IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Ivor Bull et al.	Examiner:	Wood, Elizabeth D.
Serial No.:	12/480,360	Group Art Unit:	1793
Filed:	June 8, 2009	Docket:	5328A/ENG0073-01DV
Title:	COPPER CHA ZEOLITE CATALYSTS		
Confirmation No.:	3250		

PRELIMINARY AMENDMENT

Prior to examination of this application, please enter the following claims amendments and consider the attached remarks.

Amendment to the Specification begins on page 2

Amendments to the claims begin on page 3.

Remarks being on page 7.

IN THE SPECICATION

In the specification, please amend the Title on the first line of page 1 to read:

PROCESSES FOR REUDCING REDUCING NITROGEN OXIDES USING COPPER CHA ZEOLITE CATALYSTS

IN THE CLAIMS

1. – 19. (Canceled)

20. (Currently amended) A process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process comprises contacting the gas stream with a catalyst comprising a zeolite having the CHA crystal structure and a mole ratio of silica to alumina from about 15 to about 256 and an atomic ratio of copper to aluminum from about 0.25 to about 0.50.

21. (Currently amended) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb flow through substrate.

22. (Currently amended) The process of claim 21, wherein the exhaust gas stream further comprises ammonia and at least a portion of the flow through substrate is coated with CuCHA adapted to oxidize ammonia in the exhaust gas stream.

23. (Original) The process of claim 21, wherein at least a portion of the flow through substrate is coated with Pt and CuCHA adapted to oxidize ammonia in the exhaust gas stream.

24. (Currently amended) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb wall flow substrate.

25. (Currently amended) The process of claim 24, wherein the exhaust gas stream further comprises ammonia and at least a portion of the wall flow substrate is coated with CuCHA adapted to oxidize ammonia in the exhaust gas stream.

26. (Original) The process of claim 24, wherein at least a portion of the wall flow substrate is coated with Pt and CuCHA adapted to oxidize ammonia in the exhaust gas stream.

27. (Currently amended) The process of claim 20, the gas stream is an exhaust gas stream from an internal combustion engine and the process further comprising contacting the exhaust gas stream with a catalyzed soot filter.

28. (Original) The process of claim 27, wherein said catalyzed soot filter is upstream of said catalyst.

29. (Original) The process of claim 27, wherein said catalyzed soot filter is downstream of said catalyst.

30. (Original) The process of claim 27, further comprising contacting the exhaust gas stream with a diesel oxidation catalyst.

31. (Original) The exhaust process of claim 30, wherein said diesel oxidation catalyst is upstream of said catalyst comprising a zeolite having the CHA crystal structure.

32. (Original) The exhaust process of claim 31, wherein said diesel oxidation catalyst and catalyzed soot filter are upstream from said catalyst comprising a zeolite having the CHA crystal structure.

33. (New) A process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said process comprises contacting the gas stream with a catalyst comprising a zeolite having the CHA crystal structure promoted with sufficient copper to prevent thermal degradation of the zeolite when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

34. (New) The process of claim 33, wherein the zeolite having the CHA crystal structure retains the CHA crystal as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

35. (New) The process of claim 33, wherein the zeolite retains the CHA crystal structure as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 800°C and high water vapor environments of about 10% or more for at least about 48 hours.

36. (New) The process of claim 33, wherein the zeolite contains ion-exchanged copper and an amount of non-exchanged copper sufficient to maintain NOx conversion of the catalyst in an exhaust gas stream containing nitrogen oxides after hydrothermal aging of the catalyst temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

37. (New) The process of claim 33, wherein NOx conversion of the catalyst at about 200°C after hydrothermal aging in 10% steam at 850° C for 6 hours is at least 90% of the NOx conversion of the catalyst at about 200°C prior to hydrothermal aging.

38. (New) The process of claim 33, wherein at least about 90% of the oxides of nitrogen are reduced by the catalyst over the temperature range of about 250° C to 450° C.

39. (New) The process of claim 33, further comprising adding a reductant to the exhaust gas stream upstream from the catalyst comprising a zeolite having the CHA crystal structure.

40. (New) The process of claim 39, wherein the reductant is selected from ammonia and an ammonia precursor.

41. (New) The process of claim 40, further comprising contacting the exhaust gas stream with a downstream catalyst comprising a Cu-containing zeolite having the CHA crystal structure.

42. (New) The process of claim 41, wherein the downstream catalyst further comprises a precious metal.

43. (New) the process of claim 40, wherein the catalyst comprising a zeolite having the CHA crystal structure is disposed on a wall flow filter.

REMARKS

The Title has been amended to be more consistent with the presently pending claims. Support for the amendment can be found at least in the originally filed claims and page 1, paragraph 0002 of the specification.

Claims 1 to 32 were originally filed. Claims 1-19 have been canceled. Claim 20 has been amended to correct a minor informality. Claims 21, 22, 24, 25, and 27 have been amended, support for which can be found at least at page 7, paragraph 0035 and page 9, paragraph 0043. New claims 33-43 have been added. Support for claims 33 and 36 can be found at least at page 3, paragraph 0012. Support for claims 34 and 35 can be found at least at page 29, Example 2. Support for claim 37 can be found at least at page 3, paragraph 009. Support for claim 38 can be found at least at Figures 1-4. Support for claims 39 and 40 can be found at least at page 31, paragraph 0132. Support for claims 41-43 can be found on page 32. No new matter has been added. If allowance of this application may be expedited by resolution of simple issues through a telephone conference, the Examiner is invited to call the undersigned.

If any additional fees are due, the Commissioner is hereby authorized to charge deposit account 50-3329 for such fees.

Respectfully Submitted,

DIEHL SERVILLA LLC
77 Brant Avenue
Suite 210
Clark, New Jersey 07066
732 815 0404

Date: November 18, 2009

By /Scott S. Servilla, Reg. #40806/
Scott S. Servilla
Reg. No. 40806

Electronic Acknowledgement Receipt

EFS ID:	6478848
Application Number:	12480360
International Application Number:	
Confirmation Number:	3250
Title of Invention:	Copper CHA Zeolite Catalysts
First Named Inventor/Applicant Name:	Ivor Bull
Customer Number:	48226
Filer:	Scott Servilla/Linda Murphy
Filer Authorized By:	Scott Servilla
Attorney Docket Number:	5328A
Receipt Date:	18-NOV-2009
Filing Date:	08-JUN-2009
Time Stamp:	15:29:43
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		00097384.PDF	84698 67f38ff24c3e9d8cf67a8805e450c45487c9a390	yes	7

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Preliminary Amendment	1	1
	Specification	2	2
	Claims	3	6
	Applicant Arguments/Remarks Made in an Amendment	7	7

Warnings:

Information:

Total Files Size (in bytes):	84698

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

PTO/SB/06 (07-06)
Approved for use through 1/31/2007. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875	Application or Docket Number 12/480,360	Filing Date 06/08/2009	☐ To be Mailed

APPLICATION AS FILED – PART I

	(Column 1)	(Column 2)	SMALL ENTITY ☐		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE ($)	FEE ($)		RATE ($)	FEE ($)
☐ BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A			N/A	
☐ SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A			N/A	
☐ EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A			N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	minus 20 =	*	X $ =		OR	X $ =	
INDEPENDENT CLAIMS (37 CFR 1.16(h))	minus 3 =	*	X $ =			X $ =	
☐ APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $250 ($125 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).						
☐ MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))							
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL			TOTAL	

APPLICATION AS AMENDED – PART II

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
AMENDMENT	**11/18/2009**	CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	* 24	Minus	** 32	= 0	X $ =		OR	X $52=	0
	Independent (37 CFR 1.16(h))	* 2	Minus	***3	= 0	X $ =		OR	X $220=	0
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	**0**

		(Column 1)		(Column 2)	(Column 3)					
AMENDMENT		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE ($)	ADDITIONAL FEE ($)		RATE ($)	ADDITIONAL FEE ($)
	Total (37 CFR 1.16(i))	*	Minus	**	=	X $ =		OR	X $ =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	X $ =		OR	X $ =	
	☐ Application Size Fee (37 CFR 1.16(s))									
	☐ FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.

** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest Number Previously Paid For" (Total or Independent) is the highest number found in the appropriate box in column 1.

Legal Instrument Examiner:
/Susan K. Ford/

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NUMBER	FILING OR 371(C) DATE	FIRST NAMED APPLICANT	ATTY. DOCKET NO./TITLE
12/480,360	06/08/2009	Ivor Bull	5328A

CONFIRMATION NO. 3250

PUBLICATION NOTICE

OC000000038860065

48226
BASF CATALYSTS LLC
100 CAMPUS DRIVE
FLORHAM PARK, NJ 07932

Title: Copper CHA Zeolite Catalysts

Publication No.US-2009-0285737-A1
Publication Date:11/19/2009

NOTICE OF PUBLICATION OF APPLICATION

The above-identified application will be electronically published as a patent application publication pursuant to 37 CFR 1.211, et seq. The patent application publication number and publication date are set forth above.

The publication may be accessed through the USPTO's publically available Searchable Databases via the Internet at www.uspto.gov. The direct link to access the publication is currently http://www.uspto.gov/patft/.

The publication process established by the Office does not provide for mailing a copy of the publication to applicant. A copy of the publication may be obtained from the Office upon payment of the appropriate fee set forth in 37 CFR 1.19(a)(1). Orders for copies of patent application publications are handled by the USPTO's Office of Public Records. The Office of Public Records can be reached by telephone at (703) 308-9726 or (800) 972-6382, by facsimile at (703) 305-8759, by mail addressed to the United States Patent and Trademark Office, Office of Public Records, Alexandria, VA 22313-1450 or via the Internet.

In addition, information on the status of the application, including the mailing date of Office actions and the dates of receipt of correspondence filed in the Office, may also be accessed via the Internet through the Patent Electronic Business Center at www.uspto.gov using the public side of the Patent Application Information and Retrieval (PAIR) system. The direct link to access this status information is currently http://pair.uspto.gov/. Prior to publication, such status information is confidential and may only be obtained by applicant using the private side of PAIR.

Further assistance in electronically accessing the publication, or about PAIR, is available by calling the Patent Electronic Business Center at 1-866-217-9197.

Office of Data Managment, Application Assistance Unit (571) 272-4000, or (571) 272-4200, or 1-888-786-0101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Ivor Bull et al.	Examiner:	Wood, Elizabeth D.
Serial No.:	12/480,360	Group Art Unit:	1793
Filed:	June 8, 2009	Docket:	5328A/ENG0073-01DV
Title:	COPPER CHA ZEOLITE CATALYSTS		
Confirmation No.:	3250	EFS ID	6478848

TRANSMITTAL LETTER

Further to the filing of a Preliminary Amendment filed on November 18, 2009, please remove page 2 showing an amendment to the Title and replace it with the attached replacement page 2.

Respectfully Submitted,

DIEHL SERVILLA LLC
77 Brant Avenue
Suite 210
Clark, New Jersey 07066
732 815 0404

Date: November 19, 2009

By /Scott S. Servilla, Reg. #40806/
Scott S. Servilla
Reg. No. 40806

IN THE SPECICATION

In the specification, please amend the Title on the first line of page 1 to read:

<u>PROCESSES FOR REDUCING NITROGEN OXIDES USING</u> COPPER CHA ZEOLITE CATALYSTS

Electronic Acknowledgement Receipt

EFS ID:	6483538
Application Number:	12480360
International Application Number:	
Confirmation Number:	3250
Title of Invention:	Copper CHA Zeolite Catalysts
First Named Inventor/Applicant Name:	Ivor Bull
Customer Number:	48226
Filer:	Scott Servilla/Linda Murphy
Filer Authorized By:	Scott Servilla
Attorney Docket Number:	5328A
Receipt Date:	19-NOV-2009
Filing Date:	08-JUN-2009
Time Stamp:	09:53:17
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1		00097449.PDF	74733 d84ec85f71d73eb59cc4aa5404f114b8bd8f4961	yes	2

	Multipart Description/PDF files in .zip description		
	Document Description	**Start**	**End**
	Miscellaneous Incoming Letter	1	1
	Specification	2	2
Warnings:			
Information:			
	Total Files Size (in bytes):	74733	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

<u>National Stage of an International Application under 35 U.S.C. 371</u>
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<u>New International Application Filed with the USPTO as a Receiving Office</u>
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Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/480,360	06/08/2009	Ivor Bull	5328A	3250

48226 7590 02/26/2010
BASF CATALYSTS LLC
100 CAMPUS DRIVE
FLORHAM PARK, NJ 07932

EXAMINER	
WOOD, ELIZABETH D	

ART UNIT	PAPER NUMBER
1793	

NOTIFICATION DATE	DELIVERY MODE
02/26/2010	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

sonny.nkansa@basf.com
Melanie.Brown@basf.com

PTOL-90A (Rev. 04/07)

Office Action Summary	Application No.	Applicant(s)	
	12/480,360	BULL ET AL.	
	Examiner	**Art Unit**	
	Elizabeth D. Wood	1793	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE _3_ MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on _18 November 2009_.
2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.
3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) _20-43_ is/are pending in the application.
4a) Of the above claim(s) _____ is/are withdrawn from consideration.
5)☒ Claim(s) _20-32_ is/are allowed.
6)☒ Claim(s) _33-43_ is/are rejected.
7)☐ Claim(s) _____ is/are objected to.
8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.
10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
a)☐ All b)☐ Some * c)☐ None of:
1.☐ Certified copies of the priority documents have been received.
2.☐ Certified copies of the priority documents have been received in Application No. _____.
3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08) Paper No(s)/Mail Date _6/8/09, 10/21/09, 11/25/09_.
4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

Specification

The examiner has not checked the specification to the extent necessary to determine the presence of **all** possible minor errors (grammatical, typographical and idiomatic). Cooperation of the applicant(s) is requested in correcting any errors of which applicant(s) may become aware of in the specification, in the claims and in any future amendment(s) that applicant(s) may file.

Applicant(s) is also requested to complete the status of any copending applications referred to in the specification by their Attorney Docket Number or Application Serial Number, **if any**.

The status of the parent application(s) and/or any other application(s) cross-referenced to this application, if **any**, should be updated in a timely manner.

Information Disclosure Statement

The information disclosure statements filed have been considered as set forth in MPEP 609. Once the minimum requirements of 37 C.F.R. 1.97 and 1.98 are met, the examiner has the obligation to consider the information. Consideration by the examiner of the information submitted in an IDS means nothing more than considering the documents in the same manner that other documents in Office search files are considered by the examiner while conducting a search of the prior art in a proper field of search. The initials of the examiner placed adjacent to the citations on the PTO-1449 or PTO/SB/08A and 08B, or its equivalent, mean that the examiner to the extent noted above has considered the information. See MPEP 609.05(b) Rev. 5.

Applicant should note that documents not in the English language have been considered only to the extent of statements of relevance, explanations provided in the corresponding search reports provided and provided translations.

Claim Rejections - 35 USC § 112

The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claims 33-43 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. This is a new matter rejection.

Claims 33 – 43 recite reduction of oxides of nitrogen in the presence of “a catalyst comprising a zeolite having the CHA crystal structure promoted with sufficient copper to prevent thermal degradation….”.

This recitation is not supported by the originally filed specification. A thorough reading of the specification indicates that a CuCHA zeolite such as that set forth in claim 20 which is **further** promoted with an amount of free copper results in the prevention of hydrothermal degradation. Paragraph 12 recites such a catalyst. The examples compare such catalyst to the exchanged CuCHA zeolite that does not contain “free” copper. Paragraph [0041] recites that the SCR catalyst is formed from a Cu exchanged zeoltie having free copper **in addition to** ion-exchanged copper.

In view of the foregoing, it is considered that the applicant did not have possession of the claimed process taking place in the presence of a material that is only a CHA zeolite promoter with sufficient copper to prevent thermal degradation.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

The factual inquiries set forth in *Graham* **v.** *John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

Claims 33-43 are rejected under 35 U.S.C. 103(a) as being unpatentable over Ishihara et al. (Journal of Catalysis article, Ishihara et al. (Chemistry Letters article), Ishihara et al. (Ind. Eng. Chem. Res. article) or Ishihara et al. (Studies in Surface Science and catalysis article), each taken individually.

The instantly claimed invention is directed to a method for reducing nitrogen oxides in an exhaust gas stream by employing a catalyst comprising a zeolite with the CHA crystal structure promoted with copper.

Each of the Ishihara et al. articles is concerned with the production of SAPO-34 materials. Each of the references produces a material determined by X-ray diffraction to be SAPO-34, which is exchanged with copper. Each of the references teaches that the material is employed in processes for the reduction of nitrogen oxides, substantially as claimed in the instant application. Each of the references details the material to be highly thermally stable, which would indicate to the examiner that the material inherently possesses the characteristics herein claimed by applicant, as hydrothermal stability by definition means retaining functional crystallinity, pore size, acidity and so forth. As the material of the Ishihara et al. references is indistinguishable from the instant claims and is thermally stable, the examiner can only conclude that the references include sufficient copper to prevent thermal degradation of the zeolite, thus rendering the instantly claimed process obvious. Moreover, to demonstrate this stability, the Ishihara et al. experiments detail treating the molecular sieve in a manner commensurate with that recited in the instant application. By treating the molecular sieves in a manner that mimics conditions of use (i.e. steam atmosphere, high temperatures), the figures in particular show that the material retains the ability to function with great effectiveness at 700C (or higher temperatures, although the references indicate that some loss ensues with increasing temperatures - Note page 1496 the Studies in Surface Science article which states that even calcination at 800C in wet air results in a relatively small decrease in activity). Accordingly, as the treatment method does not appear to differ substantially from that recited in the instant application, and as the references all produce materials they define to be hydrothermally stable and are not apparently patentably distinct from the Ishihara et al. disclosures, it can only be considered that the references teach the same process being recited by applicant in the instant claims. See particularly the experimental data and tables in each of the applied references.

With respect to limitations such as the presence of ammonia the use of a filter or additional catalysts, and so forth, the examiner would submit such to be well known in the art and not considered to patentably define over the disclosures of the prior art of record in the instant application.

Allowable Subject Matter

Claims 20-32 are allowable over the prior art of record. The prior art fails to teach or establish a link between the silica to alumina ratio and the copper to aluminum ratio in the final catalyst being employed in the instantly claimed process. Although it is known in the art to employ ratios that overlap these claimed recitations in ZSM-5 catalysts, it is also known in this art that CHA based catalysts are very different from MFI catalysts and there is no predictability associated with their use in SCR materials.

Accordingly, there would have been no motivation or expectation of success with respect to nitrogen reduction when employing the instantly claimed materials.

Conclusion

Applicants are advised that any evidence to be provided under 37 CFR 1.131 or 1.132 and any amendments to the claims and specification should be submitted prior to final rejection to be considered timely. It is anticipated that the next office action will be a final rejection.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Elizabeth D. Wood whose telephone number is 571-272-1377. The examiner can normally be reached on M-F, 5:30-2:00.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Curtis Mayes can be reached at 571-272-1234. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Elizabeth D. Wood/
Primary Examiner, Art Unit 1793

/E. D. W./
Primary Examiner, Art Unit 1793

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Bull et al.	Examiner	Wood, Elizabeth D.
Serial No.:	12/480,360	Group Art Unit	1732
Filed:	June 8, 2009	Docket No.:	EH5328A
		Confirmation No.:	3250

Title: COPPER CHA ZEOLITE CATALYSTS

Commissioner for Patents
P.O.Box 1450
Alexandria, VA 22313-1450

AMENDMENT AND RESPONSE UNDER 37 C.F.R. § 1.114

Sir:

Further to the final Office Action mailed on July 26, 2010, in the above-referenced application, Applicants submit this Amendment and Response along with the accompanying Request for Continued Examination. A response to the Office Action was due by October 26, 2010. This Amendment and Response is being submitted with a petition for a three-month extension of time. Accordingly, this paper is being timely filed.

Applicants request entry of the following amendments to the claims. Upon entry, the claims pending for further proceedings will be those in the claim listing that begins on page 5 of this paper.

Amendments to the Specification begin on page 3 of this paper.

Amendments to the Drawings begin on Page 4 of this paper.

Remarks begin on page 11.

In the Specification:

Please amend the Specification as follows:

In the Abstract:

Zeolite catalysts and systems and methods for preparing and using zeolite catalysts having the CHA crystal structure are disclosed. The catalysts can be used to remove nitrogen oxides from a gaseous medium across a broad temperature range and exhibit hydrothermal stable at high reaction temperatures. The zeolite catalysts include a zeolite carrier having a silica to alumina ratio from about 15:1 to about 256:1 and a copper to ~~alumina~~ aluminum ratio from about 0.25: 1 to about 1:1.

Please amend the paragraph 0122 in the Specification as follows:

The slurry preparation, coating and SCR NO_x evaluation were the same as outlined above for Example 1. As shown in Fig. [[7]] 9, Example 18 exhibited the same SCR performance as Example 3 that was prepared by twice ion-exchanges with copper sulphate plus an incipient wetness impregnation.

In the Drawings

Please amend Figure 1A as shown in the Annotated Sheet and Replacement Sheet submitted with this Amendment and Response.

IN THE CLAIMS:

1. – 19. (Cancelled)

20. (Previously presented) A process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process comprises contacting the gas stream with a catalyst comprising a zeolite having the CHA crystal structure and a mole ratio of silica to alumina from about 15 to about 256 and an atomic ratio of copper to aluminum from about 0.25 to about 0.50.

21. (Previously presented) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb flow through substrate.

22. (Previously presented) The process of claim 21, wherein the exhaust gas stream further comprises ammonia and at least a portion of the flow through substrate is coated with CuCHA adapted to oxidize ammonia in the exhaust gas stream.

23. (Original) The process of claim 21, wherein at least a portion of the flow through substrate is coated with Pt and CuCHA adapted to oxidize ammonia in the exhaust gas stream.

24. (Previously presented) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb wall flow substrate.

25. (Previously presented) The process of claim 24, wherein the exhaust gas stream further comprises ammonia and at least a portion of the wall flow substrate is coated with CuCHA adapted to oxidize ammonia in the exhaust gas stream.

26. (Original) The process of claim 24, wherein at least a portion of the wall flow substrate is coated with Pt and CuCHA adapted to oxidize ammonia in the exhaust gas stream.

27. (Previously presented) The process of claim 20, the gas stream is an exhaust gas stream from an internal combustion engine and the process further comprises contacting the exhaust gas stream with a catalyzed soot filter.

28. (Original) The process of claim 27, wherein said catalyzed soot filter is upstream of said catalyst.

29. (Original) The process of claim 27, wherein said catalyzed soot filter is downstream of said catalyst.

30. (Original) The process of claim 27, further comprising contacting the exhaust gas stream with a diesel oxidation catalyst.

31. (Original) The exhaust process of claim 30, wherein said diesel oxidation catalyst is upstream of said catalyst comprising a zeolite having the CHA crystal structure.

32. (Original) The exhaust process of claim 31, wherein said diesel oxidation catalyst and catalyzed soot filter are upstream from said catalyst comprising a zeolite having the CHA crystal structure.

33. (Currently amended) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst deposited on a substrate, the catalyst comprising a zeolite having the CHA crystal structure promoted with sufficient copper including non-exchanged copper to prevent thermal degradation of the zeolite when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

34. (Previously presented) The process of claim 33, wherein the zeolite having the CHA crystal structure retains the CHA crystal as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

35. (Previously presented) The process of claim 33, wherein the zeolite retains the CHA crystal structure as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 800°C and high water vapor environments of about 10% or more for at least about 48 hours.

36. (Previously presented) The process of claim 33, wherein the zeolite contains ion-exchanged copper and an amount of non-exchanged copper sufficient to maintain NOx conversion of the catalyst in an exhaust gas stream containing nitrogen oxides after hydrothermal aging of the catalyst temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

37. (Previously presented) The process of claim 33, wherein NOx conversion of the catalyst at about 200°C after hydrothermal aging in 10% steam at 850° C for 6 hours is at least 90% of the NOx conversion of the catalyst at about 200°C prior to hydrothermal aging.

38. (Previously presented) The process of claim 33, wherein at least about 90% of the oxides of nitrogen are reduced by the catalyst over the temperature range of about 250° C to 450° C.

39. (Cancelled)

40. (Previously presented) The process of claim 33, wherein the reductant is selected from ammonia and an ammonia precursor.

41. (Previously presented) The process of claim 40, further comprising contacting the exhaust gas stream with a downstream catalyst comprising a Cu-containing zeolite having the CHA crystal structure.

42. (Previously presented) The process of claim 41, wherein the downstream catalyst further comprises a precious metal.

43. (Previously presented) The process of claim 40, wherein the catalyst comprising a zeolite having the CHA crystal structure is disposed on a wall flow filter.

44. (Previously presented) The method of claim 33, wherein the reductant comprises urea.

45. (Previously presented) The method of claim 33, wherein and the catalyst is disposed on a honeycomb flow through substrate.

46. (New) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst comprising a zeolite having the CHA crystal structure deposited on a substrate, the zeolite promoted with copper, wherein the catalyst

exhibits less than a 10% decrease in NOx conversion with the nitrogenous reductant over a range from about 200° C to about 300° C following hydrothermal aging in 10% H_2O at 800° C for 50 hours.

47. (New) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst deposited on a substrate, the catalyst comprising a zeolite having the CHA crystal structure promoted with copper and exhibiting improved low temperature activity and hydrothermal stability compared to Cu Beta zeolite under similar conditions.

48. (New) The SCR process according to claim 47, wherein the reductant comprises ammonia.

REMARKS

Claims 20-38 and 40-45 are pending in the application. Claims 20-32 are allowed. Claims 33-38 and 40-45 are finally rejected.[1]

Claim 1 has been amended to more particularly define the subject matter the Applicants consider their invention. Specifically, claim 1 has been amended to recite that the process is a "SCR" process and that the catalyst is "deposited on a substrate." Support for the amendment can be found at least at paragraphs 37-44 and 52 of the specification as originally filed.

New claim 46 has been added directed to a particular embodiment of the disclosed SCR process. Support for the new claims can be found at least at paragraphs 9, 34 and 35, Examples 1 and 6, and Figures 2 and 3 of the specification as originally filed.

New claims 47 and 48 have been added directed to a particular embodiment of the disclosed SCR process. Support for the new claims 47 and 48 can be found at least at paragraphs 7, and 0093 (Table 1) of the specification as originally filed.

The Specification has been amended to correct typographical errors. The Abstract as originally filed referred to copper to alumina ratio, which is inconsistent with the remainder of the specification. The word "aluminum" has been substituted for "alumina." Paragraph 0122 referred to the incorrect Figure.

Figure 1A has been amended. Figure 1A as originally filed contained incorrect legends for the black diamonds and hollow diamonds. Support for this amendment can be found in Figure 1 and Table 1. In Figure 1, the solid diamonds show the aged data of Example 1 (2.41%), where the 210° C performance is 43% (as in Table 1), but in Figure 1A, Example 1 (2.41%)

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[1] The Office Action incorrectly sates that claims 20-43 are pending in application and claims 33-43 are rejected.

should be the hollow diamonds, not the solid diamonds, because the aged performance should match Figure 1 and Table 1.

No new matter has been introduced by this amendment.

Claims 33-38 and 40-47 are presented for further proceedings. Reconsideration of the claim rejections and allowance of the pending claims in view of the amendments above and the following remarks are respectfully requested.

Claim Rejections – 35 U.S.C. § 103

Claims 33-38 and 40-45 remain rejected under 35 U.S.C. § 103(a) as allegedly unpatentable over various Ishihara et al. articles (*Zeolites and Related Microporous Materials: State of the Art*, 1994 (Ishihara I); *Journal of Catalysis*, 1997 (Ishihara II); and *Ind. Eng. Chem Res.*, 1997 (Ishihara III)), each taken individually. According to the Response to Arguments section in the final Office Action:

> Applicant had amended the claims to require that the reductant be a nitrogenous compound, whereas the previous claims were silent with respect to the reductant or recited ammonia or a precursor thereof. As mentioned in the previous office action, the selection of an acceptable reductant would have been well known to those practicing in this field of technology and would not be considered a patentable improvement. Evidence of this position can be found in prior art of record in this application, such as US 7,042,261 which discloses that various reducing agents are known to be applicable with zeolite catalysts in SCR methods, including the hydrocarbons of the Ishihara references and the nitrogenous reductants now specified in the instant claims. Accordingly, the art has established equivalence between these materials. Applicant's comments regarding Appeal 2008-3469 are not convincing. The Board did recognize that all of the reductants are known and equivalent in the art. The Board indicated that in that particular application, an unexpected synergism was achieved which provided unexpected results over an otherwise obvious substitution. No such synergism is asserted for the instantly

> claimed nitrogenous reductant. In fact, the instantly claimed specification recognizes the equivalence between the reductants in paragraph [0043]. With respect to the claims reciting non-exchanged copper, whereas the Ishihara et al. documents recite merely ion-exchanged copper, the examiner is not convinced that such limitation defines over the prior art. In making the copper containing compositions, Ishihara et al. do not wash their catalyst prior to calcination. Accordingly, there is no reason to assume that "free" or "non-ion-exchanged" copper will not be present. The examiner would take the position that additional copper would be expected to be present on the catalyst. Furthermore, as indicated in the previous office action, all of the benefits/characteristics that applicant assigns in the specification to the presence of free copper are also achieved by Ishihara et al., as their compositions are taught to be highly thermally stable under water vapor conditions, at high temperatures, for long periods of time. As a result, the examiner considers that the preponderance of the evidence would indicate that Ishihara et al. have produced a catalyst nearly indistinguishable from that being employed in the instantly claimed process.

Applicants respectfully traverse this basis for rejection.

In rejecting claims under 35 U.S.C. § 103, it is incumbent upon the Examiner to establish a factual basis to support the legal conclusion of obviousness. *See In re Fine*, 837 F.2d 1071, 1073 (Fed. Cir. 1988). In so doing, the Examiner must make the factual determinations set forth in *Graham v. John Deere Co.*, 383 U.S. 1, 17 (1966), *viz.*, (1) the scope and content of the prior art; (2) the differences between the prior art and the claims at issue; and (3) the level of ordinary skill in the art. "[T]he examiner bears the initial burden, on review of the prior art or on any other ground, of presenting a *prima facie* case of unpatentability." *In re Oetiker*, 977 F.2d 1443, 1445 (Fed. Cir. 1992). To establish a *prima facie* case of obviousness, all the claim limitations must be taught or suggested by the prior art. *See In re Royka*, 490 F.2d 981, 985 (CCPA 1974). Furthermore, although the analysis need not identify explicit teachings directed to the claimed subject matter, "it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does." *KSR Int'l Co. v. Teleflex Inc.*, 127 S. Ct. 1727, 1741 (2007). "[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *In re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006), *cited with approval in KSR*, 550 U.S. at 418.

Nitrogenous and Hydrocarbon Reductants are Not Functionally Equivalent

Claim 33 as amended and new claims 46 and 47 are directed to a SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein the SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst comprising a zeolite having the CHA crystal structure promoted with copper deposited on a substrate.

None of the Ishihara articles discloses a SCR process utilizing a nitrogenous reductant. Rather, as recognized by the Examiner, Ishihara utilizes hydrocarbon reductant. According to the Examiner, however, nitrogenous and hydrocarbon reductants are equivalent NOx reduction materials. Applicants first note that this conclusion regarding equivalence does not relieve the Examiner of the burden of establishing a *prima facie* case of obviousness as per the requirements of 35 U.S.C. § 103. *See Ex parte Ng*, Appeal No. 2008-1725, for U.S. Pat. Application No. 10/979,058 (BPAI 2008) ("At the outset, we note that it is fundamental that a prior art disclosure of a functional equivalent of a claimed element does not necessarily establish the obviousness of the claimed element within the meaning of § 103. It is incumbent upon the Examiner to provide a factual basis to support the legal conclusion that the claimed element, whether a functional equivalent of a prior art element or not, would have been obvious to one of ordinary skill in the art in the context of the claimed invention.").

In any event, contrary to the Examiner's assertion, the use of a nitrogenous reductant is not equivalent to the use of hydrocarbon reductant in NOx abatement processes. As explained in the accompanying Declaration of Dr. Joseph Patchett Under 37 C.F.R. § 1.132 ("Patchett declaration"),[2] it is well known to those skilled in the art that the operating conditions under which NOx is reduced by hydrocarbon differs quite dramatically from operating conditions under which NOx is reduced by nitrogenous reductants, and there is no expectation that a catalyst which is effective under one set of conditions will be effective under another set of conditions. Notwithstanding the boilerplate language in US 7,049,261, data for hydrocarbon-based NOx abatement cannot be used to predict the effectiveness for nitrogenous reductant-based NOx abatement – the two processes simply don't correlate. Also, the architecture needed to provide and deliver nitrogenous reductants to exhaust gas streams is more extensive than that used in hydrocarbon-based NOx abatement systems. Indeed, Ishihara recognizes the non-equivalence of hydrocarbon and nitrogenous reductants for NOx abatement by noting that "[a]t present nitrogen oxides were removed with selective reduction with NH_3 for large scale plants such as electric power generation plants or three-way catalysts for gasoline engines. However, there is no effective method for removal of NOx from diesel engines." *See* Ishihara III, at 17. As explained by Dr. Patchett, if nitrogenous and hydrocarbon reductants were equivalent, Ishihara would have tested the SAPO-34 catalyst with ammonia, and not felt the need to test C_3H_6. *See* Patchett declaration, ¶ 15.

The teachings of the subject application are not to the contrary. According to the Examiner, paragraph 0043 recognizes the equivalence between nitrogenous and hydrocarbon reductants. However, paragraph 0043 actually states that "[i]n specific embodiments, the reducing agent is ammonia" and that "in accordance with a broader scope of the invention, the reductant could include . . . hydrocarbon." Later, in paragraph 0052, the application states that "[t]he catalyzed reaction of ammonia and nitrogen oxides is therefore sometimes referred to as the selective catalytic reduction ("SCR") of nitrogen oxides or, as sometimes herein, simply as the "SCR process." Thus, the specification teaches that the term "SCR process," as recited in claims 33 and 46, specifically requires a nitrogenous reductant (such as ammonia). As explained by Dr. Patchett, although the application contemplates the use of hydrocarbons in some broader aspects, nothing would suggest to one of skill in the art that the applicants were equating the use of nitrogenous and hydrocarbon reductants in NOx abatement processes. *See* Patchett declaration, ¶ 16. As such, Ishihara fails to teach or suggest a SCR process as defined in the subject application.

Applicants would also like to address the Examiner's Assertion that in Appeal No. 2009-3469, the Board recognized that all reductants are equivalent in the art. In actuality, the Board did no such thing. The Board actually stated, "There does not appear to be any dispute that ***urea and ammonia*** are well known reducing agents for reducing NOx in engine exhaust gas." *See* page 13 (emphasis added). The Board reached no conclusion regarding equivalence between hydrocarbons and nitrogenous reductants. Indeed, the fact that the Board found that the prior art taught synergism from using hydrogen and a hydrocarbon for NOx reduction (as recognized by the Examiner), and that there was no evidence that replacing the hydrogen and hydrocarbon with urea or ammonia would achieve the same synergistic effect, is consistent with Dr. Patchett's conclusion that nitrogenous and hydrocarbon reductants are not are recognized equivalents in NOx abatement processes. Thus, the Examiner's assertion regarding equivalence is merely an unsubstantiated allegation lacking any factual basis and is, in fact, contrary to the evidence of record. *See Ex parte Ito*, Appeal No. 1998-0223, for U.S. Pat. Appl'n No. 08/351,749 (BPAI 1998) ("We find that the Examiner has presented no evidence to base the conclusion of obviousness other than assumption that suggested modification of Humble '343 would have been a matter of mere substitution of art recognized equivalents. Such assertion by the Examiner cannot replace the requirement of factual evidence."); *Ex parte Turnquest*, Appeal No. 2007-4242, for U.S. Pat. Appl'n No. 10/064,283 (BPAI 2008) ("We are in agreement with Appellants that the Examiner has not provided sufficient evidence or explanation to support a finding that Hastelloy® C0276 is an art recognized equivalent of the alloys used for Basu's sealing brush bristles. The Examiner has not explained why one of ordinary skill in the art would have concluded that a corrosion resistant alloy such as Hastelloy® C-276 would be a suitable substitute for Basu's conventional high temperature alloy sealing brush materials.").

Thus, according to Dr. Patchett, taken together, there is nothing in Ishihara to provide a reason to useSAPO-34 as a suitable catalyst candidate for use in a nitrogenous reductant-based SCR process, particularly over any of the hundreds of other known zeolite preparations. Each of these preparations has various characteristics capable of affecting its catalytic activity, such as silicon content, metal type and loading, crystal size and shape, pore size, etc. There is simply no way to predict *a priori* which of the hundreds of these zeolite preparations will be effective to convert NOx in any given process. *See* Patchett declaration, ¶ 19. As such, this is not a case where obvious to try is the proper test for obviousness. *See Takeda Chem. Indus. v. Alphapharm Pty., Ltd.*, 492 F.3d 1350, 1359 (Fed. Cir. 2007) ("Rather than identify predictable solutions for antidiabetic treatment, the prior art disclosed a broad selection of compounds any one of which could have been selected as a lead compound for further investigation. Significantly, the closest prior art compound (compound b, the 6-methyl) exhibited negative properties that would have directed one of ordinary skill in the art away from that compound. Thus, this case fails to present the type of situation contemplated by the [*KSR*] Court when it stated that an invention may be deemed obvious if it was 'obvious to try.' The evidence showed that it was not obvious to try.").

Dr. Patchett concludes that even if one of skill in the art had decided to test Ishihara's Cu-SAPO-34 catalyst in a nitrogenous reductant-based SCR process, there would have been no basis to conclude that it would have been effective to reduce NOx. *See* Patchett declaration, ¶ 20. As noted above, operating conditions under which NOx is reduced by hydrocarbon differs quite dramatically from operating conditions under which NOx is reduced by nitrogenous reductants, meaning that data for hydrocarbon-based NOx abatement cannot be used to predict the effectiveness for nitrogenous reductant-based NOx abatement. Also, as noted above, each zeolite preparation has various characteristics capable of affecting its catalytic activity, which may be independent or interdependent. Thus, there is simply no way one of skill in the art could predict whether or not Ishihara's Cu-SAPO-34 would be effective as a catalyst in a nitrogenous reductant-based SCR process, let alone exhibiting the characteristics recited in instant claims 33, 46 and 47. *See In re Dow Chem. Co.*, 837 F.2d 469, 473 (Fed. Cir. 1988) ("Both the suggestion and the expectation of success must be founded in the prior art, not in applicant's disclosure.").

Because the Examiner's has failed to establish equivalence between nitrogenous and hydrocarbon reductants for use in NOx abatement processes, Applicants submit that the Examiner ultimate conclusion of obviousness rests on nothing more than impermissible hindsight. *See Ex parte Harding*, Appeal No. 2002-1053, for U.S. Pat. Appl'n No. 09/702,981 (BPAI 2003) ("[W]e agree with the appellants . . . that the applied prior art does not establish that Wood's tensioning roll and the spring-biased movable dancer arms of Simmons are 'art recognized equivalents.' . . . In our view, the only suggestion for modifying Simmons to meet the above-noted limitations stems from hindsight knowledge derived from the appellants' own disclosure. The use of such hindsight knowledge to support an obviousness rejection under 35 U.S.C. § 103 is, of course, impermissible."); MPEP § 2144.06 ("In order to rely on equivalence as a rationale supporting an obviousness rejection, the equivalency must be recognized in the prior art, and cannot be based on applicant's disclosure or the mere fact that the components at issue are functional or mechanical equivalents."). Accordingly, Applicants submit that claims 33-38 and 40-45 (as well as new claim 46) are not unpatentable over any of the Ishihara references, alone or in combination, and respectfully request that the rejection be withdrawn.

Ishihara Teaches Away

In addition to the lack of equivalence, Dr. Patchett also explains that one of skill in the art would not have sought to use the particular catalyst in Ishihara in a nitrogenous reductant-based SCR process, such as that recited claims 33, 46 and 47. According to Dr. Patchett, using Ishihara I as representative, Figure 1 shows that the Cu-SAPO-34 catalyst had very low NOx conversion activity over the critical temperature range of 200-300° C, which includes a typical operating temperature range for diesel engines. In contrast, as shown in Figures 1, 1A, 2 3 and 4 of the subject application, the CuCHA catalysts had excellent NOx conversion activity over this same range. In addition, Figure 4 of Ishihara I shows that the Cu-SAPO-34 catalyst exhibited extremely low NOx activity of less than about 15% at 350° C following hydrothermal treatment at 800° C and 3% H_2O water for 2 hours. In contrast, as shown in Figure 3 of the subject application, the CuCHA catalyst exhibited significantly better NOx activity (greater than 90% conversion) following hydrothermal treatment at 800° C and 10% H_2O for 50 hours, which are characteristics recited in new claim 46. *See* Patchett declaration, ¶ 17. It is noted that Figures 1 and 4, while not showing the same level of results as in Figure 4, the NOx conversion after hydrothermal aging at 800° C exceeded 85% conversion. Figures 1 and 4, together with Table 1, support new claim 47.

Dr. Patchett notes that it is important to recognize that the reaction conditions for the two catalysts were different: Ishihara used a space velocity of only 8,500 h^{-1} (*see* page 1494), which is not realistic of typical diesel operating conditions, whereas the space velocity used in the subject application was 80,000 h^{-1}, which is typical of diesel conditions. As one of skill in the art knows, a catalyst tested at higher space velocities results in lower NOx conversion than the same catalyst tested under the same conditions but at a lower space velocity. Thus, according to Dr. Patchett, Ishihara's catalyst would have even lower NOx conversion activity if tested under true engine conditions, as was done in the subject application. Also, the C_3H_6 used as the reductant is not typical of diesel exhaust – more typical would be the larger decane. *See* Patchett declaration, ¶ 18.

Furthermore, in this regard, other researchers have observed the poor results in Ishihara. See *Kim et al., Water Tolerance of DeNOx SCR Catalysts Using Hydrocarbons: Findings,* *Improvements and Challenges,* Korean J. Chem. Eng 18 (5), 725-40 at p. 736 (2001) (attached as Exhibit A), noting that while hydrothermally stable, "both catalysts [CU-SAPO and CuMFI] after aging at 800 C showed the catalyst deactivation within the reaction temperatures covered." It is respectfully submitted that a person of ordinary skill in the art would have readily recognized that while Ishihara may have referred to the SAPO-34 materials as hydrothermally stable, there would be no interest in these materials as low temperature catalysts in view of their extremely poor low temperature NOx conversion after aging.

Moreover, Kim et al. noted after surveying the literature at the time of the article:

> The reversibility of the catalyst deactivation by the existence of water in the feed gas stream may be an experimental evidence for the competitive adsorption of the reactants including water &ring the course of the reaction. It has also been observed for the decomposition of NO over excessively ion-exchanged Cu-zeolite. However, it becomes complicated due to the chemical alteration of metal ions to metal oxides after aging in a wet stream, as extensively discussed. **This implies that no single cause can elucidate the catalyst deactivation by water for the reduction of NO by HCs. It varies with the catalyst, the reductant and the operating condition employed for the reduction**.

Id. (emphasis added)

The above quoted passage from the Kim et al. article makes clear that catalyst deactivation by water cannot be attributed to a single cause. More importantly, the literature notes that deactivation varies with **the catalyst, the reductant and the operating conditions** employed for the reduction. The above statements quote from Kim et al. also bear on the lack of functional equivalence between hydrocarbon reductants and nitrogenous reductants. In consideration of the above, no prediction could be made with respect to the reduction of NOx with an ammonia environment under operating conditions that are different from those in Ishihara.

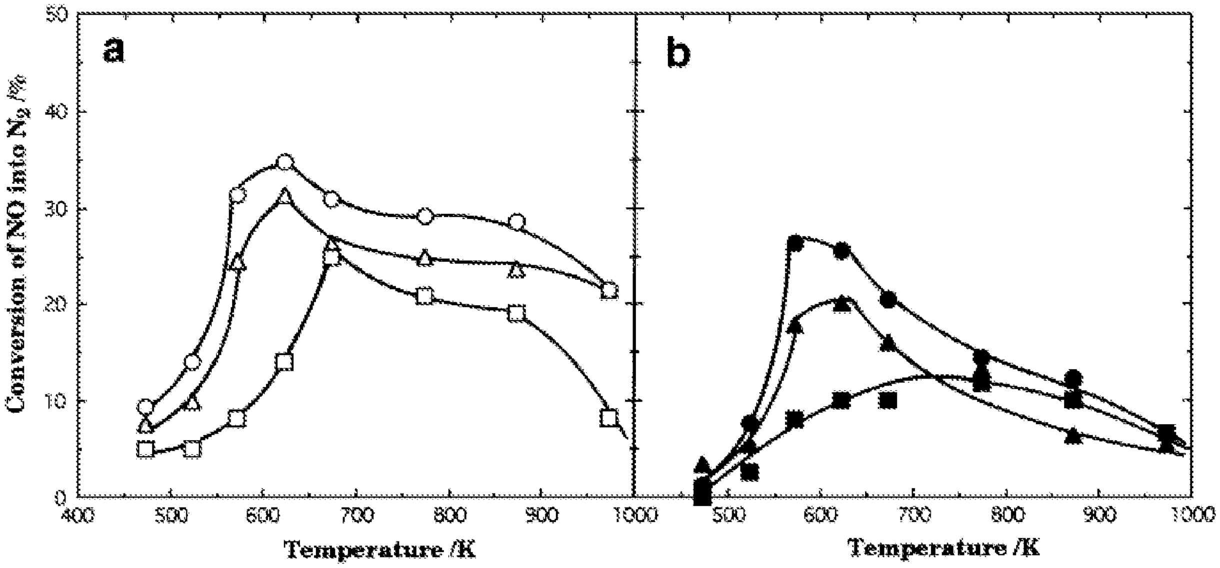
Unexpected Results

Finally, in addition to the results discussed above and in the specification of the instant patent application, the Declaration of Stanley Roth, Ph.D. provides evidence of unexpected results. The expectation of Cu zeolites generally prior to the present invention was that they would not maintain NOx conversion across a broad temperature range after exposure to hydrothermal conditions. Roth Declaration, ¶ 11. As shown in the Roth Declaration, the Ford Motor Company researchers noted that "no reported Cu/zeolite SCR formulation was able to yield suitable low temperature NOx performance after exposure to hydrothermal conditions consisting of 1 hour at 950° C." Roth Declaration, ¶ 12. A Ford Motor Company research paper, attached as Exhibit C to the Roth Declaration and entitled "*Enhanced Durability of Cu/Zeolite Based SCR Catalyst*," further noted:

> Among the dozens of Cu/zeolite formulations tested in past years, no formulation has been able to withstanding exposure up to 900 °C while maintaining stable NOx performance at 200 "C. Under the 1 hour/900 °C aging condition, the 2007 SCR catalyst retained 90% NOx conversion at 200 °C. All older SCR formulations have achieved no better than 20% NOx conversion.

The results in the instant patent application, even for Example 1, all exhibited better than 40% NOx conversion at 200° C after extended aging at 800° C. The Ishihara reference shows merely about 5% conversion after only moderate exposure of 3% H_2O and 2 hours. See Figure 4a in

Ishihara reproduced below in which the hollow squares show the performance of Cu SAPO-34 after aging at 800° C in 3% H_2O for only 2 hours:



Compared with any of the results in the instant patent application, even Examples 1 and 4, the fresh and aged NOx conversions are unexpectedly good compared to Ihsihara et al. In view of the above, it is respectfully submitted that the pending claims are patentable over the cited references.

New Claims 47-48

In the non-final office action of February 26, 2010, it was asserted that the applicants were not in possession of the invention of claims 33-43 as then presented. Claim 47 is supported by the specification at least at paragraphs 0007, 0009, 0036 and Example 1. As noted in Dr. Patchett's declaration, and discussed above, the invention is not limited to catalysts having the

CHA crystal structure and non-exchanged copper to prevent thermal degradation. The application amply supports claims 47 and 48, as an amount of non-exchanged copper is not essential to practice of the invention, but merely provides "enhanced" by non-exchanged copper. See Patchett Declaration, ¶ 8.

Secondary Considerations

While it is maintained that based on the above remarks, the Final Office Action has failed to establish a prima facie case of obviousness, it is respectfully submitted the secondary considerations further weigh in favor patentability of the claims in the instant application. In *Graham*, the Supreme Court stated that "secondary considerations as commercial success, long felt but unsolved needs, failure of others, etc., might be utilized to give light to the circumstances surrounding the origin of the subject matter sought to be patented. As indicia of obviousness or nonobviousness, these inquiries may have relevancy." *See Graham*, 383 U.S. at 17-18. Thus, objective evidence of secondary considerations must be considered in making an obviousness decision. *See Stratoflex, Inc. v. Aeroquip Corp.*, 713 F.2d 1530, 1538-39 (Fed. Cir. 1983). Any initial obviousness determination is reconsidered anew in view of the proffered evidence of nonobviousness. *See In re Rinehart*, 531 F.2d 1048, 1052 (CCPA 1976); *In re Eli Lilly & Co.*, 902 F.2d 943, 945 (Fed. Cir. 1990).

The attached Roth Declaration shows that prior to the present invention, there was skepticism by experts that Cu-zeolites could be used to remediate NOx in diesel engines. In 2005, Dr. Roth, in his capacity as research group leader for NOx control catalysts at Engelhard Corporation (the predecessor in interest to the assignee of the instant application) attempted to secure a Department of Energy (DOE) funding for a proposal to study Cu-zeolites for SCR o

NOx. However, the experts at the DOE concluded that Cu-exchanged zeolites lack the hydrothermal stability needed to be commercially viable for SCR of NOx with ammonia for diesel engines. Roth Declaration, ¶ 6. In fact, Dr. Roth was told that several reviewers and the DOE grant manager felt Cu zeolites were far too unstable to be commercially feasible. Roth Declaration, ¶ 7. The DOE further stated that "several other investigators who are presumable experts in the area" were equally skeptical about the prospects of using Cu zeolites for SCR of NOx in diesel engines. Roth Declaration, ¶ 8. Such expressions of skepticism and disbelief by experts is strong evidence of non-obviousness. See *Environmental Designs, Ltd. v. Union Oil Co-.,* 713 F. 2d 693, 698 (Fed. Cir. 1983), *cert. denied*, 464 U.S. 1043 (1984) ("Expressions of disbelief by experts constitute strong evidence of nonobviousness. *United States v. Adams, 383 U.S. 39, 52, 15 L. Ed. 2d 572, 86 S. Ct. 708 (1966).*").

The Roth Declaration also provides evidence of long-felt need. As explained in the Roth Declaration, the very recent literature, recognizing the excellent results provided by the instant invention have called the problem of NOx reduction in lean burn engines such as diesel engines "daunting." Roth Declaration, ¶ 10. At the time of the invention, impending Tier 2 Bin 5 standards were requiring higher NOx conversion, which the authors at Ford Motor Company recognized as "especially challenging" for temperatures in the range of 200° to 350° C. While there were Cu/zeolite catalysts that delivered fresh performance, their performance degraded over time as a result of high temperature deactivation. Roth Declaration, ¶ 11. The present invention satisfied a long-standing need, and the Ford Motor Company researchers indicated that the material used in the process of the present invention was a "remarkable" Cu/zeolite that showed high NOx conversion in the low temperature range. Roth Declaration, ¶ 11. The instant situation is similar to that in the Environmental Designs case cited above, where the Federal Circuit affirmed a district court decision finding that the claimed process filled a long felt need in the face of stricter environmental regulations. The claimed process in Environmental Designs also had been denigrated by the experts and the court concluded that the invention as a whole would not have been obvious at the time it was made to one of ordinary skill in the art. *See Environmental Designs,* 713 F.2d at 697-98 ("That the need was legislatively recognized in this case does not militate against its existence. There as a long felt need to remove as much sulfur as possible from the air we breathe.")

CONCLUSION

It is believed that claims 33-38 and 40-47 are now in condition for allowance, early notice of which would be appreciated. No additional fees are believed due. If any additional fees are due, the Commissioner is authorized to charge Deposit Account No. 50-3329. Please contact the undersigned if any further issues remain to be addressed in connection with this submission.

Date: January 24, 2011 Respectfully submitted,

By: /Scott S. Servilla, Reg. #40806/
Scott S. Servilla
Reg. No. 40,806
Tel. No. (732) 815-0404

BASF Corporation
100 Campus Drive
Florham Park, New Jersey 07932

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BASF CORPORATION
100 CAMPUS DRIVE
FLORHAM PARK, NJ 07932

EXAMINER	
WOOD, ELIZABETH D	
ART UNIT	**PAPER NUMBER**
1732	
NOTIFICATION DATE	**DELIVERY MODE**
02/01/2012	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

sonny.nkansa@basf.com
Melanie.Brown@basf.com

PTOL-90A (Rev. 04/07)

Office Action Summary	Application No.	Applicant(s)	
	12/480,360	BULL ET AL.	
	Examiner	Art Unit	
	ELIZABETH WOOD	1732	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *24 January 2011*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.

4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *20-38 and 40-48* is/are pending in the application.

5a) Of the above claim(s) _____ is/are withdrawn from consideration.

6)☐ Claim(s) _____ is/are allowed.

7)☒ Claim(s) *20-38 and 40-48* is/are rejected.

8)☐ Claim(s) _____ is/are objected to.

9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

10)☐ The specification is objected to by the Examiner.

11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

12)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

13)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☐ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date *1/24/11, 2/24/11, 5/6/11, 7/15/11, 12/20/11, 1/24/12*.
4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

Continued Examination Under 37 CFR 1.114

A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on January 24, 2011 has been entered.

Specification

The examiner has not checked the specification to the extent necessary to determine the presence of **all** possible minor errors (grammatical, typographical and idiomatic). Cooperation of the applicant(s) is requested in correcting any errors of which applicant(s) may become aware of in the specification, in the claims and in any future amendment(s) that applicant(s) may file.

Applicant(s) is also requested to complete the status of any copending applications referred to in the specification by their Attorney Docket Number or Application Serial Number, **if any**.

The status of the parent application(s) and/or any other application(s) cross-referenced to this application, if **any**, should be updated in a timely manner.

Information Disclosure Statement

The information disclosure statements filed have been considered as set forth in MPEP 609. Once the minimum requirements of 37 C.F.R. 1.97 and 1.98 are met, the examiner has the obligation to consider the information. Consideration by the examiner of the information submitted in an IDS means nothing more than considering the documents in the same manner that other documents in Office search files are considered by the examiner while conducting a search of the prior art in a proper field of search. The initials of the examiner placed adjacent to the citations on the PTO-1449 or PTO/SB/08A and 08B, or its equivalent, mean that the examiner to the extent noted above has considered the information. See MPEP 609.05(b) Rev. 5.

Applicant should note that documents not in the English language have been considered only to the extent of statements of relevance, explanations provided in the corresponding search reports provided and provided translations.

Status of Claims

The allowability of claims 20-32 is hereby WITHDRAWN. The following is a complete disposition of pending claims 20-38 and 40-48.

Claim Rejections - 35 USC § 112

The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

The following is a quotation of the second paragraph of 35 U.S.C. 112:

> The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter which the applicant regards as his invention.

The following is a quotation of the fourth paragraph of 35 U.S.C. 112:

Subject to the [fifth paragraph of 35 U.S.C. 112], a claim in dependent form shall contain a reference to a claim previously set forth and then specify a further limitation of the subject matter claimed. A claim in dependent form shall be construed to incorporate by reference all the limitations of the claim to which it refers.

Claims 22, 23, 25, 26, 33, 34, 36, 45, 47 and 48 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

With respect to claims 22, 23, 25, 26, they recite the language “adapted to”. This terminology is unclear and is not defined by the specification. The word “adapted” implies some particular feature independent from the identity of the composition to produce such characteristic. If the result naturally flows from the identity of the composition, then the language is redundant as there has been no adaptation.

Claim 33 recites “sufficient copper including non-exchanged copper to prevent thermal degradation of the zeolite”. As "sufficient" is an undefined term, and the specification provides no direct nexus between the amount of non-exchanged copper and thermal degradation in the absence of participation from any other features of the composition, the claim is unclear.

Claim 36 further recites “contains …an amount of non-exchanged copper sufficient to maintain NOx conversion". As the “amount" is an undefined term, and the specification provides no direct nexus between the amount of non-exchanged copper and the conversion in the absence of participation from any other features of the composition, the claim is unclear. The language “to maintain" is also unclear. The most minimal performance would fall within this limitation, which is clearly not the intent of the invention.

Claim 34 should recite "structure" after "crystal" in line 2.

Claim 45 recites "wherein and the" which is unclear.

Claim 47 recites a comparison to beta zeolite under "similar conditions" which provides "improved" activity and stability. The improvement is not defined, demonstrated or categorized, (and is also a relative term with no point of reference) and "similar" conditions are insufficient for an adequate comparison. Applicant apparently relies merely on this functional language if to support novelty, and thus renders the claim indefinite.

Claims 34 and 35 are rejected under 35 U.S.C. 112, 4th paragraph, as being of improper dependent form for failing to further limit the subject matter of the claim upon which it depends, or for failing to include all the limitations of the claim upon which it depends. These claims merely recite retention of the crystal structure of the zeolite under certain conditions. This recitation in no way limits the process steps of the process under consideration in this application. Applicant may cancel the claim(s), amend the claim(s) to place the claim(s) in proper dependent form, or present a sufficient showing that the dependent claim(s) complies with the statutory requirements.

Claims 33-38 and 40-48 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the enablement requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention.

The specification does not provide sufficient information as to the manner in which an artisan would determine whether the composition employed in the process of claim 33 actually prevents thermal degradation. No degree of degradation is specified, and the artisan would be forced to test myriad compositions within the scope of the claims to determine whether or not such degradation was prevented, as well as make a determination regarding the degree of degradation. Such is clearly a situation involving undue experimentation. The same reasoning applies with respect to the “amount of non-exchanged copper sufficient to maintain NOx conversion”. As other factors regarding process steps and catalyst compositional limitations are also in play, and there is no demonstration of a nexus between this single limitation and the maintenance of conversion, the burden of undue experimentation would fall on those attempting to make a determination as to the compositions within the scope of these claims. The language “exhibits less than a 10% decrease in NOx conversion” in claim 46 provides slightly more guidance, but remains functional in nature and no catalyst limitations are recited that would account for such a characteristic. Accordingly, the skilled artisan would be required to test a potentially infinite number of supported copper promoted CHA materials to determine which would fall within the scope of the claim. Claim 47 further recites “exhibiting improved low temperature activity and hydrothermal stability compared to Cu Beta zeolite under similar conditions”. This terminology also would require the artisan to test untold numbers of catalysts to determine if this improvement is obtained, thus amounting to a situation requiring undue experimentation to determine the scope of the claims under examination.

Claim Rejections - 35 USC § 103

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

The factual inquiries set forth in *Graham* v. *John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966), that are applied for establishing a background for determining obviousness under 35 U.S.C. 103(a) are summarized as follows:

1. Determining the scope and contents of the prior art.
2. Ascertaining the differences between the prior art and the claims at issue.
3. Resolving the level of ordinary skill in the pertinent art.
4. Considering objective evidence present in the application indicating obviousness or nonobviousness.

This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

Claim 20 is rejected under 35 U.S.C. 103(a) as being unpatentable over US 6,709,644 to Zones et al. in view of the Ishihara et al. article "copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6".

Zones et al. is relied on for the disclosure that a chabazite zeolite having a ratio of silica to alumina consistent with the instantly claimed invention and containing copper is known to be effective in a process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen, preferably in the exhaust stream of an internal combustion engine. Zones et al. differs from the instantly claimed invention in the failure to specifically recite that the ratio of copper to aluminum is within the herein claimed range. However, Zones et al. do specify that the amount of copper to be employed is that capable of catalyzing the reduction of oxides of nitrogen in an excess of oxygen. Accordingly, Zones et al. firmly establish the required amount of copper as a result effective variable for nitrogen reduction processes. See particularly column 1, column 4 and the examples.

Ishihara et al. are relied on for the analogous process for reducing oxides of nitrogen using a SAPO-34 catalyst composition (CHA) of high silica to alumina ratio and containing on the order of 3 to 4% copper, thus establishing the effective amount required to use for this process. Accordingly it would have been obvious to employ this amount of copper in the compositions of Zones et al. during nitrogen reduction processes to arrive at the instantly claimed process. The amount of copper employed by Ishihara et al. in the catalyst and process of Zones et al. will be expected to result in a composition having an atomic ratio of copper to aluminum of from about 0.25 to about 0.50 as claimed in the instant application. See particularly the experimental section of Ishihara et al.

Claim 21-26 are rejected under 35 U.S.C. 103(a) as being unpatentable over US 6,709,644 to Zones et al. in view of the Ishihara et al. article “copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6” as applied to claim 20 above and further in view of US 2006/0039843 to Patchett et al.

With respect to claims 21 - 26 there are further requirements that the catalyst be disposed on a honeycomb flow thru substrate, the exhaust gas comprises ammonia, and portions of the substrate are coated with copper CHA. Patchett et al. are relied on for the disclosure of a substantially related process for the reduction of nitrogen oxide emissions in the exhaust stream of an internal combustion engine, employing SCR catalyst compositions. Patchett et al. disclose that several SCR catalysts containing a copper-exchanged zeolite coated on a wall flow or flow through substrates substantially as claimed in the instant application and adoption of this feature would have3 been obvious to the skilled artisan practicing in this field and desirous of placing the catalyst composition as a part of an entire emission treatment system. Patchett et al. further teach that the substrate comprising the SCR catalyst also contains an ammonia destruction catalyst composition comprising a platinum group metal, and it is clear that the excess ammonia in the exhaust stream is oxidized. The examiner takes the position that the skilled artisan would have found it obvious to employ any known system organization of the component parts, as taught by Patchett et al., since the system described in the instant process claims is notoriously well known in this field of endeavor. See particularly the figures and description thereof and pages 1-2.

Claims 27, 28, and 30-32 are rejected under 35 U.S.C. 103(a) as being unpatentable over US 6,709,644 to Zones et al. in view of the Ishihara et al. article “copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6” as applied to claim 20 above and further in view of US 2005/0031514 to Patchett et al.

These claims further require the presence of oxidation and/or catalyzed soot filter upstream of an SCR catalyst. Patchett et al. are relied on for the disclosure of a substantially related process for the reduction of nitrogen oxide emissions in the exhaust stream of an internal combustion engine, employing SCR catalyst compositions . Patchett et al. disclose that analogous SCR catalysts containing a copper-exchanged zeolite composition may be used in concert with one or more of a diesel oxidation catalyst and a soot filter upstream of the SCR catalyst as claimed in the instant application and adoption of this feature would have3 been obvious to the skilled artisan practicing in this field and desirous of placing the catalyst composition as a part of an entire emission treatment system. The examiner takes the position that the skilled artisan would have found it obvious to employ any known system organization of the component parts, as taught by Patchett et al. See particularly the figures and pages 2-6.

Claims 27 and 29 are rejected under 35 U.S.C. 103(a) as being unpatentable over US 6,709,644 to Zones et al. in view of the Ishihara et al. article "copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6" as applied to claim 20 above and further in view of US 2004/0098973 to Tennison et al.

With respect to claims reciting a soot filter in downstream location, Tennison et al. are is relied on for the disclosure of a substantially related process for the reduction of nitrogen oxide emissions in the exhaust stream of an internal combustion engine, employing SCR catalyst compositions . Tennison et al. disclose a zeolite containing SCR catalyst and a catalyzed filter down stream substantially as claimed in the instant application and adoption of this feature would have been obvious to the skilled artisan practicing in this field and desirous of placing the catalyst composition as a part of an entire emission treatment system. The examiner takes the position that the skilled artisan would have found it obvious to employ any known system organization of the component parts, as taught by Tennison et al. See particularly the claims and paragraphs {0006], [0009], [0010] and [0025].

Claims 33-48 are rejected under 35 U.S.C. 103(a) as being unpatentable over Ishihara et al. (Journal of Catalysis article), Ishihara et al. (Chemistry Letters article), Ishihara et al. (Ind. Eng. Chem. Res. article) or Ishihara et al. (Studies in Surface Science and catalysis article), each taken individually in view of US 7,049,261 to Nam et al. and US 2006/0039843 to Patchett et al.

The instantly claimed invention is directed to a method for reducing nitrogen oxides in an exhaust gas stream by employing a catalyst comprising a zeolite with the CHA crystal structure promoted with copper in the presence of a nitrogenous reductant.

Each of the Ishihara et al. articles is concerned with the production of SAPO-34 materials. Each of the references produces a material determined by X-ray diffraction to be SAPO-34, which is exchanged with copper. Each of the references teaches that the material is employed in processes for the reduction of nitrogen oxides, substantially as claimed in the instant application. Each of the references details the material to be highly thermally stable, which would indicate to the examiner that the material inherently possesses the characteristics herein claimed by applicant, as hydrothermal stability by definition means retaining functional crystallinity, pore size, acidity and so forth. As the material of the

Ishihara et al. references is indistinguishable from the instant claims and is thermally stable, the examiner can only conclude that the references include sufficient copper to prevent thermal degradation of the zeolite, thus rendering the instantly claimed process obvious. Moreover, to demonstrate this stability, the Ishihara et al. experiments detail treating the molecular sieve in a manner commensurate with that recited in the instant application. By treating the molecular sieves in a manner that mimics conditions of use (i.e. steam atmosphere, high temperatures), the figures in particular show that the material retains the ability to function with great effectiveness at 700C (or higher temperatures, although the references indicate that some loss ensues with increasing temperatures - Note page 1496 the Studies in Surface Science article which states that even calcination at 800C in wet air results in a relatively small decrease in activity). Accordingly, as the treatment method does not appear to differ substantially from that recited in the instant application, and as the references all produce materials they define to be hydrothermally stable and are not apparently patentably distinct from the Ishihara et al. disclosures, it can only be considered that the references teach the same process being recited by applicant in the instant claims. See particularly the experimental data and tables in each of the applied Ishihara et al. references.

The Ishihara references differ from the instant claims in the requirement that the reductant be nitrogenous.

Nam et al. are relied on for the disclosure that related copper zeolites known to abate nitrogen oxides across a broad temperature range can be used for both nitrogenous and hydrocarbon reductant processes. Accordingly, in view of this teaching of equivalence, the examiner takes the position that the skilled artisan armed with the prior art of record would have a more than reasonable expectation that the compositions of Ishihara would be equally effective in NOx abatement with any nitrogenous reluctant.

With respect to the limitation regarding the presence of non-exchanged copper, it is pointed out that as the Ishihara et al references do not wash their catalyst prior to calcination, it is reasonable to conclude that "free" or "non-exchanged" copper will be present, and the presence thereof will result in the claimed “sufficient to maintain NOx conversion” and the specified NOx conversions after hydrothermal aging which are substantially shown by the Ishihara et al. references. Furthermore, Nam et al. teach that the composition containing 2.5% to 3.5% copper had sufficient excess copper (after ion-exchange) to provide copper ions that lump into a mass, forming a metal oxide. This is substantially what the examiner considers occurs in the Ishihara et al. references and in applicant’s catalyst, particularly in view of the fact that all of the applied prior art teaches their composition to be highly thermally stable under water vapor conditions, high temperatures and for long periods of time. In view of this, it is considered that claims reciting retention of CHA crystal structure would naturally flow from the Ishihara et al. documents. Further, claims reciting certain decreases in conversion after hydrothermal again are within the purview of the Ishihara compositions, as is also the limitation regarding improved low temperature activity and hydrothermal stability. Additionally, Nam et al.

specifically teach low temperature activity. All of these claimed features are considered clearly shared by the prior art catalyst materials(in contrast to the affidavit arguing unexpected results due to low temperature performance). As a result, the examiner considers that the preponderance of the evidence on this record indicates that the references of record render the instantly claimed process obvious. See particularly columns 1-3.

The Ishihara et al. references additionally fail to teach a supported material, particularly supported on a wall slow filter or honeycomb flow through substrate. The Ishihara et al. references also fail to teach a further downstream catalyst also comprising a CuCHA zeolite which can contain precious metal.

Patchett et al. are relied on for the disclosure of a substantially related process for the reduction of nitrogen oxide emissions in the exhaust stream of an internal combustion engine, employing SCR catalyst compositions . Patchett et al. disclose that several SCR catalysts containing a copper-exchanged zeolite coated on a wall flow or flow through substrates substantially as claimed in the instant application and adoption of this feature would have3 been obvious to the skilled artisan practicing in this field and desirous of placing the catalyst composition as a part of an entire emission treatment system. Patchett et al. further teach that the substrate comprising the SCR catalyst also contains an ammonia destruction catalyst composition comprising a platinum group metal, and it is clear that the excess ammonia in the exhaust stream is oxidized. The examiner takes the position that the skilled artisan would have found it obvious to employ any known system organization of the component parts, as taught by

Patchett et al., as the system described in the instant process claims is notoriously well known in this field of endeavor.

Response to Arguments

Applicant's arguments with respect to the previous rejections are moot in view of the new grounds of rejection. However, it should be noted that the examiner has considered the arguments and affidavit asserting that there is no equivalence between nitrogen oxide reducing processes employing nitrogenous reductants as compared to hydrocarbon reductants. The examiner's position with respect thereto is set forth in the hereinabove rejection(s), but the following is added for emphasis. The examiner does not agree that the instant specification is clearly directed to nitrogenous reductants only. The skilled artisan possessing the claimed disclosure would not find it unobvious to experiment with hydrocarbon reductants, as the specification clearly indicates such are within the broad aspects of the disclosure, and because the claims themselves are not so limited. Applicant argues differences in the conditions of the processes and that they “do not correlate”, and that the Ishihara material has inferior “low temperature activity”. This is not convincing as there is nothing on this record that links an improvement in such activity to the claims under examination. The Ishihara reference clearly that significant conversion at temperatures across a wide range. Further, there is significant prior art of record in this application (Halasz article and US 7049261, among others) as well as **numerous** documents provided by the applicant from reexamination proceeding

95/001,453 that support the equivalence between the two reductants; thus the examiner has weighed the evidence on this record of the opinion affidavit and argument as compared to the prior art and other affidavits asserting that one of ordinary skill in this field of endeavor would indeed consider the reductants equivalent and finds that the preponderance of the evidence in this file wrapper supports the position that regardless of the mechanism of the reaction, one of ordinary skill in the art has a more than reasonable expectation that a catalyst that functions with an ammonia reductant will also function with a hydrocarbon reductant.

Applicant should note the article to Centi et al. that teaches that copper zeolites are active in a wider range of NO transformations than other catalyst systems. Centi et al. further teach both low and high temperature applications, and notes that various copper zeolites function for HC, NH3 and CO transformations, in contrast to the arguments being presented in the instant application.

Applicant additionally argues that the Ishihara reference teach away from the conditions of the instant process, it is considered that the conditions under which the testing took place are not relevant because these reference specify that their catalysts can be used for NOx abatement in the exhaust gas of diesel or lean-burn engines. As a result, it is considered that this disclosure indicates functionality of the compositions in the herein claimed process. Clearly Ishihara teach significant conversions of NO at temperatures as low as 300C, and further clearly teach low temperature reduction of oxides of nitrogen across a broad temperature range. Where the claims recite amounts of copper , such are completely commensurate with the amounts employed by the Ishihara et al. references and Nam et al. applied hereinabove.

Conclusion

Applicants are advised that any evidence to be provided under 37 CFR 1.131 or 1.132 and any amendments to the claims and specification should be submitted prior to final rejection to be considered timely. It is anticipated that the next office action will be a final rejection.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to ELIZABETH WOOD whose telephone number is (571)272-1377. The examiner can normally be reached on M-F, 6:30-3:00.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Curtis Mayes can be reached on 571-272-1234. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Elizabeth D. Wood/
Primary Examiner, Art Unit 1732

/E. W./
Primary Examiner, Art Unit 1732

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

First Named Inventor:	Ivor Bull	Examiner	Wood, Elizabeth D.
Serial No.:	12/480,360	Group Art Unit	1732
Filed:	Jun 8, 2009	Docket No.:	EH5328A
		Confirmation No.:	3250
Title:	Processes For Reducing Nitrogen Oxides Using Copper CHA Zeolite Catalysts		

AMENDMENT/RESPONSE UNDER 37 C.F.R. § 1.111

This paper is being submitted in response to the Non-Final Office Action dated February 1, 2012, in the above-identified patent application. The three month period for reply to the Office Action expires on May 1, 2012. Accordingly, this paper is being timely filed.

Amendments to the Claims begin on page 2.

Remarks begin on page 9.

IN THE CLAIMS

1. – 19. (Cancelled)

20. (Currently Amended) A process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process comprises contacting the gas stream with a catalyst comprising a zeolite having the CHA crystal structure and a mole ratio of silica to alumina from about 15 to about ~~256~~ 100 and an atomic ratio of copper to aluminum from about 0.25 to about 0.50.

21. (Previously presented) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb flow through substrate.

22. (Currently Amended) The process of claim 21, wherein the exhaust gas stream further comprises ammonia and at least a portion of the flow through substrate is coated with CuCHA ~~adapted to oxidize ammonia in the exhaust gas stream~~.

23. (Currently Amended) The process of claim 21, wherein at least a portion of the flow through substrate is coated with Pt and CuCHA ~~adapted~~ to oxidize ammonia in the exhaust gas stream.

24. (Previously Presented) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the catalyst is disposed on a honeycomb wall flow substrate.

25. (Currently Amended) The process of claim 24, wherein the exhaust gas stream further comprises ammonia and at least a portion of the wall flow substrate is coated with CuCHA ~~adapted to oxidize ammonia in the exhaust gas stream~~.

26. (Currently Amended) The process of claim 24, wherein at least a portion of the wall flow substrate is coated with Pt and CuCHA ~~adapted~~ to oxidize ammonia in the exhaust gas stream.

27. (Currently amended) The process of claim 20, wherein the gas stream is an exhaust gas stream from an internal combustion engine and the process further comprises contacting the exhaust gas stream with a catalyzed soot filter.

28. (Original) The process of claim 27, wherein said catalyzed soot filter is upstream of said catalyst.

29. (Original) The process of claim 27, wherein said catalyzed soot filter is downstream of said catalyst.

30. (Original) The process of claim 27, further comprising contacting the exhaust gas stream with a diesel oxidation catalyst.

31. (Original) The exhaust process of claim 30, wherein said diesel oxidation catalyst is upstream of said catalyst comprising a zeolite having the CHA crystal structure.

32. (Original) The exhaust process of claim 31, wherein said diesel oxidation catalyst and catalyzed soot filter are upstream from said catalyst comprising a zeolite having the CHA crystal structure.

33. (Currently Amended) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst deposited on a substrate, the catalyst comprising a zeolite having the CHA crystal structure having a silica to alumina mole ratio less than about 50 and promoted with ~~sufficient~~ copper to provide a copper to aluminum atomic ratio of about 0.25 to about 0.50 ~~including non exchanged copper~~ ~~to prevent thermal~~, the catalyst resistant to significant degradation of ~~the~~ ~~zeolite~~ fresh NOx conversion performance of the catalyst when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

34. (Cancelled)

35. (Cancelled)

36. (Currently Amended) The process of claim 33, wherein the zeolite contains ~~ion exchanged~~ copper ~~and an amount of non exchanged copper sufficient to~~ and the catalyst maintains about 90% of fresh NOx conversion ~~of the catalyst~~ in an exhaust gas stream containing nitrogen oxides

after hydrothermal aging of the catalyst temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours.

37. (Previously presented) The process of claim 33, wherein NOx conversion of the catalyst at about 200°C after hydrothermal aging in 10% steam at 850° C for 6 hours is at least 90% of the NOx conversion of the catalyst at about 200°C prior to hydrothermal aging.

38. (Previously presented) The process of claim 33, wherein at least about 90% of the oxides of nitrogen are reduced by the catalyst over the temperature range of about 250° C to 450° C.

39. (Cancelled)

40. (Previously presented) The process of claim 33, wherein the reductant is selected from ammonia and an ammonia precursor.

41. (Previously presented) The process of claim 40, further comprising contacting the exhaust gas stream with a downstream catalyst comprising a Cu-containing zeolite having the CHA crystal structure.

42. (Previously presented) The process of claim 41, wherein the downstream catalyst further comprises a precious metal.

43. (Previously presented) The process of claim 40, wherein the catalyst comprising a zeolite having the CHA crystal structure is disposed on a wall flow filter.

44. (Previously presented) The method of claim 33, wherein the reductant comprises urea.

45. (Currently amended) The method of claim 33, wherein ~~and~~ the catalyst is disposed on a honeycomb flow through substrate.

46. (Currently amended) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst comprising a zeolite having the CHA crystal structure deposited on a substrate, the zeolite promoted with copper, wherein the catalyst exhibits less than a 10% decrease in fresh NOx conversion with the nitrogenous reductant over a range from about 200° C to about 300° C following hydrothermal aging in 10% H_2O at 800° C for 50 hours.

47. (Currently Amended) A SCR process for the reduction of oxides of nitrogen contained in an exhaust gas stream from an internal combustion engine wherein said SCR process comprises contacting the gas stream with a nitrogenous reductant and a catalyst deposited on a substrate, the catalyst comprising a zeolite having the CHA crystal structure having a silica to alumina mole ratio less than about 50 and promoted with copper to provide a copper to aluminum atomici ratio of about 0.25 to about 0.50 and exhibiting ~~improved low temperature activity and hydrothermal stability compared to Cu Beta zeolite under similar conditions~~ higher NOx

conversion at about 210 °C after hydrothermal aging at about 850 °C in 10% steam for 6 hours, as compared to Cu Beta zeolite having a silica to alumina ratio of about 35 and a copper to aluminum ratio of about 0.36 and prepared, tested and hydrothermally aged under the same conditions as the zeolite having the CHA crystal structure.

48. (Previously presented) The SCR process according to claim 47, wherein the reductant comprises ammonia.

49. (New) The process of claim 33, wherein the mole ratio of silica to alumina is from about 15 to about 50.

50. (New) The process of claim 49, wherein the mole ratio of silica to alumina is from about 25 to about 40.

51. (New) The process of claim 33, wherein the zeolite is resistant to poisoning by long chain hydrocarbons.

52. (New) The process of claim 33, wherein the substrate comprises a wall flow substrate.

53. (New) The process of claim 33, wherein at least a portion of the wall flow substrate is coated with CuCHA.

54. (New) The process of claim 53, wherein at least a portion of the wall flow substrate is coated with Pt and CuCHA.

55. (New) The process of claim 33, wherein the catalyst is disposed downstream from a diesel

engine and an injector adds a urea reductant to an exhaust gas stream from the engine upstream of the catalyst.

INTERVIEW SUMMARY

The undersigned appreciates the courtesies extended by Examiner Wood in conducting an interview with the undersigned and Dr. Ahmad Moini at the United States Patent and Trademark Office on March 29, 2012. During the interview, Dr. Moini and the undersigned reviewed the unique advantages of the claimed invention and the differences between the claimed invention and the cited prior art. The proceedings in Reexamination Control Number 95/001,453, which involves the patent granted from the parent application of the instant application.

REMARKS

Claims 20-38 and 40-48 are pending in the application. Claims 20-38 and 40-48 are rejected. Claims 34, 35 and 39 have been cancelled. No claims are allowed.

Claims 20, 22-27, 33, 36, 45, 46 and 47 have been amended to more clearly describe and distinctly claim the subject matter the Applicants consider their invention. Claims 27 and 45 have been amended to correct minor informalities.

New claims 49-55 have been added. No new matter has been added by this amendment.

Claim Rejections – 35 U.S.C. § 112

Rejections under 35 U.S.C. 112, second paragraph

Claims 22, 23, 25, 26, 27, 33, 34, 36, 45, 47 and 48 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. The "adapted to" language objected to in the office action has been removed from the claims, rendering this rejection moot.

Claim 33 was rejected for reciting the language "sufficient copper. . . " Claim 33 has been amended to remove the language "sufficient copper. . . ". Claim 33 now recites that the catalyst is promoted with copper to provide a specific copper to aluminum ratio and and the catalyst is resistant to significant degradation of fresh NOx conversion performance of the catalyst when exposed hydrothermal aging conditions. Support for this amendment can be found throughout the specification, and Example 3, among other examples shows that there is little degradation of the fresh performance of the catalyst, which shown in Table 1 and paragraph 0094, in that samples retained up to 95% of their fresh NOx conversion after hydrothermal aging.

Claim 36 has also been amended to remove the "sufficient to . . ." language objected to by the Examiner. Claim 36 has also been amended to recite that the catalyst maintains 90% of fresh NOx conversion after aging. Support for this amendment can be found at least at pargarph 0009 of the originally filed specification. More specifically, claim 47 has been amended to recite the claimed zeolite has higher NOx conversion at about 210 °C after hydrothermal aging at 850 °C in 10% steam for 6 hours, as compared to Cu Beta zeolite having a silica to alumina ratio of about 35 and a copper to aluminum ratio of about 0.36 and prepared, tested and hydrothermally aged under the same conditions as the zeolite having the CHA crystal structure. This is clear from the Examples.

Claim 47 has been amended to specifically recite the conditions under which the beta zeolite and the claimed zeolite were compared, based upon the Examples, namely Comparative Example 11 with the examples in accordance with the claimed invention.

Rejection of Claims 34 and 35 under 35 U.S.C. 112, 4th paragraph

Claims 34 and 35 are rejected under 35 U.S.C. 112, 4th paragraph, as being of improper dependent form for failing to further limit the subject matter of the claim upon which it depends, or for failing to include all the limitations of the claim upon which it depends. While the Applicants disagree with this basis of the rejection, claims 34 and 35 have been canceled without prejudice to refilling claims containing these limitations at a later time.

However, it should be noted that MPEP Section 608.01(n) states, with reference to 37 CFR 1.75(c): "Any claim which is in dependent form but which is so worded that it, in fact is not, as, for example, it does not include every limitation of the claim on which it depends, will be required to be canceled as not being a proper dependent claim; and cancelation of any further claim depending on such a dependent claim will be similarly required." The Examiner cites no further authority for the rejection of claims 34 and 35. However, claims 34 and 35 as submitted meet the standard set forth in MPEP Section 608.01(n)—claims 34 and 35 include as presented include every limitation of claim 33. On this basis alone, the rejection should be withdrawn.

Original Claim 34 recited that the zeolite having the CHA crystal structure retains the CHA crystal structure as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 600°C and high water vapor environments of about 10% or more for at least about 6 hours. Original Claim as 35 recited that the zeolite retains the CHA crystal structure as indicated by X-ray powder diffraction over the range of 15 to 38.5 degrees two theta when exposed to temperatures of at least about 800°C and high water vapor environments of about 10% or more for at least about 48 hours. The claim from which claims 34 and 35 depend, claim 33, does not recite this limitation. The Office Action states that this in no way limits the process steps of the process under consideration in the application.

However, claims 34 and 35 as originally presented recited a feature of the zeolite that is not recited in claim 33. The Federal Circuit has observed that "practice has long recognized that claims may be multiplied ... to define the metes and bounds of the invention in a variety of different ways. Thus two claims which read differently can cover the same subject matter." *Tandon Corp. v. United States Int'l Trade Comm'n*, 831 F.2d 1017, 1023 (affirming the International Trade Commission's holding that "the inclusion of the term 'non-gimballed' in claim 5 did not require that claims 1 and 12 be read to encompass a gimballed first transducer").

Thus, claim 33, which does not include the limitation with maintain crystallinity, for example, perhaps a moderate amount crystallinity loss is possible, while claims 34 and 35 exclude catalysts lose crystallinity as defined.

Enablement Rejection of Claims 33-38 and 40-48

Claims 33-38 and 40-48 are rejected under 35 U.S. C. 112, first paragraph, as failing to comply with the enablement requirement. It is respectfully submitted that claims 33-38 and 40-48 are now enabled. The claims now recite specific conditions for testing and hydrothermal aging, and that the claimed catalyst exhibits "higher" NOx conversion over a specific Cu-Beta. These conditions are clearly set forth in the working and comparative examples, and use nearly identical language in the Examples. The stated conditions are all well within the abilities of one of ordinary skill in the art because they are clearly laid out in the Examples. A specific test under a specific set of conditions to compare with a specific Cu-Beta zeolite having a Cu/Al and silica to alumina ratio is provided. As such, no undue experimentation is required.

Claim Rejections – 35 U.S.C. § 103

Rejections Based on Zones in View of Ishihara

Claim 20 is rejected under 35 U.S.C. §103(a) as being unpatentable over United States Patent No. 6,709,644 ("Zones") in view of the Ishihara et al. article "Copper Ion-Exchanged SAPO-34 as a Thermostable Catalyst for Selective Reduction of NO with C3H6" ("Ishihara").

Claim 21-26 are rejected under 35 U.S.C. §103(a) as being unpatentable over Zones et al. in view of Ishihara as applied to claim 20 above and further in view of US 2006/0039843 to Patchett et al.

Claims 27, 28, and 30-32 are rejected under 35 U.S.C. §103(a) as being unpatentable over Zones in view of Ishihara as applied to claim 20 above and further in view of US 2005/0031514 to Patchett et al.

Claims 27 and 29 are rejected under 35 U.S.C. §103(a) as being unpatentable over Zones in view of the Ishihara as applied to claim 20 above and further in view of US 2004/0098973 to Tennison et al.

Each of the above rejections is based on Zones in view of Ishihara. As was discussed at length in the interview, Zones does not disclose or suggest the use of a zeolite having the CHA crystal structure with the recited silica to alumina ratio or the specific copper to aluminum ratio. Moreover, Zones is silent on the use of a reductant in a selective catalytic reduction process for reducing oxides of nitrogen. Dr. Zones himself has provided a declaration dated February 7, 2011 attesting to this in Reexamination Control number 95/001,453:

> 10. The '644 patent does not specifically disclose or suggest that the zeolite having the CHA crystal structure is useful for selective catalytic reduction of oxides of nitrogen in the presence of a reductant, such as ammonia. There is no discussion, suggestion or example in the '644 patent indicating that a zeolite having the CHA crystal structure containing copper exhibits improved selective catalytic reduction of oxides of nitrogen at temperatures below 350° C compared to other zeolites, or that a zeolite having the CHA crystal structure and containing copper maintains excellent conversion of oxides of nitrogen after hydrothermal aging at temperatures in excess of 650° C and 10% H_2O. I understand that many zeolites containing copper and other metals have had limited application as selective catalytic reduction catalysts in diesel engines because of problems related to maintenance of good nitrogen oxide conversion upon hydrothermal exposure at temperatures in excess of 650° C.

As was discussed at length in the interview, all zeolites that are promoted with a promoter metal such as copper, cobalt, nickel, ceria, etc. are expect to have **some** activity in the reduction of oxides of nitrogen. But the question of obviousness of the presently claimed invention is not whether the claimed process would have exhibited **some** activity, but whether the claimed process would have **excellent** activity at temperatures below 350° C that is maintained after hydrothermal aging. Failure to consider the excellent attributes of the copper promoted CHA materials of the present invention including excellent low temperature conversion after hydrothermal aging, resistance to poisoning from hydrocarbons and low generation (make) of N_2O, a greenhouse gas, fails to consider the invention as a whole.

It has long been the law that ascertaining the differences between the prior art and the claims at issue requires interpreting the claim language, and considering **both the invention** and the prior art references **as a whole**. "In delineating the invention as a whole, we look not only to the subject matter which is literally recited in the claim in question... but also to those properties of the subject matter which are inherent in the subject matter *and* are disclosed in the specification. . . Just as we look to a chemical and its properties when we examine the obviousness of a composition of matter claim, it is this invention *as a whole,* and not some part of it, which must be obvious under 35 U.S.C. 103." *In re Antonie*, 559 F.2d 618, 620, 195 USPQ 6,8 (CCPA 1977) (emphasis in original).

In the case *In re Goodwin*, 576 F.2d 375, 376 (C.C.P.A. 1978) *aff'd*, 599 F.2d 1060 (C.C.P.A. 1979), the court upheld patentability of process claims directed to applying carbon monofluoride lubricants to glass mold cavities heated up to 700° F when the Margrave reference disclosed carbon monofluorides useful as solid lubricants and stable in oxidizing atmospheres at temperatures up to 800° C in combination with a second reference that disclosed a similar glass molding process. However, the CCPA reversed the Board, holding that "[t]hePTO has shown no evidence to overcome appellants' argument that 'on a fair reading of Margrave et al. there is no suggestion of the use of carbon monofluoride at a temperature in excess of 800° C and particularly not those temperatures of use taught in the disclosure of the subject application, i. e., 982° -1204° C.'" *Id.* at 377. In so holding, the court noted that "[w]hile the prior art teaches use of the compounds as lubricants with characteristics that are valuable to appellants, it also teaches their use below temperatures necessarily used in appellants' technology." *Id.*

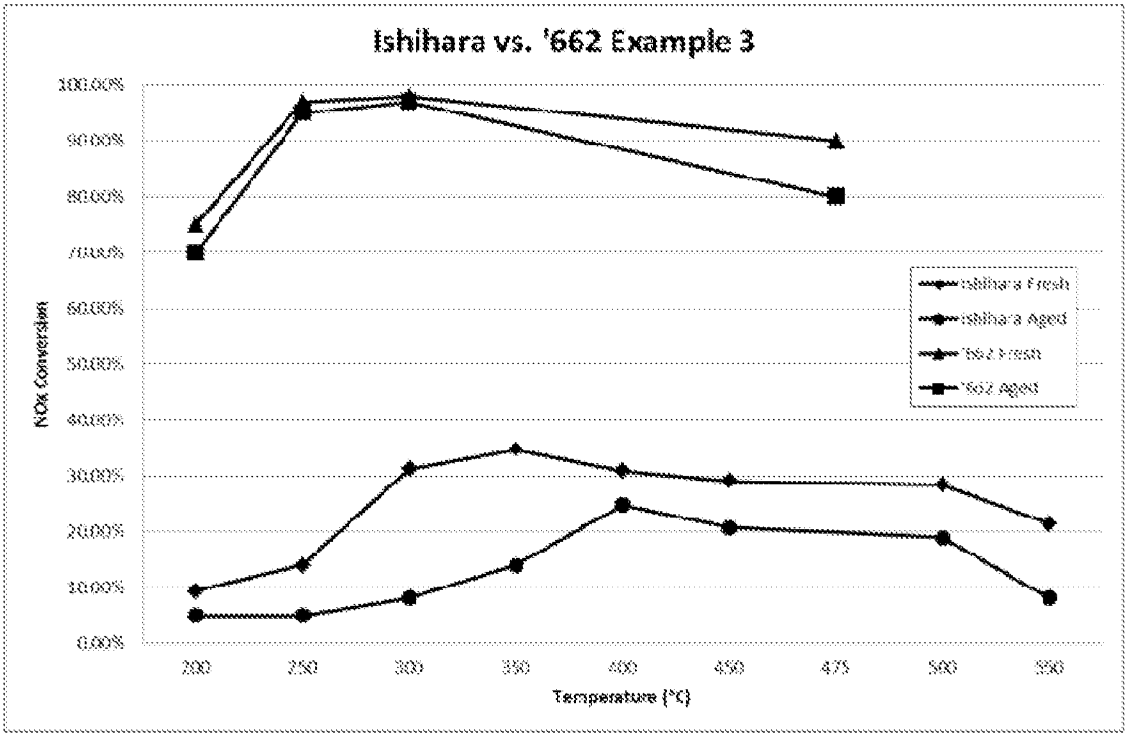
In Zones, there is no recognition whatsoever that the zeolite having the CHA crystal structure promoted with any amount of copper would be particularly useful for excellent low temperature NOx conversion after aging, low generation of N_2O or resistance to poisoning from hydrocarbons.

Ishihara is relied upon in the Office Action as allegedly teaching a process for reducing oxides of nitrogen using a SAPO-34 catalyst composition (CHA) of high silica to alumina ratio and containing 3 to 4% copper. The Office Action concludes that it would have been obvious to employ this amount of copper in the compositions of Zones to arrive at the instantly claimed process.

As stated in the *KSR* decision, "it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does." 550 U.S at 401. The requirement was restated in in *Esai Co. Ltd. v. Dr. Reddy's Labs., Inc.*, 533 F.3d 1353, 1359 (Fed. Cir. 2009): "the Supreme Court's analysis in *KSR* presumes that the record before the time of invention would supply some reasons for narrowing the prior art universe to a "finite number of identified, predictable solutions."

As was discussed at length in the interview, Ishihara provides no reason to select a CHA structured material to narrow the prior art universe of molecular sieves to materials having the

CHA crystal structure. The results from Figure 5(a) of Ishihara, which were under milder hydrothermal aging conditions and at testing conditions than used in the Examples of the present patent application that would be expected to generate much higher conversions, are directly compared with Example 3 of the present invention.



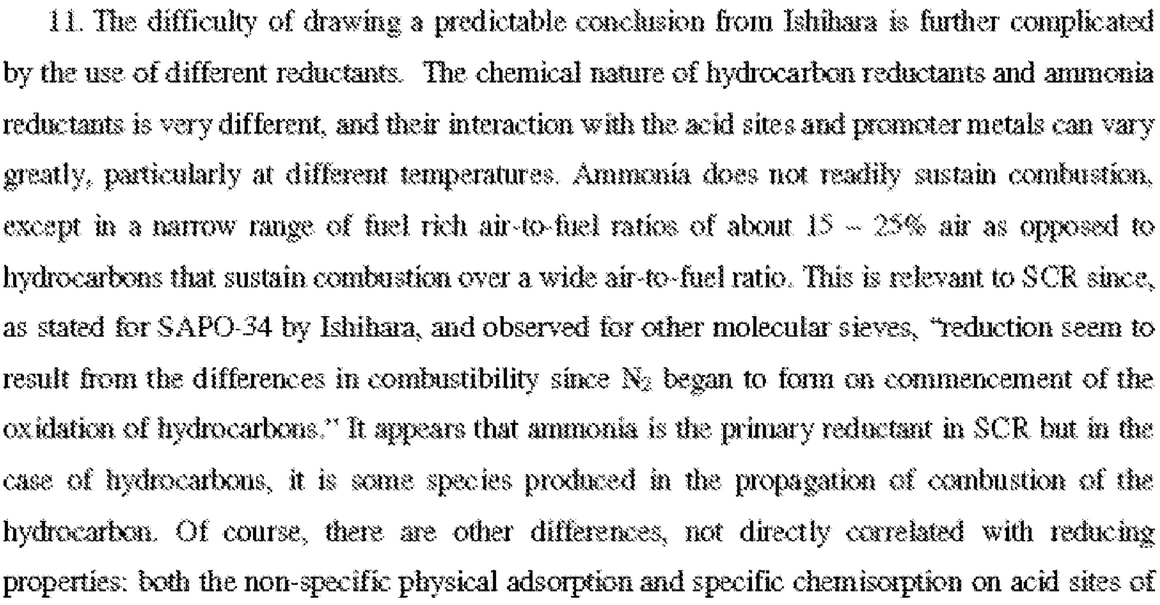
As the above graph plainly shows, the aged conversion in Ishihara (which was aged at less severe conditions than in the Examples of the instant patent application and at much lower space velocity (which would provide higher conversion) was below 10% at 300° C and below. Ishihara hardly provides a reason to use a CHA structured material that provides excellent low temperature NOx conversion, regardless of the reductant used. For at least the above reasons, a *prima facie* case of obviousness has not been established by the combination of Zones and Ishihara. If anything, Ishihara teaches away from CHA structured materials because the NOx conversion at low temperatures after aging is extremely poor. At 350° C, the NOx conversion after aging at 800° C in 3% H2O is approximately 14%. Compared to the fresh samples shown in Figure 1 of Ishihara, the decline in NOx conversion at 300° C was approximately 73%, which was a higher percentage decline in NOx conversion than the CuZSM-5 material tested. It is also noted that the samples in Ishihara were run at a low space velocity (8500 h-1). Typical space velocities in automotive applications are approximately ten times the space velocity in Ishihara (as tested in the instant patent appliation), and higher space velocity testing results in lower conversion. The CuSAPO-34 material showed a significant degradation of catalytic activity after hydrothermal aging at moderate conditions of 3% H_2O. Moreover, the fresh conversion at 300° C is significantly reduced from about 30% to less than 10% after aging.

Hydrocarbon SCR v. Ammonia SCR

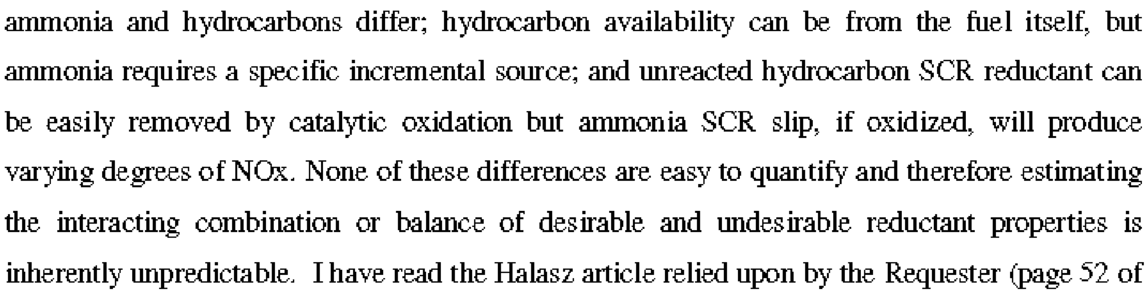
The differences between hydrocarbon SCR and ammonia SCR were also discussed during the interview. Aside from Ishihara teaching that materials with the CHA structure were poor candidates for low temperature NOx conversion after aging, Ishihara used a hydrocarbon reductant. As explained by Dr. Haller in a first declaration submitted in the Reexamination Control No. 95/001,143:

> 9. With respect to reduction of oxides of nitrogen in the presence of a reducing agent, in general, different reducing agents preferentially adsorb on different sites in different forms and lead to different mechanisms of action. In other words, the activity and mechanism of action of a particular reducing agent are not good predictors of the reactivity of different reducing agents on a particular zeolite catalyst. Alkenes, e.g., ethene or propene, are particularly effective reducing agents for NO on metal exchanged zeolites and it is generally agreed that these alkenes are preferentially adsorbed on acid sites. In contrast, while ammonia is a base that will adsorb on acid sites, "Ammonia readily reacts with copper ions especially in zeolite cavities forming copper-ammine complexes that have been characterized by several techniques such as adsorption measurements [24, 31], X-ray diffraction [313], ESR [38, 314-316], IR [38, 315, 317] and X-ray absorption [268] spectroscopies." *See* G. Centi and S. Perathoner, Applied Catalysis A: General 132, 1995, page 216, first sentence in section 4.3 (Exhibit C). It is for this reason that NO reduction by hydrocarbons and NO reduction by ammonia on Cu zeolites do not generally have parallel behavior and why using the results of hydrocarbon reduction of NO is not a good guide to NO reduction by ammonia on the same Cu zeolite, let alone for two different Cu zeolite catalysts when the structure type and/or composition of the zeolites are different.

In a second Declaration submitted in Reexamination Control No. 95/001,143, Dr. Haller stated:



11. The difficulty of drawing a predictable conclusion from Ishihara is further complicated by the use of different reductants. The chemical nature of hydrocarbon reductants and ammonia reductants is very different, and their interaction with the acid sites and promoter metals can vary greatly, particularly at different temperatures. Ammonia does not readily sustain combustion, except in a narrow range of fuel rich air-to-fuel ratios of about 15 – 25% air as opposed to hydrocarbons that sustain combustion over a wide air-to-fuel ratio. This is relevant to SCR since, as stated for SAPO-34 by Ishihara, and observed for other molecular sieves, "reduction seem to result from the differences in combustibility since N_2 began to form on commencement of the oxidation of hydrocarbons." It appears that ammonia is the primary reductant in SCR but in the case of hydrocarbons, it is some species produced in the propagation of combustion of the hydrocarbon. Of course, there are other differences, not directly correlated with reducing properties: both the non-specific physical adsorption and specific chemisorption on acid sites of



ammonia and hydrocarbons differ; hydrocarbon availability can be from the fuel itself, but ammonia requires a specific incremental source; and unreacted hydrocarbon SCR reductant can be easily removed by catalytic oxidation but ammonia SCR slip, if oxidized, will produce varying degrees of NOx. None of these differences are easy to quantify and therefore estimating the interacting combination or balance of desirable and undesirable reductant properties is inherently unpredictable. I have read the Halasz article relied upon by the Requester (page 52 of

Moreover, the literature cited by the Requester in Reexamination Control No. 95/001,453 proves that there is no predictability even between different hydrocarbon reductants. Figure 3 of Ishihara shows almost 60% conversion with a propene reductant between 300 and 625 °C, but the study is on a fresh, not aged material. In addition, the conversion is ZERO at 200 °C and below 20% at 250 °C. See Second Haller Decl. ¶11.

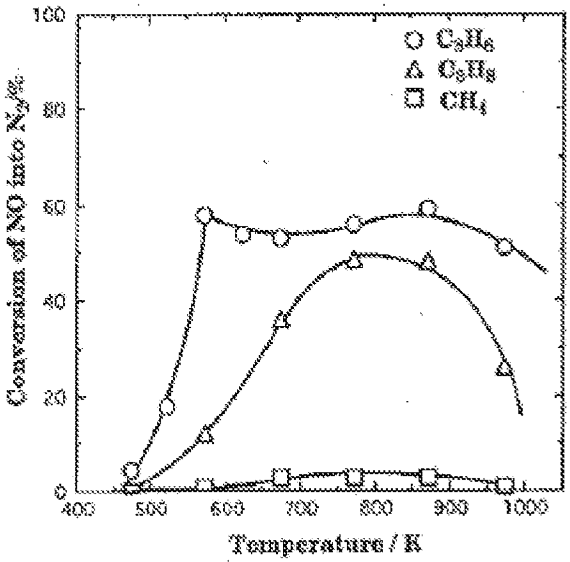


FIG. 3. Effects of different hydrocarbons as reductant on the activity of Cu-SAPO-34 for NO reduction (P_{NO} = 1000 ppm, $P_{hydrocarbon}$ = 1000 ppm, P_{O_2} = 5%, W/F = 0.3 g·s cm^{-3}).

Very recent literature shows the unpredictability in the art when different reductants are used. Korhonen et al. Chem.Comm 47 2011 800, cited in an IDS in this application shows that the ammonia SCR performance is dramatically better than propene SCR behavior for Cu-SSZ-13. The Korhonen study was for a Cu-SSZ-13 material having a silica to alumina ratio of 18, and a Cu/Al of 0.18. While the Cu/Al ratio is slightly outside the range in the instant claims, this study is useful as a direct comparison of material with the CHA crystal structure and containing copper for ammonia SCR and hydrocarbon SCR. In Figure 1 of Korhonen et al., an aluminosilicate with the CHA crystal structure showed **no** NOx conversion with a propene reductant at 200 °C and about 30% NOx conversion at 250 °C. A review of Figure 1 from the Korhonen et al article reveals the dramatic difference in SCR activity between propene and ammonia as reductants.

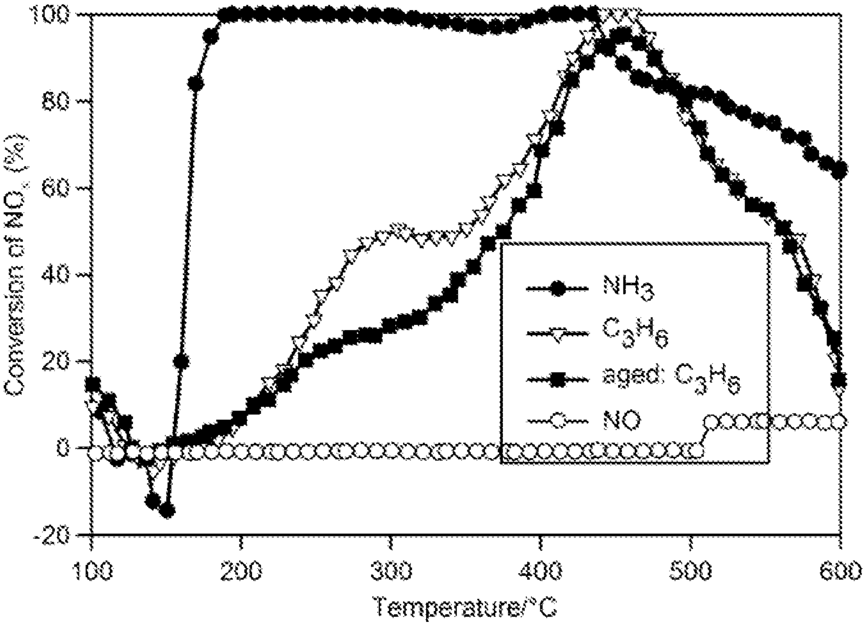


Fig. 1 Conversion of NO_x for CuCHA during NO decomposition (open circles) and during either NH_3- (filled circles) or C_3H_6-SCR (fresh catalyst: open triangles, aged catalyst: filled squares). Feed: 4000 ppm NO for NO decomposition and 1000 ppm NO, 1000 ppm NH_3 or C_3H_6, and 5% O_2 for NH_3- or C_3H_6-SCR.

During the interview, the Halasz article cited in the Office Action was discussed. Dr. Moini pointed out that Halasz tested ammonia only at 573 K, which is above the temperature region of interest in the '662 patent, and Halasz plainly shows that propene and propane, both hydrocarbon reductants, exhibited completely different behavior over the same ZSM-5 catalyst. This is shown in Figures 5 and 7 of Halasz, where NO conversion reached nearly 80% after 60 minutes for propene, and less than about 40% for propane.

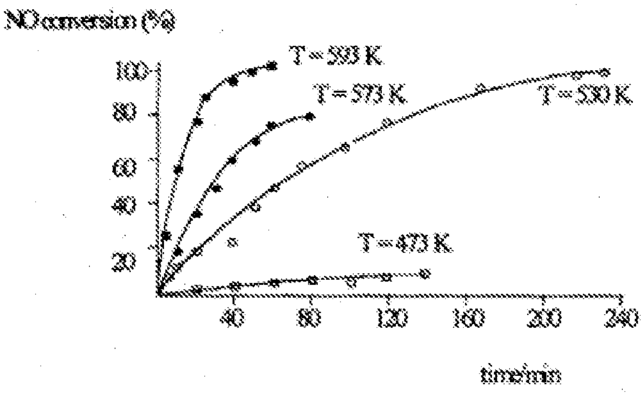


Fig.5. Temperature dependence of NO transformaton over Cu-ZSM-5/con. in the presence of propene.

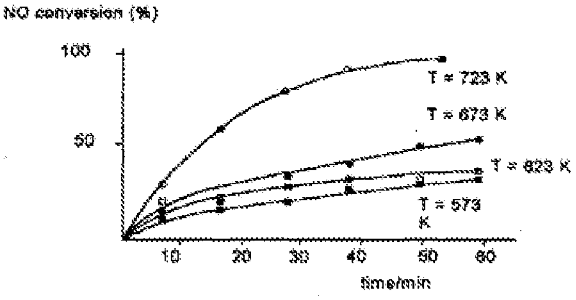


Fig.7. Temperature dependence of NO transformation over Cu-ZSM-5/con. catalyst in the presence of propane

Halasz shows that there is no predictability among different reductants in an SCR reaction. For all of the above reasons, Zones in view of Ishihara fails to establish a prima facie case of obviousness. The Patchett references are cited only to show the features of dependent claims, and the Patchett references to not remedy the deficiencies in the combination of Zones and Ishihara, withdrawal of the rejections is respectfully requested.

Rejections Over Ishihara et al. in View of Nam

Claims 33-48 are rejected under 35 U.S.C. §103(a) as being unpatentable over Ishihara et al. (Journal of Catalysis article), Ishihara et al. (Chemistry Letters article), Ishihara et al. (Ind. Eng. Chem. Res. article) or Ishihara et al. (Studies in Surface Science and catalysis article), each taken individually in view of US 7,049,261 to Nam et al. (Nam) and US 2006/0039843 to Patchett (Patchett).

The rejection asserts that each of the Ishihara articles teaches a material that is highly thermally stable. However, as was discussed in the interview, even if a material is "thermally stable," the material is not of interest if the material has poor catalytic activity after hydrothermal aging. The above discussion of Ishihara demonstrates that there would be no reason to use a material with the CHA crystal structure as an SCR catalyst because the NOx conversion below 300° C was less than 10%.

Nam is relied upon as allegedly teaching that related copper zeolites are known to abate nitrogen oxides across a broad temperature range for both nitrogenous and hydrocarbon reductant processes. However, the only mention in Nam of hydrocarbon reducing agents is in the Background section at column 1, lines 41-43, where hydrocarbon reductants are mentioned as possible reductants together with ammonia, urea, and the like. There are no examples or experiments showing predictability between or among different reductants for zeolites promoted with copper. The discussion above, including the discussion of the Halasz article and the recent literature, shows that the art is not predictable with respect to NOx conversion activity between or among different reductants. Patchett is relied upon for the disclosure of the reduction of nitrogen oxide emissions in the exhaust stream of an internal combustion engine, employing SCR catalyst compositions as part of an emissions treatment system, but Patchett does not remedy the deficiency in the combined teachings of Ishihara and Nam.

Accordingly, withdrawal of the rejection of claims 33-48 is respectfully requested.

Secondary Considerations

While is it not believed that an extensive presentation of secondary considerations is necessary in view of the discussion above that the cited art fails to establish a *prima facie* case of obviousness, an abbreviated discussion of the secondary considerations discussed in Reexamination Control No. 95/001,453 is provided herein.

Skepticism and Long-Felt Need

As the Declaration of Dr. Roth in the instant application (and the Roth Declarations in the Reexamination) shows, there was a great deal of skepticism that a Cu Zeolite could be used as an SCR catalyst in lean burn engines due to problems with loss of activity after hydrothermal aging. Furthermore, the discussion in the Ford paper discussed in paragraphs 11 and 12 of the Roth Declaration submitted in the instant application indicated that there was a long-felt need of a zeolite that provided excellent conversation in the range of 200-350° C and maintained high conversion after hydrothermal aging. The Second Roth Declaration submitted in Reexamination Control No. 95/001,453 shows that there was a need in the art that existed for at least 15 and more likely 20 years for an SCR catalyst exhibiting the properties provided by the present invention.

Unexpected Results

Examples representative of the claimed invention include Example 2- Cu/Al 0.33; Example 3- Cu/Al 0.38; Example 4- Cu/Al 0.44; Example 1A- Cu/Al 0.40 in the '662 patent demonstrate that aged performance for samples aged at 800°C for 50 hours or 850 °C for 6 hours, which represent more extreme aging conditions than in any of the references. The aged NOx conversion performance of the catalyst defined by the claims exceeded 50%, and several examples exceed 60%. In addition, the sample sent to Ford (discussed in the Second Ravindran Delcaration in Reexamination Control no. 95/001,453), having a silica/alumina=30 and Cu/Al= 0.45, is also representative of the claimed invention. In the Second Moini Declaration submitted in Reexamination Control No. 95/0014,453 Dr. Moini provides further data obtained after the filing date of the '662 patent that provides wider ranges of silica to alumina (up to 49.2) and copper to aluminum (ranging from 0.25 to 0.32) demonstrating the excellent aged performance of the material of the claimed invention.

CONCLUSION

It is believed that the pending claims are now in condition for allowance, early notice of which would be appreciated. No fees are believed due with this submission. If any fees are due at this time, the Commissioner is authorized to charge Deposit Account No. 50-3329. Please contact the undersigned if any further issues remain to be addressed in connection with this submission.

Respectfully submitted,

Dated: May 1, 2012

By: /Scott S. Servilla, Reg. #40806/
Scott S. Servilla
Reg. No. 40806
Diehl Servilla LLC
33 Wood Ave S
Second Floor, Suite 210
Iselin, NJ 08830

Telephone: (732) 815-0404
Attorney for Applicant

UNITED STATES PATENT AND TRADEMARK OFFICE

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
12/480,360	06/08/2009	Ivor Bull	5328A	3250

48226 7590 07/18/2012
BASF CORPORATION
100 PARK AVENUE
FLORHAM PARK, NJ 07932

EXAMINER	
WOOD, ELIZABETH D	
ART UNIT	PAPER NUMBER
1732	

NOTIFICATION DATE	DELIVERY MODE
07/18/2012	ELECTRONIC

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Notice of the Office communication was sent electronically on above-indicated "Notification Date" to the following e-mail address(es):

sonny.nkansa@basf.com
Melanie.Brown@basf.com
linda.komorowski@basf.com

PTOL-90A (Rev. 04/07)

Office Action Summary	**Application No.** 12/480,360	**Applicant(s)** BULL ET AL.
	Examiner ELIZABETH WOOD	**Art Unit** 1732

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE *3* MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *5/1/12*.
2a)☒ This action is **FINAL**. 2b)☐ This action is non-final.
3)☐ An election was made by the applicant in response to a restriction requirement set forth during the interview on _____; the restriction requirement and election have been incorporated into this action.
4)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

5)☒ Claim(s) *20-33,36-38 and 40-55* is/are pending in the application.
5a) Of the above claim(s) _____ is/are withdrawn from consideration.
6)☒ Claim(s) *20-32* is/are allowed.
7)☒ Claim(s) *33,36-38 and 40-55* is/are rejected.
8)☐ Claim(s) _____ is/are objected to.
9)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

10)☐ The specification is objected to by the Examiner.
11)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
12)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

13)☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
a)☐ All b)☐ Some * c)☐ None of:
1.☐ Certified copies of the priority documents have been received.
2.☐ Certified copies of the priority documents have been received in Application No. _____.
3.☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☐ Notice of References Cited (PTO-892)
2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
3) ☒ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date *4/17/12, 5/23/12*.
4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____ .
5) ☐ Notice of Informal Patent Application
6) ☐ Other: _____.

Umicore AG & Co. KG
Exhibit 1009

Specification

The examiner has not checked the specification to the extent necessary to determine the presence of **all** possible minor errors (grammatical, typographical and idiomatic). Cooperation of the applicant(s) is requested in correcting any errors of which applicant(s) may become aware of in the specification, in the claims and in any future amendment(s) that applicant(s) may file.

Applicant(s) is also requested to complete the status of any copending applications referred to in the specification by their Attorney Docket Number or Application Serial Number, **if any**.

The status of the parent application(s) and/or any other application(s) cross-referenced to this application, if **any**, should be updated in a timely manner.

Claim Rejections - 35 USC § 112

The following is a quotation of the first paragraph of 35 U.S.C. 112:

> The specification shall contain a written description of the invention, and of the manner and process of making and using it, in such full, clear, concise, and exact terms as to enable any person skilled in the art to which it pertains, or with which it is most nearly connected, to make and use the same and shall set forth the best mode contemplated by the inventor of carrying out his invention.

Claims 33, 36-38, 40-45 and 47-55 are rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the written description requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to reasonably convey to one skilled in the relevant art that the inventor(s), at the time the application was filed, had possession of the claimed invention. This is a new matter rejection.

The specification fails to support claims to a process employing a catalyst as claimed having a silica to alumina mole ratio of less than about 50, with no lower end point. As catalysis is extremely unpredictable, it is essential that specific ratios and ranges as supported by the specification be introduced into claims. Furthermore, there is not sufficient evidence on the file record to support that the specific claimed characteristics and nothing else are responsible for producing a catalyst resistant to significant degradation of performance, (for example, the amount of copper oxide present, which the specification discusses as a participant in the prevention of hydrothermal degradation of the nitrogen oxide conversion), the support material employed, and so forth). In other words, there is provided no specific nexus of all components responsible for the achieved results. Further, the term “significant” is neither defined by nor supported in the specification, so the extent of the metes and bounds of the term cannot be quantified and thus represents new matter. It is further not certain that claim 36 further limits the process in claim 33 in any way in addition to requiring undue experimentation. The catalyst of claim 33 already contains copper, and there is no discussion of any compositional limitation required to cause the catalyst to maintain the specified conversion.

Claim 46 remains rejected under 35 U.S.C. 112, first paragraph, as failing to comply with the enablement requirement. The claim(s) contains subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention.

Claim 46 recites a conversion process wherein the catalyst is identified only as CHA with copper, employing the language “exhibits less than a 10% decrease in fresh NOx conversion” that is merely functional in nature and no catalyst limitations are recited that would account for such a characteristic. Claim 36 also recites only an amount of conversion obtained after aging. Accordingly, the skilled artisan would be required to test a potentially infinite number of supported copper promoted CHA materials to determine which would fall within the metes and bounds of the claims. Such is clearly a situation involving undue experimentation. As many other factors regarding process steps (i.e. type of reductant) and catalyst compositional limitations(i.e. supported, amounts of promoters, ratio of silica to alumina) are also in play, and there is no demonstration of any nexus between all of the compositional and process limitations that would be required to achieve such conversion (and the claims are certainly not limited to all possibilities), the burden of undue experimentation would fall heavily on those attempting to make a determination as to the unlimited number of potential compositions within the scope of these claims.

Allowable Subject Matter

Claims 20-32 are allowable over the prior art of record. The prior art rejections of all claims as set forth in the office action of February 1, 2012 are withdrawn. The examiner considers that applicant has more than met the burden required to establish the unexpected nature of this field of technology, the unpredictability associated therewith and has demonstrated that the prior art itself is replete with evidence of this position. Accordingly, the examiner takes the position that there is no expectation of predictable catalytic behavior in the analysis of the catalyst employed in the claimed process and under the specified conditions of the claimed process.

Response to Arguments

Applicant's arguments filed May 1, 2012 have been fully considered and are persuasive except to the extent set forth hereinabove.

Conclusion

Applicant's amendment necessitated the new ground(s) of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a). Applicant is reminded of the extension of time policy as set forth in 37 CFR 1.136(a).

A shortened statutory period for reply to this final action is set to expire THREE MONTHS from the mailing date of this action. In the event a first reply is filed within TWO MONTHS of the mailing date of this final action and the advisory action is not mailed until after the end of the THREE-MONTH shortened statutory period, then the shortened statutory period will expire on the date the advisory action is mailed, and any extension fee pursuant to 37 CFR 1.136(a) will be calculated from the mailing date of the advisory action. In no event, however, will the statutory period for reply expire later than SIX MONTHS from the date of this final action.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to ELIZABETH WOOD whose telephone number is (571)272-1377. The examiner can normally be reached on M-F, 6:30-3:00.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Curtis Mayes can be reached on 571-272-1234. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free). If you would like assistance from a USPTO Customer Service Representative or access to the automated information system, call 800-786-9199 (IN USA OR CANADA) or 571-272-1000.

/Elizabeth D. Wood/
Primary Examiner, Art Unit 1732

/E. W./
Primary Examiner, Art Unit 1732

.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In *Inter Partes* Reexamination of:)
: Examiner: DIAMOND, ALAN D
BULL ET AL.)
: Group Art Unit: 3991
Reexamination Control No. 95/001,453)
: Confirmation No: 2755
Patent No. 7,601,662)
:
Issued: October 13, 2009)
:
For: COPPER CHA)
ZEOLITE CATALYSTS :

Mail Stop Inter Partes Reexam
Central Reexamination Unit
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF STANLEY ROTH, PH.D. UNDER 37 C.F.R. § 1.132

I, Stan Roth, do declare and say as follows:

1. I am currently the research group leader for diesel oxidation catalysts and soot filters for BASF Corporation, located in Iselin, New Jersey. In 2005, I held the position of research group leader for NOx control catalysts for Engelhard Corporation, which was subsequently acquired by BASF Corporation.

2. I received a doctorate degree in Inorganic Chemistry in 1982 from University of Illinois. I have been involved in the research and development of catalysts since 1986, and since 1995 I have worked in the areas of research and development of catalysts for automotive emissions, in particular diesel engines.

3. I am familiar with United States Patent No. 7,601,662 ("the '662 patent"), which is directed to a catalyst comprising a zeolite having the CHA crystal structure, a silica to alumina

ratio of about 15 and an atomic ratio of copper to aluminum exceeding about 0.25, with specific claims directed to silica to alumina ratios in the range of 15 to 40 and copper to aluminum ratios in the range of about 0.25 to 0.50. Such catalysts are useful for the abatement of nitrogen oxides in lean burn engines such as diesel engines, particularly by selective catalytic reduction in excess oxygen in the presence of a reductant such as ammonia. I understand that the '662 patent presently under reexamination in the United States Patent and Trademark Office, and that all of the claims have been rejected as allegedly being obvious over various cited references.

4. In 2005, I contacted a university professor, whom Engelhard was working with to obtain Department of Energy (DOE) funding for a proposal to study Cu-zeolites for selective catalytic reduction (SCR) of nitrogen oxides (NOx). Exhibit A attached hereto is a copy of the e-mail correspondence with the university professor on the DOE proposal, with the names of the professor, DOE review personnel and other personnel redacted. As shown on page 7 of Exhibit B, the grant proposal was wait-listed because the DOE grant monitor concluded that "Cu-exchanged zeolites lack the hydrothermal stability needed to be commercially viable for SCR of NOx with ammonia for diesel engines."

5. After receiving the information that the grant proposal had been wait-listed, I wrote back to the professor asking if the proposal could be reconsidered. The professor explained that "some reviewers, and my DOE grant manager simply think Cu-exchanged zeolites are far to [sic, too] unstable to water to be commercially feasible, so they do not want to fund work in the area." (Exhibit A, at page 5).

6. After writing to the professor a second time, the professor quoted the DOE contact as stating:

> "Clarifying the water-stability issue, without revealing proprietary knowledge, would be a good point to address in a new version. I have

> heard the same negative comment about the prospects for Cu-zeolites from several other investigators who presumably are also experts in this area. Thus, it is imperative to argue/present evidence that dispels such belief. More that the practicality of the concept, such as prospects for large-scale commercialization, the BES reviewers will be seeking for the rationale that will lead to new/corrected mechanistic understanding underlying such stability (or lack thereof)."

(Exhibit A, page 3).

7. The professor further quoted one of the reviewers as stating:

> "The structure-property-processing relationships that the PI's describe as the scientific goals are meritorious and worthy of support. The PI's weaken their position considerably, however, by emphasizing the technology of SCR in diesel vehicles when in fact propose to study de-NOx via ammonia over Cu-exchanged mordenite. Moreover, the PI's completely side step the issue of catalysts deactivation in the presence of water; I believe this to be the primary reason why metal-exchanged zeolites have limited application. It is interesting to note that not a single metal-zeolite for SCR was commercialized in the USA in the 1990'2 (see John Armor, App. Cat. A, V222, page 407(2001))."

(Exhibit A, pages 3-4).

8. The statements made by the DOE contact and reviewers represented the view of many researchers and those skilled in the art that Cu-zeolites could not be used as catalysts for the SCR of NOx because of the inability to maintain NOx conversion upon exposure to hydrothermal conditions—namely temperatures in excess of 650° C and H_2O of 10%. Even the recent literature, recognizing the results achieved in the '662 patent have called the problem of NOx reduction in lean burn engines as "daunting". (Exhibit B, first page).

9. The challenge before the invention of the '662 patent was to provide a zeolite material promoted with a metal or metal ion that exhibited high NOx conversion across a wide temperature range, including temperatures in the range of 200° to 350° C and that maintained high NOx conversion after hydrothermal aging of temperatures above 650° C, and in some cases

as high as 800° C or 900° C. The researchers at Ford summarized the problem in the research paper attached as Exhibit C (first page):

> Passenger and light duty diesel vehicles will require up to 90% NOx conversion over the Federal Test Procedure (FTP) to meet future Tier 2 Bin 5 standards. This accomplishment is especially challenging for low exhaust temperature applications that mostly operate in the 200° - 350° C temperature regime. Selective catalytic reduction (SCR) catalysts formulated with Cu/zeolites have shown the potential to deliver this level of performance fresh, but their performance can easily deteriorate over time as a result of high temperature thermal deactivation.

10. In 2006, I am aware that Engelhard Corporation provided samples of a Cu-zeolite having the CHA crystal structure deposited on a substrate to Ford Motor Company for SCR testing, and I understand that this is the material tested and described in Exhibit C, a research paper by Ford Motor Company entitled "Enhanced Durability of a Cu/Zeolite Based SCR Catlayst. As noted in Exhibit C (first page), it was believed that Fe-zeolites exhibited superior hydrothermal durability compared to Cu-zeolites. After testing the samples that were sent to Ford, the Ford researchers concluded that the material of the '662 patent is "remarkable". (Exhibit C, last page).

> In past years, no reported Cu/zeolite SCR formulation was able to yield stable low temperature NOx performance after exposure to hydrothermal conditions consisting of 1 hour at 950° C. Within the last year, a remarkable Cu/zeolite SCR formulation was identified with high NOx conversion in the 200° C – 350° C temperature range.

11. The material claimed in the '662 patent has been sold for use as a SCR catalyst for the removal of NOx in diesel engines in several different automotive manufacturer vehicle platforms. The material of the '662 patent has met a long-standing and previously unfulfilled need - a metal zeolite that exhibits both excellent NOx conversion over a wide temperature range, including the range of 200° to 350° C, and that maintains high conversion after exposure to hydrothermal conditions. This has allowed automotive manufacturers to meet increasingly stringent NOx standards that went into effect in 2010.

12. The Research & Development Council of New Jersey has recognized the inventors of the '662 patent with the 2010 Thomas Alva Edison Patent Award in the environmental category, which recognizes the outstanding work done by New Jersey scientists and inventors by honoring the most exceptional efforts.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-identified patent.

Respectfully submitted,

Dated: January 20, 2011

By: ______________________
Stanley Roth, Ph.D.

EXHIBIT A

Stan Roth/RD/ENGELHARD

09/28/2005 02:55 PM

To James[redacted].edu>
cc
Subject RE: proposal on Cu-zeolites for NOx SCRLink

Jim,

I have been out of the country for the past week. How did we leave this issue of your DOE proposal?

From my perspective you can go ahead as planned in your memo below. Hopefully our discussion has been useful. You can modify your introduction to include the comparative zeolite requirements for HC-SCR and NH3-SCR. Let me know if you require me to slightly modify my 2005 memo to state that "Preliminary experimental data shows thermal durability to 800°C"

In the zeolite literature there are probably many examples of structures with hydrothermal durability to the 700-800°C range. The big issue appears to be your DOE reviewers that have experience limited to the Cu-ZSM5 HC-SCR example, where catalytic performance quickly died after modest hydrothermal aging.

I understand that you like Mordinite because it's symmetry makes calculations easier. And that many of your papers have concerned work on ZSM-5. Is part of the problem with your DOE proposal that you are stressing continual work on these zeolites?

Moving forward, I would not really recommend either of these zeolites for the NH3-NOx application. Do we want to take our relationship to the next step, and have Engelhard supply you with samples for evaluation/modelling. This will of course require confidentiality/secrecy agreements, and in the past it has taken months to iron out all the legal implications. In cases were the University requires retention of patent rights, Engelhard has declined to participate in potentially useful programs. The alternative is to keep the relationship on an informal basis. That limits the relevance of your work to model catalyst systems, but also puts no limitations on publication of the results. Let me know you thoughts on this subject.

Regards,
Stan

[redacted] <[redacted].edu>

09/16/2005 05:05 PM

To: Stan_Roth@engelhard.com
cc:
Subject: RE: proposal on Cu-zeolites for NOx SCR

Hi Stan,

Thanks very much for the explanation. I knew part of it, but what you said really clarified the issues for me.

I would like to go ahead and resubmit my proposal mostly as is but with more explanation of the stabilization issue, as that was the only major objection to our proposal, which otherwise was very favorably reviewed.

So, my plan is to change our intro to include some of [redacted]'s data from [redacted], and some data from [redacted] [redacted] of the [redacted] Institute.

With your permission, I will also clarify some of the stability issues using the info only from your Sept 16 email, and none of your proprietary info.

I would like to also ask if I could reuse the letter you had given me in January 2005, but with a current date?

Hopefully that will be enough. The DOE really wants me to resubmit by mid-September to meet their January review, so I am unfortunately being rushed in my revisions.

Thanks again for your help!

Best wishes,
Jim

James [redacted]
Professor
Department of Chemical and Materials Engineering
[redacted] University
[redacted]
[redacted] (fax)

-----Original Message-----
From: Stan_Roth@engelhard.com [mailto:Stan_Roth@engelhard.com]
Sent: Friday, September 16, 2005 12:38 PM
To: James [redacted]
Cc: [redacted]; Stan_Roth@engelhard.com
Subject: RE: proposal on Cu-zeolites for NOx SCR

Jim,

Thank you for these reviewer quotes.
At last I finally understand where the objections to your proposals are comming from.

5-10 years ago there was much effort worldwide on the reaction of HC+NOx, oven known as active lean NOx or HC-SCR. There are propably 500+ literature references to this catalyst concept. There were two main types of catalyst used for this reaction:
(1) Pt-ZSM5 which functioned from 180-250°C but had as it's main weakness that the reaction was not selective and produced predominately N_2O rather than N_2.
(2) Cu-ZSM5 which was had an activity window from 300-500°C, did not produce N_2O, but had as it's main weaknees that the catalyst deactivated and could not survive extended hydrothermal treatment over 550°C. The mechanism of deactivation was clearly demonstrated to be loss of strong

acid sites in the zeolite that were responsible for coke formantion. The reaction pathway involved the seqauential reaction of HC on the acid sites to form coke. The reaction of NO on Cu to form NO2 and the reaction of NO2 with "coke" to form NO and N2.

NH3-SCR catalysts do not have the same deactivation mechansim because the strong acid sites do not play a role in the rate determining step of the reaction. Yet it appears as if the reviewers, who are not experts in the field, are taking what little they have deard about unrelated chemisty and drawing the conclusion that your proposed project is not based on a catalyst that can survive under realistic conditions.

How do we go forward?

Regards,
Stan

P.S. I will be out of the office for the next week visiting automotive/truck customers in Europe. We can talk again when I return.

James[redacted]
<[redacted] To: Stan_Roth@engelhard.com
[redacted].edu> cc: [redacted] <[redacted].edu>
Subject: RE: proposal on Cu-zeolites for NOx SCR
09/14/2005 02:55
PM

Hi Stan,

Our DOE contact is [redacted]. Here is the latest quote from him:
"Clarifying the water-stability issue, without revealing proprietary knowledge, would be a good point to address in a new version. I have heard the same negative comment about the prospects for Cu-zeolites from several other investigators who presumably are also experts in this area. Thus, it is imperative to argue/present evidence that dispels such belief. More that the practicality of the concept, such as prospects for large-scale commercialization, the BES reviewers will be seeking for the rationale that will lead to new/corrected mechanistic understanding underlying such stability (or lack thereof)."

Also, a quote from one of the reviewers was:
"The structure-property-processing relationships that the PI's describe as the scientific goals are meritorious and worthy of support. The PI's weaken their position considerably, however, by emphasizing the technology of SCR

in diesel vehicles when in fact propose to study de-NOx via ammonia over Cu-exchanged mordenite. Moreover, the PI's completely side step the issue of catalysts deactivation in the presence of water; I believe this to be the primary reason why metal-exchanged zeolites have limited application. It is interesting to note that not a single metal-zeolite for SCR was commercialized in the USA in the 1990'2 (see John Armor, App. Cat. A V222, page 407(2001))."

So, I think their major concern is instability of the zeolite, either due to dealumination or inactivation of the Cu. Any help you could provide would be greatly appreciated. [redacted] [redacted] just gave me approval to include her latest results presented at DEER 2005 meeting, which helps greatly but doesn't specify the metal in the zeolite. So, if you could give me any info re. stability of Cu-exchanged zeolites, I would greatly appreciate it.

Thanks very much!

Jim

James [redacted]
Professor
Department of Chemical and Materials Engineering
[redacted] University
[redacted]
([redacted]) [redacted]
[redacted] (fax)

-----Original Message-----
From: Stan_Roth@engelhard.com [mailto:Stan_Roth@engelhard.com]
Sent: Wednesday, September 14, 2005 11:34 AM
To: James [redacted]
Subject: RE: proposal on Cu-zeolites for NOx SCR

Jim,

Is the issue one of your contact at DOE not understanding the fundamental hydrothermal stability of zeolites. If that is the case I can probably pull together some papers/patents that show zeolites can remain stable for HC adsorption or acid catalysis after being exposed to high temperatures.

Or is the issue one of stability of Cu in the zeolite matrix, and its ability to retain SCR specific activity after exposure to high temperatures.

Who is your DOE contact. I know some of the DOE people that have been involved in funding advanced combustion and catalyst programs. Specifically Gurpreet Singh and Kevin Stork.

Regards,
Stan

James [redacted]
<[redacted] To:
Stan_Roth@engelhard.com
.[redacted].edu> cc:
Subject: RE: proposal on
Cu-zeolites for NOx SCR
09/14/2005 12:45
PM

Dear Stan,

The information you present below would make ALL the difference between our receiving or not receiving a grant from DOE. Some reviewers, and my DOE grant manager, simply think Cu-exchanged zeolites are far to unstable to water to be commercially feasible, so they do not want to fund work in the area.

One option would be for you to verbally share that information with my DOE grant officer, but ask him to keep it confidential.

Another option is if I quote the information below but do not name the company, but inform the reviewers that DOE has been told.

Please think about this, as without help from you or [redacted], the DOE grant officer thinks work in this area is useless.

I am also waiting to hear from [redacted] [redacted] at [redacted], as she has shared some exciting data privately with our group, and I am hoping I will be allowed to include or refer to it.

Best wishes,
Jim

James [redacted]
Professor
Department of Chemical and Materials Engineering
[redacted] University
[redacted]
([redacted]) [redacted]
([redacted] (fax)

-----Original Message-----

From: Stan_Roth@engelhard.com [mailto:Stan_Roth@engelhard.com]
Sent: Wednesday, September 14, 2005 9:29 AM
To: James [redacted]
Subject: Re: proposal on Cu-zeolites for NOx SCR

Jim,

Under laboratory aging conditions of air + steam we have SCR catalysts based on Cu-zeolite that have survived 50h at 800°C without significant loss in SCR activity and still exhibit >90% NOx conversion at inlet temp >300°C. At lower temperatues the performance drops due to oxidation of NO not due to thermal durability of the Cu-zeolite.

This information is confidential to Engelhard and I am uncertain how to support your program without disclosure of our product performance. Such a catalyst will likely not be in commercial application until 2010.

Is there any way to support your program without disclosure of confidential information?

It sounds to me as if DOE has a reviewer who does not have much experience with zeolites.

Regards,
Stan

James [redacted]
[redacted] To:
Stan_Roth@engelhard.com
[redacted].edu> cc:
Subject: proposal on
Cu-zeolites for NOx SCR
09/06/2005 03:07
PM

Dear Stan,

I hope all is well with you. I've been waiting to hear on my DOE proposal, which was "wait-listed" and although it was close, it was finally not approved for funding. The major criticism from one reviewer (and echoed by the DOE grant monitor) is that Cu-exchanged zeoliteslack the hydrothermal stability needed to be commercially viable for SCR of NOxwith ammonia for diesel engines.

I greatly appreciate the support letter you wrote for me last year, which was helpful, but due to proprietary issues it was not quite strong enough to address the reviewers concerns.

DOE has encouraged me to resubmit the proposal in the next 1-2 weeks, if I can obtain stronger evidence of the hydrothermal stability of the zeolites. I am asking [redacted] [redacted] at [redacted] for help and to be able to include some of her data, but I would also greatly appreciate it if you again give me a letter of support, especially one that directly addresses the hydrothermal stability concerns.

I very much want to continue work in this area, but without stronger evidence of hydrothermal stability I will not be able to address the reviewers concerns and obtain funding from DOE. So, I would greatly appreciate any help you can give, in the form of a modified letter from last year, and/or any data I can point to.

Thanks very much.

Sincerely,

James [redacted]

Professor

Department of Chemical and Materials Engineering

[redacted]University

[redacted]

[redacted]

([redacted]

([redacted] (fax)

EXHIBIT B

Journal of Catalysis 275 (2010) 187–190

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JOURNAL OF CATALYSIS

Priority Communication

Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH_3

Ja Hun Kwak, Russell G. Tonkyn, Do Heui Kim, János Szanyi, Charles H.F. Peden *

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, United States

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ABSTRACT

Superior activity and selectivity of a Cu ion-exchanged SSZ-13 zeolite in the selective catalytic reduction (SCR) of NO_x with NH_3 were observed, in comparison with Cu-beta and Cu-ZSM-5 zeolites. Cu-SSZ-13 was not only more active in the NO_x SCR reaction over the entire temperature range studied (up to 550 °C), but also more selective toward nitrogen formation, resulting in significantly lower amounts of NO_x by-products (i.e., NO_2 and N_2O) than the other two zeolites. In addition, Cu-SSZ-13 demonstrated the highest activity and N_2 formation selectivity in the oxidation of NH_3. The results of this study strongly suggest that Cu-SSZ-13 is a promising candidate as a catalyst for NO_x SCR with great potential in after-treatment systems for either mobile or stationary sources.

1. Introduction

The abatement of environmentally harmful NO_x compounds (NO, NO_2, and N_2O) emitted from mobile or stationary power sources remains a challenging task for the catalysis community. In particular, conventional three-way catalysts used in the exhaust after treatment technologies of internal combustion engines prove ineffective when the engine is operated under highly oxidizing conditions (to achieve better fuel efficiency). The problem is daunting, since reduction chemistry (NO_x to N_2) has to be carried out under highly oxidizing conditions. Several approaches have been proposed for lean-NO_x abatement, each of them with its own specific sets of problems. The two technologies that seem to have clear advantages among the processes proposed are the selective catalytic reduction either with hydrocarbons (HC-SCR) or with ammonia (NH_3-SCR), and lean-NO_x traps (LNT). For the NH_3-SCR technology, transition metal (in particular Fe and Cu) ion-exchanged zeolite catalysts have shown high activity and N_2 selectivity.

The most extensive studies have been carried out on Cu^{2+} ion-exchanged ZSM-5 (Cu-ZSM-5) zeolites, first shown to exhibit high NO decomposition rates and NO_x SCR activities in the 1980s [1–7]. More recently, Cu^{2+}-exchanged beta zeolite (Cu-beta) has been shown to have excellent activity in the SCR of NO_x with NH_3, and metal-exchanged beta zeolites are generally found to have greater hydrothermal stability than similar ZSM-5 catalysts [8]. In the very recent patent literature, Cu^{2+} ion-exchanged SSZ-13 (Cu-SSZ-13) has been reported to exhibit NO_x conversions of 90–100% over a wide temperature range in the NH_3-SCR process, and its activity exceeded 80% even after extensive high-temperature hydrothermal aging [9]. The SSZ-13 zeolite has chabazite (CHA) structure with a relatively small pore radius (~3.8 Å) in an eight-membered ring [10]. The enhanced thermal stability of the Cu-SSZ-13 catalyst has been attributed to the location of copper ions within the cage; i.e., just outside the six-membered rings of the zeolite framework, as evidenced by XRD analysis [11]. Although, high catalytic activity has been reported in the patent literature for the Cu-SSZ-13 catalyst under a specific set of reaction conditions, no comparisons have been made with other, widely studied NH_3-SCR catalysts (i.e., Cu-ZSM-5 and Cu-beta) under the same reaction conditions. Here, we report on the performance of a Cu-SSZ-13 catalyst in the SCR of NO_x with NH_3, particularly focusing on the activity and N_2 selectivity in comparison with those of Cu-beta and Cu-ZSM-5. We also compare the NH_3 oxidation activities/selectivities of these catalysts under highly oxidizing conditions. Our results confirm that the activity and selectivity of the Cu-SSZ-13 catalyst for both NO_x SCR with NH_3 and NH_3 oxidation are superior to those of both Cu-beta and Cu-ZSM-5.

2. Experimental

The SSZ-13 zeolite was synthesized using the methods recently published by Fickel and Lobo [11], reported to give a material with a Si/Al_2 ratio of ~12. The structure-directing agent used in the synthesis, N,N,N-trimethyl-1-adamantanamine iodide, was synthesized using the procedure reported by Zones [10]. After synthesis,

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* Corresponding author. Fax: +1 509 376 2837.
E-mail address: chuck.peden@pnl.gov (C.H.F. Peden).

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the SSZ-13 was calcined at 550 °C for 5 h in air before ion exchange in order to remove the zeolite framework structure-directing agent. Copper ions were exchanged into the zeolite in an aqueous ion-exchange process, using 0.1 M $Cu(NO_3)_2$ solutions; solution volumes were such that they contained twice the amount of Cu^{2+} needed for complete ion exchange. After ion exchange over 1 day at room temperature, the catalysts were filtered, thoroughly washed with distilled water, and dried overnight at 100 °C. To ensure complete ion exchange, this process was carried out a second time with an aqueous solution of Cu^{2+} of the same initial concentration. The dried catalysts were pre-calcined at 500 °C in laboratory air for 2 h before reaction tests. The CHA structure in Cu-SSZ-13 was confirmed with XRD measurement.

For comparison purposes, Cu^{2+}-exchanged ZSM-5 and beta zeolites were prepared from commercially available zeolites (ZSM-5 (CBV-3024, $Si/Al_2 = 30$) and beta (CP-814C, $Si/Al_2 = 38$), both from Zeolyst International Co.), using the same ion-exchange and calcination procedures applied to the preparation of the Cu-SSZ-13 sample, except for varying the Cu^{2+} concentration of the solution to match the Si/Al_2 ratios of the particular zeolite.

The NO_x SCR activities were measured in a flow-through powder reactor system using gas mixtures containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2. The total flow rate was held at 300 sccm over the 120–130 mg catalyst powder samples (SV $\sim$ 30,000 h^{-1}). The temperature was varied from 550 to 160 °C in approximately 50 °C steps, as measured by a small type K thermocouple inserted directly into the center of the catalyst powder bed. The NH_3 oxidation reaction was carried out under similar reaction conditions in the absence of NO in the gas mixture. The reactant and product gas mixtures (NO, NO_2, N_2O, and NH_3) were analyzed using FTIR spectroscopy (Nicolet Magma 760 with OMNIC Series software) in a heated, 2-m path-length gas cell. Our reported NO_x conversions (%) are defined as $\{NO_{inlet} - (NO + NO_2 + 2 * N_2O)_{outlet}/NO_{inlet}\} * 100$.

3. Results and discussion

NO_x conversions as a function of reaction temperatures between 150 and 550 °C are shown in Fig. 1 over the three Cu-zeolites studied. Both Cu-ZSM-5 and Cu-SSZ-13 catalysts exhibit maximum conversion (>95%) at temperatures somewhat above 250 °C, while the maximum conversion over Cu-beta in the same temperature range is slightly lower (90%). Note that the Cu-SSZ-13 catalyst maintains its high conversion (>90%) up to 500 °C, while the NO_x conversion of Cu-ZSM-5 begins to decline above 300 °C. Even at 550 °C, the highest temperature of this study, Cu-SSZ-13 exhibits a respectably high conversion of 83%. The order of activity of these catalysts in the high-temperature region (350–550 °C) is as follows: Cu-SSZ-13 > Cu-ZSM-5 > Cu-beta.

In addition to NO_x conversion, significant differences in product selectivity were observed for the three zeolite catalysts studied. Fig. 2 displays the amounts of by-products NO_2 (a) and N_2O (b) formed in the SCR reaction. At reaction temperatures above 300 °C, Cu-ZSM-5 and Cu-beta produce significant amounts of NO_2, and at 500 °C the amounts of NO_2 produced over these two catalysts are 30 and 25 ppm, respectively, much higher than the <10 ppm measured over the Cu-SSZ-13. N_2O formation profiles as a function of reaction temperature, shown in Fig. 2b, also exhibit large differences among the three Cu ion-exchanged zeolite catalysts. The N_2O level over the Cu-SSZ-13 is very low (<5 ppm) over the entire temperature range studied, while the Cu-beta catalyst shows a double maxima in N_2O concentrations at low and high

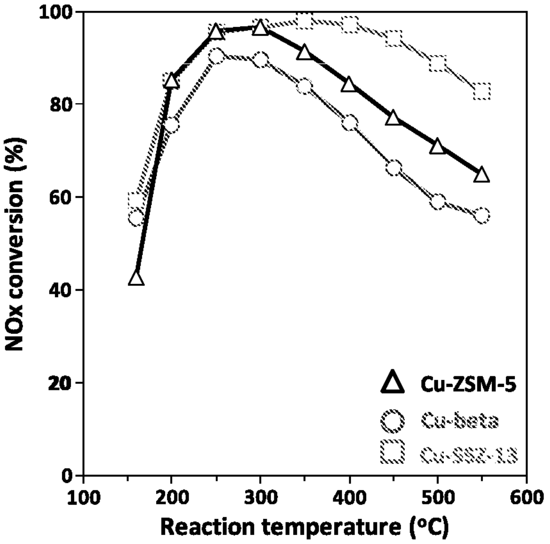

Fig. 1. NO_x conversion profiles for Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

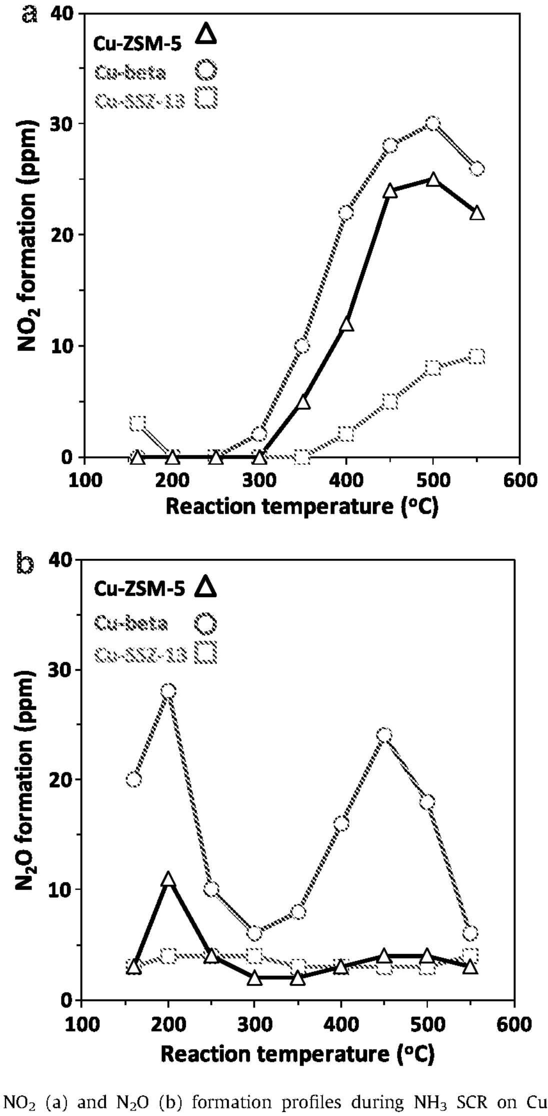

Fig. 2. NO_2 (a) and N_2O (b) formation profiles during NH_3 SCR on Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NO, 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

temperatures; i.e., 27 ppm at 200 °C and 24 ppm at 450 °C, respectively. The Cu-ZSM-5 catalyst produced a similar N_2O formation profile to Cu-beta, but the amounts of N_2O formed were much smaller. These N_2O formation profiles are likely related to the reaction mechanisms of the NO_x reduction reactions. For example, our results demonstrate that reaction intermediates (e.g., NO_x–NH_3 adsorbed complexes) on Cu-SSZ-13 take a more selective reaction route toward the production of N_2 than do the complexes on the Cu-beta and Cu-ZSM-5 catalysts.

The differences in activity and selectivity of the three zeolites studied may be related to fundamental differences in the known structures of these zeolites, i.e., the pore sizes and locations of the copper ions. The order of high-temperature NH_3 SCR reactivity discussed earlier is the inverse of the order in pore size, i.e., SSZ-13 having the smallest pores (~4 Å, 8-membered ring) being the most active, ZSM-5 with medium size pore opening (~5.5 Å, 10-membered ring) having medium activity, and beta with the largest pores (~7 Å and ~5.5 Å, 12-membered ring) having the lowest activity and N_2 selectivity. For these three catalysts, the smaller size pores seem to be preferred for the desirable reaction pathways; however, detailed mechanistic studies need to be conducted to substantiate the correlation between pore size and activity/selectivity. In summary, both the activity and selectivity of NO_x SCR with NH_3 for Cu-SSZ-13 are superior to those of Cu-ZSM-5 and Cu-beta over the entire temperature range studied (up to 550 °C).

The differences observed in the ammonia SCR reactivities and N_2 formation selectivities for the three catalysts studied may also be related (at least in part) to their abilities to oxidize ammonia. Therefore, we performed NH_3 oxidation reactions over the three different Cu-zeolite catalysts in the absence of NO and the results are presented in Fig. 3. Ammonia conversions (Fig. 3a) reveal that the light-off temperature for NH_3 oxidation is the lowest for Cu-SSZ-13, indicating its superior intrinsic NH_3 oxidation ability. For this catalyst, the NH_3 oxidation reaction lights off at around 200 °C and reaches a conversion level of more than 90% at ~300 °C. The NH_3 conversion profiles for Cu-beta and Cu-ZSM-5 are shifted to higher temperatures by ~50 and ~100 °C, respectively, relative to that of Cu-SSZ-13.

The concentrations of NO_x ($NO + NO_2 + N_2O$) in the reaction effluent, which are regarded as by-products during NH_3 oxidation to N_2, are plotted in Fig. 3b. The Cu-beta catalyst produced relatively higher levels of these by-products, with a maximum of about 55 ppm at 350 °C, while the Cu-ZSM-5 catalyst produced significant amounts of by-products at 550 °C. The relative lack of NO_x formation during ammonia oxidation on the Cu-SSZ-13 catalyst implies that most of the NH_3 is converted to N_2 over a wide temperature range for this catalyst. The near absence of further oxidization to N_2O, NO, or NO_2, as was the case for the Cu-beta and Cu-ZSM-5 catalysts, suggests again that the environment within the Cu-SSZ-13 catalyst may provide optimum conditions for selective conversion of reaction intermediates to N_2.

According to the results of previous studies, noble metal catalysts, including Pt [12], have been found to be very active in ammonia oxidation, but rather non-selective to N_2 formation, while transition metal oxides such as MnO_2 and CuO [13] have higher N_2 selectivity, but require significantly higher temperatures. Cu-SSZ-13, on the other hand, can meet the two important requirements: excellent NH_3 oxidation activity and N_2 selectivity over a wide temperature range. Thus, for example, the use of Cu-SSZ-13 as an NH_3 oxidation catalyst at the downstream end of a NO_x SCR with NH_3 unit might provide flexibility for controlling the dose of urea introduced before the SCR catalyst, since any excess of NH_3 can perhaps be removed more easily over the catalyst bed.

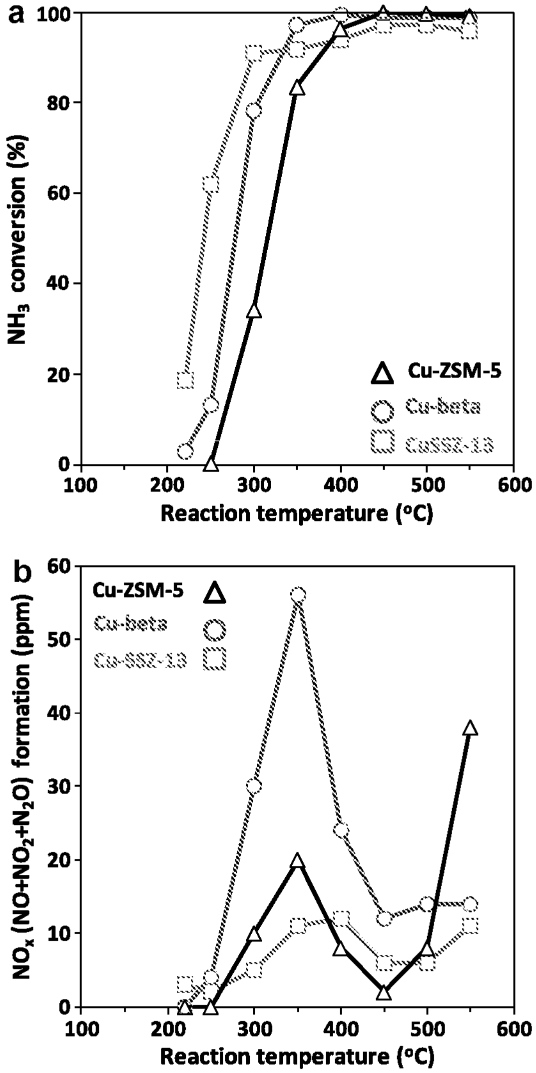

Fig. 3. (a) NH_3 conversion profiles and (b) NO_x product distributions during the NH_3 oxidation reaction on Cu-SSZ-13 (squares), Cu-beta (circles), and Cu-ZSM-5 (triangles) at various temperatures in a gas mixture containing 350 ppm NH_3, 14% O_2, and 2% H_2O with a balance of N_2.

4. Conclusions

Under the same reaction conditions for NO_x SCR with NH_3, Cu-SSZ-13 demonstrates superior activity and N_2 formation selectivity in comparison with Cu-beta and Cu-ZSM-5 zeolites. We find that Cu-SSZ-13 is more active for NO_x conversion over the entire temperature range studied (160–550 °C). Moreover, the Cu-SSZ-13 is also more selective toward the formation of N_2, producing lower amounts of undesired by-products such as NO_2 and N_2O. Our results also demonstrate that Cu-SSZ-13 has superior performance for NH_3 oxidation (lower light-off temperature) than Cu-beta and Cu-ZSM-5 zeolites, while also producing significantly lower amounts of (over-oxidized) NO_x species. These results suggest that Cu-SSZ-13 is an excellent candidate catalyst for use in practical NH_3 SCR of NO_x and/or NH_3 oxidation applications (the after-treatment systems of various mobile or stationary sources). Detailed mechanistic studies are currently under way in our laboratory to understand the origin of the different activities and selectivities observed for these three catalysts in both the NO_x SCR and NH_3 oxidation reactions.

Acknowledgments

Financial support was provided by the US Department of Energy (DOE), Office of FreedomCar and Vehicle Technologies. Portions of this work were performed in the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL). The EMSL is a national scientific user facility and supported by the US DOE, Office of Biological and Environmental Research. PNNL is a multi-program national laboratory operated for the US Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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EXHIBIT C

2008-01-1025

Enhanced Durability of a Cu/Zeolite Based SCR Catalyst

Giovanni Cavataio, Hung-Wen Jen, James R. Warner, James W. Girard,
Jeong Y. Kim and Christine K. Lambert
Ford Motor Company

ABSTRACT

Passenger and light duty diesel vehicles will require up to 90% NOx conversion over the Federal Test Procedure (FTP) to meet future Tier 2 Bin 5 standards. This accomplishment is especially challenging for low exhaust temperature applications that mostly operate in the 200 - 350°C temperature regime. Selective catalytic reduction (SCR) catalysts formulated with Cu/zeolites have shown the potential to deliver this level of performance fresh, but their performance can easily deteriorate over time as a result of high temperature thermal deactivation. These high temperature SCR deactivation modes are unavoidable due to the requirements necessary to actively regenerate diesel particulate filters and purge SCRs from sulfur and hydrocarbon contamination. Careful vehicle temperature control of these events is necessary to prevent unintentional thermal damage but not always possible. As a result, there is a need to develop thermally robust SCR catalysts. Fe/zeolite formulations are known to exhibit superior hydrothermal stability over Cu/zeolite formulations. However, current Fe/zeolite formulations are not very active for NOx conversion in the desired 200 – 350°C temperature regime under conditions having low NO_2/NOx ratios. From previous studies, Cu/zeolite formulations have demonstrated never-to-exceed temperatures up to 775°C. In this work, a laboratory flow reactor was utilized to hydrothermally age and evaluate the latest state-of-the-art Cu/zeolite formulations. Results confirm remarkable high temperature hydrothermal stability up to 950°C while maintaining stable low temperature NOx activity. A broad range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range. The aging time was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. The catalyst performance was evaluated under a synthetic exhaust gas mixture commonly known as the "Standard" SCR reaction.

INTRODUCTION

The operating conditions over the Federal Test Procedure (FTP) results in high NOx emissions in the 200 – 350°C temperature range. From current light-duty diesel applications, the future Tier 2 Bin 5 emission standards will require up to 90% reduction in the tailpipe NOx emissions.

Implementation of zeolite based components has been extensively studied for application in gasoline and diesel aftertreatment devices. However, the harsh high exhaust temperatures observed in typical gasoline vehicles have limited their widespread use. On the other hand, the relatively milder diesel exhaust temperatures have encouraged continued development of zeolites as a major component in aftertreatment devices.

One promising diesel aftertreatment technology containing zeolite is the Selective Catalytic Reduction (SCR) of NOx with an ammonia-based reductant such as aqueous urea. As stated in equation (1), NOx reduction is possible due to the high selectivity of the ammonia (NH_3) and nitrogen oxide (NO) reaction to form elemental N_2. In the absence of nitrogen dioxide (NO_2), this reaction is referred to as the "Standard" SCR reaction [1]. Additionally, the SCR reaction containing 50% NO and 50% NO_2 is referred to as the "Fast" SCR reaction (equation 2).

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{"Standard"} \quad (1)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad \text{"Fast"} \quad (2)$$

Vanadium, Fe/zeolite, and Cu/zeolite based SCR formulations are very active for the "Standard" SCR reactions. However, vanadium based formulations have been shown to easily deactivate when exposed to temperatures necessary to actively regenerate Diesel particulate filters (DPFs) with oxygen [2]. This cannot be avoided since a DPF is currently required to meet Tier 2 Bin 5 particulate matter (PM) emission standards. Fe/zeolites have been shown to be much more durable to high temperature exposure. However, in the absence of NO_2, Fe/zeolites lack the low temperature (200 - 350°C) NOx activity necessary for high FTP efficiency. In this critical temperature range, Cu/zeolite formulations have been reported to have much lower sensitivity to the NO_2/NOx ratio. As a result, Cu/zeolite formulations have been shown to achieve high NOx conversion at the desired low operating temperatures. Their lack of hydrothermal stability above 775°C has drawn questions about their long-term in-use durability and robustness to occasional over-temperature events.

Improvements in the thermal durability of Cu/zeolite based SCR formulations has been highly desirable and pursued by many research institutes and catalyst suppliers.

This paper discusses the performance and hydrothermal durability of an enhanced Cu/zeolite based SCR formulation exhibiting durable low temperature NOx activity under a wide matrix of time-at-temperature aging conditions. On key aged samples, surface area measurements and Cu reduction measurements are performed to investigate changes in the zeolite and Cu state, respectively.

EXPERIMENTAL

SAMPLE PREPARATION

A full size monolith washcoated with a state-of-the-art Cu/zeolite based SCR formulation was obtained from a catalyst supplier in 2007. The cordierite-based monolith measured 20.3cm diameter x 15.2cm length with 400 cells per square inch (CPSI) and 4.5 mil wall thickness. The SCR monolith was completely cored and cut into 160 round samples measuring 2.54cm diameter x 2.54cm length. From this, a normal distribution was observed where the 95% confidence interval around the mean mass was determined to be ± 0.4%. Older formulations mentioned in this paper did not necessarily exhibit the same distribution in mass.

HYDROTHERMAL AGING

As configured in Diagram 1, sample cores were hydrothermally aged in flowing gas from an automated flow reactor system. The total flow rate utilized was 6.44 liters/min. The synthetic gas composition consisted of 14% O_2, 5% H_2O, 5% CO_2, and balance N_2. For each aging, three samples measuring 2.54cm diameter x 2.54cm length were placed in a quartz reactor tube and labeled A, B, and C. The three SCR samples were separated by 30mm to ensure well distributed gas flow in all channels. An uncoated cordierite monolith was placed upstream to serve as a gas heat exchanger. The uncoated monolith ensured an isothermal gas temperature across each sample. Samples positioned in location "A" were used for surface area measurements. Samples positioned in location "B" were used for temperature-programmed reduction measurements (TPR). Samples positioned in location "C" were used for the NOx conversion evaluation tests.

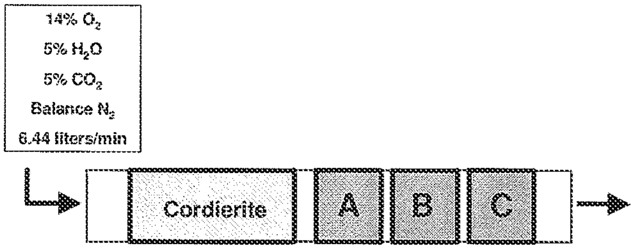

DIAGRAM 1. Sample configuration during hydrothermal aging.

A wide range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range of a promising Cu/zeolite SCR formulation. The hydrothermal aging duration was varied from 1 hour to 256 hours while the aging temperature was varied from 670℃ to 1100℃. Totaling 1116 aging hours, Table 1 defines the 24 different aging conditions utilized in this study. Special attention was considered to determine the short-term never-to-exceed (NTE) temperature and the long-term SCR durability necessary to withstand the temperature resulting from DPF regeneration events. For a given aging duration, the NTE is defined as the temperature at which the NOx conversion decay accelerates significantly.

Temp. (℃)	Hydrothermal Aging Duration (hours)								
	1	2	4	8	16	32	64	140	256
670							X		
700	X				X	X	X		X
750									
800	X				X	X	X	X	X
850							X		
900	X		X	X	X		X		
950	X	X	X	X					
1000	X								
1100	X								

TABLE 1. Time-at-temperature hydrothermal aging matrix.

LABORATORY CATALYST EVALUATION

Fundamental catalyst activity data were obtained using an automated laboratory-scale flow reactor system. Custom-written LabVIEW based software with National Instruments data acquisition hardware controlled MKS mass flow controllers and Lindberg Mini-Mite tubular furnaces. A computer controlled evaluation protocol was developed and run for each sample to decrease the test-to-test variations commonly observed by manual operation. Table 2 shows the simulated diesel exhaust gas composition flowed through each sample core to study the "Standard" SCR reaction.

Gas Compositon	Concentration
NO (ppm)	350
NO_2 (ppm)	0
NH_3 (ppm)	350
O_2 (%)	14
CO_2 (%)	5
H_2O (%)	5
Balance	N_2

TABLE 2. Simulated gas composition used to study performance for the "Standard" SCR reaction.

For all evaluations, the total gas flow rate was held constant at 6.44 liters/min while the sample size was held constant at 2.54cm diameter x 2.54cm length. As a result, a space velocity equal to 30,000/hr was used in this study. For the typical light-duty diesel vehicle operating over the FTP drive cycle, this space velocity corresponds to a SCR monolith size between 100% - 150% of the engine swept volume.

The SCR inlet gas temperature was maintained with one preheat tubular furnace followed by a second tubular furnace. SCR samples were loaded in quartz tubing and placed in the second tubular furnace. A Thermo Electron Antaris IGS FTIR Gas Analyzer with a heated sample cell was used at the outlet of the reactor to measure NO, NO_2, N_2O, NH_3, CO_2, and H_2O levels. To cover the full exhaust temperatures expected on diesel vehicles, data were taken at SCR inlet gas temperatures from approximately 150°C to 700°C in 25-50°C steps. The computer-controlled evaluation protocol stepped the reaction temperature setting from a high temperature to low temperature for a prescribed duration. At each temperature setting, the duration was chosen so that post SCR gas composition was allowed enough time to completely equilibrate.

The flow reactor used in this study was examined to determine the test-to-test variability of the entire measurement system. Among numerous variables, the FTIR measurement, the thermocouple measurement, and precision of the mass flow controllers may collectively contribute large discrepancies in the data. This may make it difficult to conclude with confidence that one result is statistically different than another result. Repeated evaluation runs were made on a single pre-aged (64hr/670°C) SCR sample to determine the 95% confidence interval. Five evaluation runs were performed over the entire temperature range.

SURFACE AREA MEASUREMENTS

A Micromeritics ASAP 2400 instrument in conjunction with the well-known Brunauer, Emmet, and Teller (BET) equation was employed to determine the surface area of each SCR sample. The BET equation determines the surface area by establishing the relationship between the volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage [3].

TEMPERATURE PROGRAMMED REDUCTION (TPR)

The Cu state within zeolite formulations changes during the SCR reaction and after hydrothermal aging. These physical-chemical changes yield different reduction temperatures. The TPR results reveal direct evidence of changing Cu-species in the catalyst and may be correlated to the deactivation of SCR activity after aging.

Temperature-Programmed-Reduction (TPR) was conducted on a Micromeritics AutoChem II 2920 instrument. Part of a catalyst sample (location "B") was sliced off and cut into small pieces, about 3 mm long. These small pieces were then loaded into a quartz reactor for TPR. Typically, 0.5 gram of sample was used in the experiment. The temperature was measured with a thermocouple in the catalyst bed. Prior to TPR, the catalyst sample was pretreated in 10%O_2/He at 600°C for 30 minutes and then cooled down to room temperature in 10%O_2/He. After the pretreatment, the gas flow was changed to 9%H_2/Ar at 20 ml/min. During TPR, the catalyst bed was heated to 600°C at a linearly increasing rate of 10°C/min. The change in H_2 concentration was monitored using Thermal-Conductivity-Detector (TCD). The consumption of H_2 indicated the reduction of oxidized Cu.

RESULTS AND DISCUSSION

FLOW REACTOR VARIABILITY

The variability of the evaluation flow reactor was determined by running a pre-aged SCR sample five times. The steady state "Standard" SCR reaction results for each of the five runs are overlaid in Figure 1. In addition, the 95% confidence interval around the mean

NOx conversion is shown in Figure 2. From Figure 1, the NOx conversion traces are virtually line on line for operating temperatures below 600°C. Above 600°C, the NOx conversion drops slightly after each subsequent evaluation run. For this particular SCR formulation, the explanation for this slight deactivation has to do with the additional aging the sample experiences during high temperature performance evaluations. This trend becomes more apparent with data presented later in this paper. Figure 2 more clearly defines the variability in the overall flow reactor system. The data from Figure 1 was manipulated in Minitab to yield the 95% confidence interval at each evaluation temperature. For evaluation temperatures below 600°C, the 95% confidence interval around the mean NOx conversion was better than ±2%. Due to catalyst deactivation with testing, the higher temperature points showed variability up to ±6%.

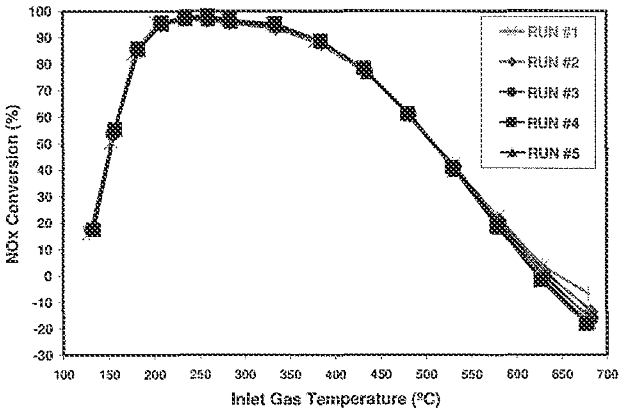

FIGURE 1. NOx conversion results for the STANDARD SCR REACTION. Five consecutive evaluation runs on a single sample aged 64 hours at 670°C.

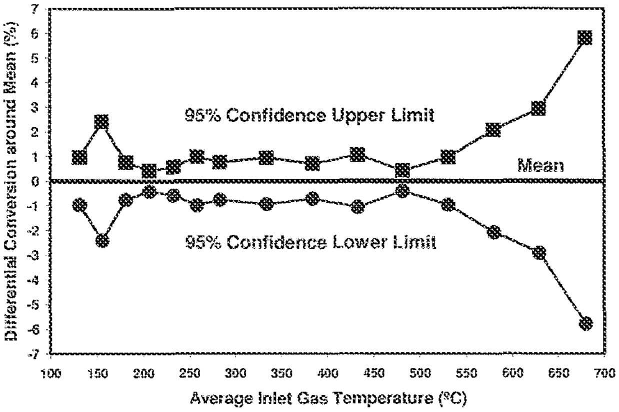

FIGURE 2. Calculated from Figure 1, the differential NOx conversion variability around the mean as determined by the 95% confidence interval.

RECENT SCR DURABILITY IMPROVEMENTS

Since current and future diesel aftertreatment systems contain DPFs, SCR formulations are required to withstand the high temperature process of regenerating soot-loaded particulate filters. A robust engine control strategy that lessens the variability of the actual regeneration temperature is critical to the durability of the SCR. For this study, the target active DPF temperature has been determined to be 670°C. Also, the total cumulative duration for the full vehicle useful life has been determined to be 64 hours. Therefore, the long-term hydrothermal stability of base metal-zeolite SCR catalysts for typical light-duty diesel applications must be able to endure, at minimum, 670°C for 64 hours.

Figure 3 shows the recent progress that has been made in Cu/zeolite SCR development. Many Cu/zeolite formulations have been aged and evaluated between 2005 and 2007. Steady improvements of NOx conversion have been made in the low temperature range (200 – 350°C). For example, at 200°C, the NOx conversion has been enhanced from 70% to 90%. In addition, the 2007 state-of-the-art SCR maintained 90%+ NOx conversion over a much larger temperature range. However, note that the enhanced low temperature activity came with a trade-off in the performance above 400°C.

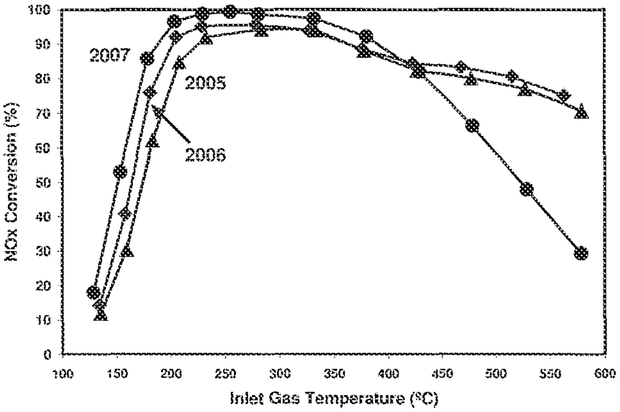

FIGURE 3. NOx conversion results for the STANDARD SCR REACTION. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

As shown in Figure 4, the three SCR formulations generate measurable levels of N_2O as a by-product. The N_2O formation has a bi-modal profile as a function of temperature. The low temperature N_2O formation around 200°C is a result of NH_3 oxidation by NO whereas the high temperature N_2O formation around 525°C is mainly from the oxidation of NH_3 by O_2. The latest SCR formulation generates much less N_2O. At 200°C, the 2007 SCR formulation yielded up to 3 times less N_2O compared to the two older formulations.

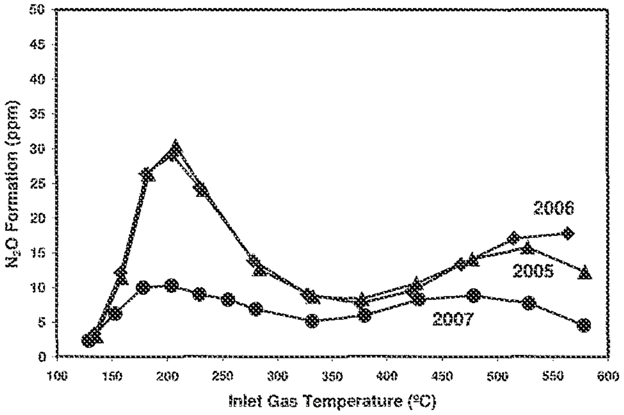

FIGURE 4. N_2O formation results for the STANDARD SCR REACTION in Figure 1. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670 °C.

Durable low temperature NOx performance is desirable for light-duty diesel applications. However, a considerable amount of NOx is emitted at high temperature during the time when the vehicle undergoes an active DPF regeneration. This added NOx emission must be compensated by additional NOx conversion during low temperature operation. As mentioned previously, the high temperature NOx performance of the 2007 SCR catalyst drops sharply as the temperature increases beyond 400 °C (Figure 3). Figure 5 plots the NH_3 oxidation of the three catalysts in the absence of NOx. Ammonia is more strongly oxidized by the 2007 SCR catalyst. In addition, a clear inflection point at 400 °C is observed which corresponds to the formation of NOx (Figure 6). As a result, the NOx performance in Figure 3 declines rapidly due to, in part, the remake of NOx from NH_3 oxidation (Figure 6).

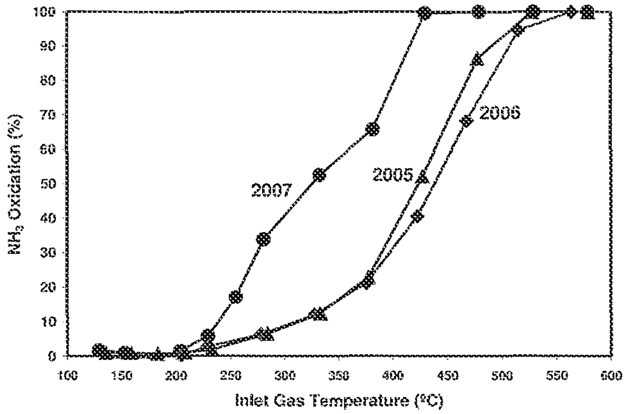

FIGURE 5. NH_3 conversion results for the ammonia oxidation reaction in the absence of NOx. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670 °C.

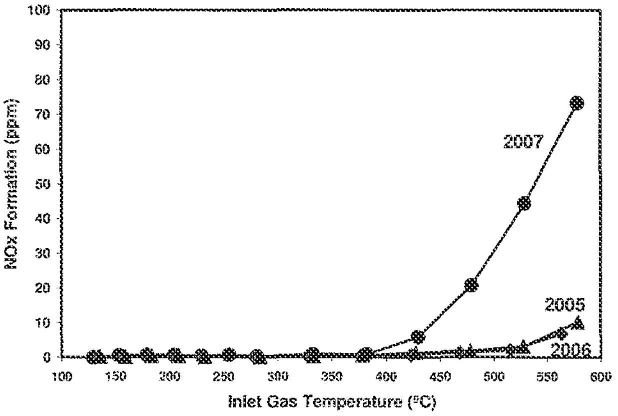

FIGURE 6. NOx formation (ppm) results for the ammonia oxidation reaction in the absence of NOx (FIGURE 5). Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670 °C.

Unrefined engine exhaust temperature control during DPF regeneration events coupled with inexact temperature measurement may expose SCR catalysts to an occasional unexpected over-temperature. As a result, the SCR formulations are screened with a robustness test protocol consisting of hydrothermal exposure at 900 °C for 1 hour. These types of data are used to define the short-term never-to-exceed (NTE) temperature. The NTE testing provides a higher degree of discrimination among similar performing formulations compared to the less severe 64hr/670 °C standard aging.

Figure 7 illustrates the remarkable progress that has been made in the past year with the durability of the 2007 Cu/zeolite based SCR formulation. Among the dozens of Cu/zeolite formulations tested in past years, no formulation has been able to withstanding exposure up to 900 °C while maintaining stable NOx performance at 200 °C. Under the 1 hour/900 °C aging condition, the 2007 SCR catalyst retained 90% NOx conversion at 200 °C. All older SCR formulations have achieved no better than 20% NOx conversion. The enhanced durability of the 2007 SCR formulations has been mainly attributed to advances in the zeolite type and composition.

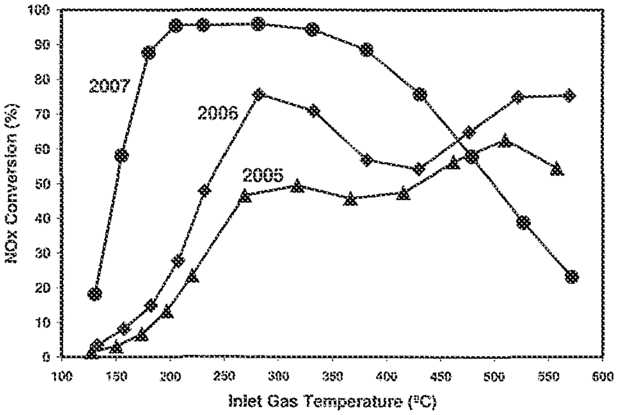

FIGURE 7. NOx conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900°C.

Based on these encouraging results, a more severe time-at-temperature aging study was undertaken with the 2007 SCR formulation defined in Figure 7. The aging and evaluation helped determine the full robustness map of this promising Cu/zeolite based SCR formulation.

TIME-AT-TEMPERATURE PERFORMANCE

Current diesel engines require a DPF to meet the Tier 2 particulate matter standards. As a result, the SCR must be able to tolerate extreme temperature swings due to typical and non-typical active DPF regenerations. Also, the durability requirement of the SCR formulation will hinge largely on the location of the SCR relative to the DPF. SCR formulations placed directly upstream must withstand high exhaust temperatures generated from the engine or over a DOC. SCR formulations placed directly downstream of the DPF will need to withstand extended temperatures coming from soot regeneration. However, the most severe conditions will likely arise from future combination systems where the DPF filter is coated with a SCR formulation. Clearly, for promising SCR formulations in close relationship to the DPF, there is a need to determine the full temperature based durability map to better assess the thermal robustness.

A broad range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range. The aging time was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. The catalyst NOx performance was based on the "Standard" SCR reaction, the "Fast" SCR reaction, and ammonia oxidation reaction (in the absence of NOx).

For the typical light-duty driving conditions, the "Standard" SCR reaction is considered to be the most challenging since little or no NO_2 is expected below 250°C.

The effect of long-term hydrothermal aging at 700°C versus duration was carried out in the laboratory. The duration was varied from 1 hour to 256 hours while the aging temperature was held constant at 700°C. NOx conversion as a function of temperature was measured on each individual sample. Results show that the 2007 Cu/zeolite SCR catalyst demonstrated outstanding stability (Figure 8). Recall that the 64 hour aging duration has been calculated to be an equivalent of 120,000 miles for a typical light-duty diesel. As long as the SCR catalyst temperature does not exceed 700°C, these results heighten the industry's confidence for successfully implementing a Cu/zeolite SCR formulation into production.

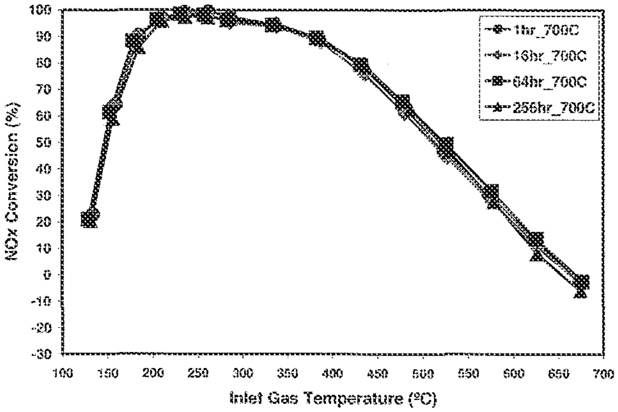

FIGURE 8. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 700°C for 1 hour – 256 hours.

For configurations where the SCR catalyst is placed upstream of the DPF, temperatures greater than 700°C are not expected normally. However, higher temperatures may be apparent for SCR catalysts placed immediately downstream of a DPF and for SCR formulations coated on the DPF itself. Therefore, the effect of long-term hydrothermal aging for up to 256 hours at 800°C was also conducted. The results showing the NOx conversion as a function of temperature are plotted in Figure 9. The Cu/zeolite SCR catalyst proved to demonstrate durable NOx conversion up to 64 hours. Further aging out to 140 hours and then out to 256 hours resulted in a continual decline in the low temperature NOx conversion. The high temperature NOx conversion declines steadily from 1 hour to 64 hours but then mildly improves from 64 hours to 256 hours. Recall, the high NOx conversion becomes negative due to aggressive oxidation of NH_3 with O_2 to yield NOx.

Given the observed hydrothermal aging limitation of 64 hours at 800°C, these data provide encouragement for the potential development of a single combined SCR/DPF substrate where the SCR formulation is coated within the DPF substrate. This consolidation would provide smaller vehicle packaging and lower cost possibilities.

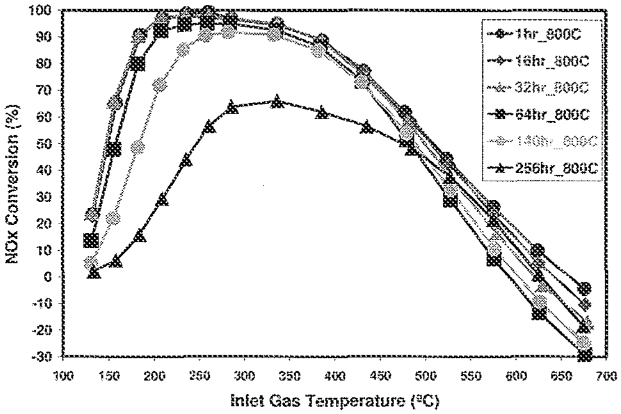

FIGURE 9. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 800°C for 1 hour – 256 hours.

Figure 10 shows the NOx conversion results for samples hydrothermally aged at 900°C for durations from 1 hour to 64 hours. Durable NOx conversion is observed up to 4 hours. The Cu/zeolite cannot tolerate 8 hours and the performance is completely destroyed with the individual samples aged out to 16 hours and beyond.

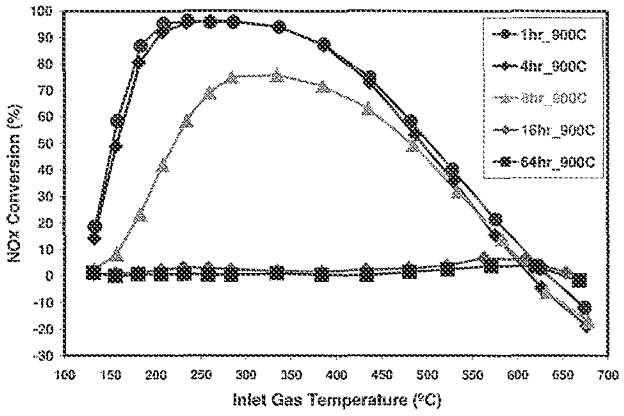

FIGURE 10. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 900°C for 1 hour – 64 hours.

Figure 11 shows the NOx conversion results for samples hydrothermally aged at 950°C for 1, 2, 4, and 8 hours. The Cu/zeolite formulation can only tolerate 1 hour exposure to 950°C. There is a significant drop in performance after 2 hours and complete deactivation after only 4 hours of exposure.

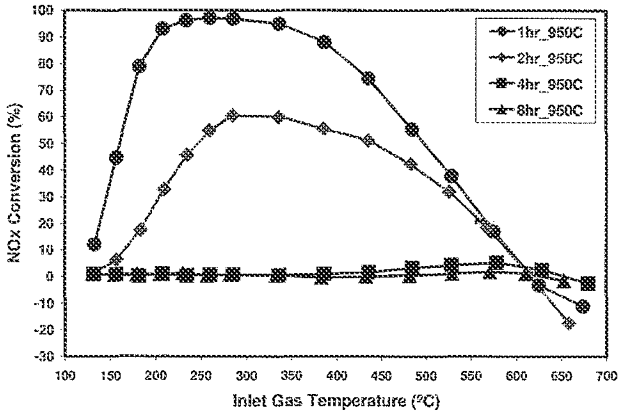

FIGURE 11. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 950°C for 1 hour – 8 hours.

For a 1 hour exposure, the short-term never-to-exceed (NTE) temperature is defined as the maximum temperature the SCR formulation can tolerate without showing signs of significant deactivation. This is particularly helpful for use by engine control calibration engineers. Figure 12 shows the NOx conversion results for samples hydrothermally aged for 1 hour with temperatures ranging from 700°C to 1100°C. The results indicated that the NTE temperature was 950°C but without much margin for error. For example, at 250°C, increasing the aging temperature from 950°C to 1000°C decreased the NOx conversion from 95% to 18%. At 1100°C, the NOx conversion was further reduced to 0%. It was clear that structural damage occurred and further work to understand the deactivation will be carried out in the near future.

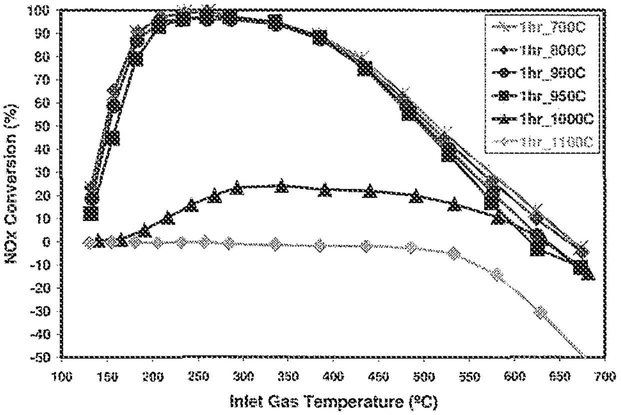

FIGURE 12. Short-term Never-To-Exceed (NTE) Temperature: NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 1 hour from 700°C – 1100°C.

Figure 13 shows the NOx conversion results for samples hydrothermally aged for 64 hours and temperature exposure from 670°C to 900°C. For the baseline, 64 hours at 670°C aging (120k mi equivalent), the Cu/zeolite activity data clearly shows > 90% NOx conversion in the 200°C – 350°C temperature window. However, the maximum temperature for this extended duration is 800°C. An additional 50°C, corresponding to 850°C, had a severe impact on the catalyst durability.

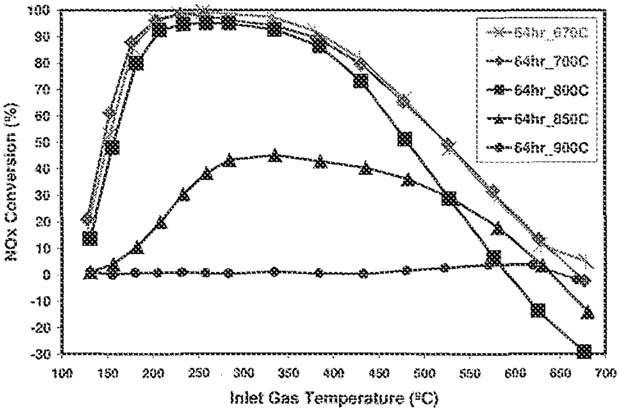

FIGURE 13. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

The same identical samples presented in Figures 8 - 13 were further evaluated under two other SCR reactions. These reactions were the "Fast" SCR Reaction and "Ammonia Oxidation" Reaction in the absence of NOx. Comparison of Figure 13 and Figure 14, the data resulting from the "Fast" SCR Reaction experiments yielded the same trends in NOx performance as the "Standard" SCR Reaction but with slightly better activity at the low to moderate temperatures.

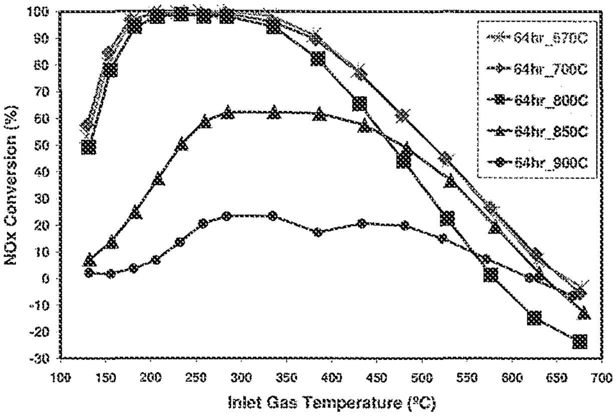

FIGURE 14. NOx conversion results for the FAST SCR REACTION. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

As illustrated in Figure 15, the ammonia oxidation evaluation in the absence of NOx yielded curves showing the deactivation of the catalyst with respect to time-at-temperature. The results show a similar deactivation trend as the NOx performance.

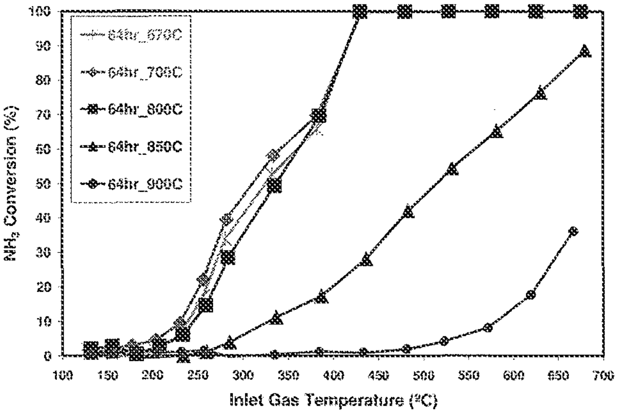

FIGURE 15. NH_3 conversion results for the AMMONIA OXIDATION REACTION in the absence of NOx. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

The results just described were for samples aged for 64 hours but at varying temperatures. Furthermore, the corresponding samples aged at the various other aging conditions showed a similar deactivation trend as the corresponding NOx performance. As a result, these data sets of NOx conversion and NH_3 oxidation have been excluded from this paper for brevity.

BET SURFACE AREA MEASUREMENTS

The BET surface area of samples located in aging position "A" were measured to determine if a trend can be developed with the NOx activity measurements. For post mortem analysis, this type of relationship is particularly useful for determining the likely temperature exposure experienced on field returned SCR parts. The zeolite framework is known to de-aluminate steadily with mild temperatures and suddenly at high temperatures. These changes are accompanied with changes in the total surface area.

The normalized BET surface area results for samples aged up to 950°C are presented in Figure 16. The results have been normalized to the sample aged for 1 hour at 700°C. For all samples aged at 700°C, the surface remained relatively stable. A 10% reduction in surface area was observed with the 256hours/700°C aged sample. This observation is in good agreement with the NOx performance data. Recall from Figure 8 that there was no significant change in the NOx performance for all samples aged at 700°C. At 800°C, the surface area dropped suddenly from the 64 hour aging to the 140 hour aging. This drop-off in surface area corresponds to the drop-off in NOx performance observed in Figure 9. At 900°C, the surface area declined after 4 hours of aging. This also corresponds quite well with Figure 10 where the first sign of NOx conversion deterioration occurred beyond 4 hours of aging. At 950°C, the results on Figure 16 show that the surface area immediately drops after the 1st hour of aging. This coincides nicely with the NOx performance data presented in Figure 11.

Comparing the NOx performance data in the previous section to the surface area data in this section, a general trend exists that links the sudden drop in NOx conversion with the sudden drop in surface area. The first 20% drop in surface area is associated with a marginal impact on the NOx conversion. However, the rapid decline in NOx conversion is associated with the aged samples measuring greater than 20% decrease in the surface area.

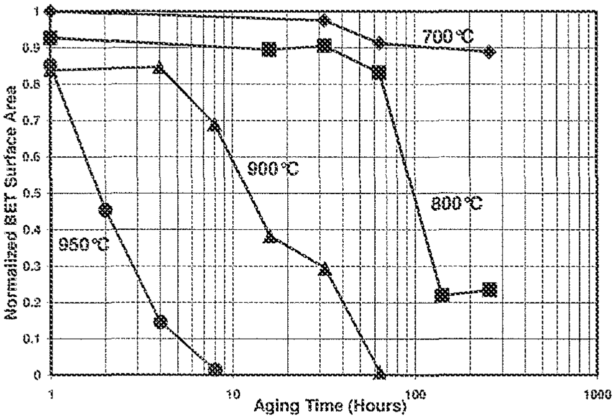

FIGURE 16. Normalized BET surface area results from laboratory aged samples at as function of time 1 - 256 hours and temperatures between 700°C – 950°C.

Figure 17 shows the normalized BET surface area for two sets of samples aged as a function of temperature. The first set of samples was aged for 1 hour in duration to represent the short-term never-to-exceed (NTE) temperature. The second set of samples was aged for 64 hours in duration to represent the long-term SCR durability needed for DPF regeneration conditions. For the 1 hour case, results indicated that the surface area steadily dropped as the temperature was increased to 950°C. However, the SCR surface area completely collapsed by increasing the temperature by an additional 50°C. The surface area for the 64 hour aged samples also collapsed sharply once the temperature exceeded 800°C. Vehicle events resulting in conditions beyond 1hr/950°C or 64hr/800°C will cause catastrophic deactivation from both the NOx conversion and surface area points of view.

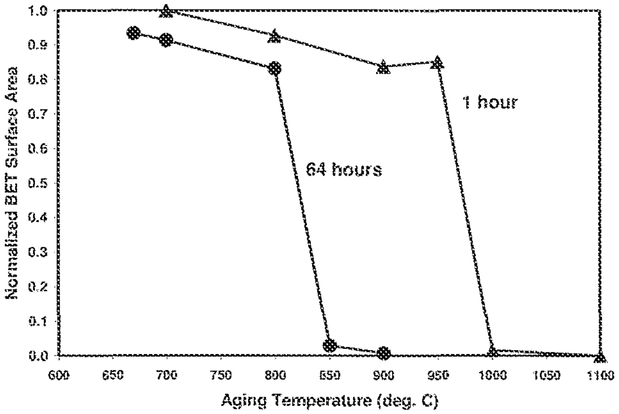

FIGURE 17. Normalized BET surface area results from laboratory 1 hour and 64 hour aged samples as a function of temperature.

TEMPERATURE PROGRAMMED REDUCTION (TPR)

Different Cu-species can yield different reduction temperatures. Therefore, the TPR result may reveal direct evidence of changing Cu-species in the catalyst and may be correlated to the deactivation of SCR activity after aging.

The effect of aging temperature on TPR for the 2007 SCR catalyst is shown in Figure 18. As the aging temperature increased from 800°C to 950°C, the reduction peak at 330°C increased proportionally. The upward shift in TPR peak temperatures, due to the increase in aging temperature, was reported for zeolite-based SCR catalysts [4]. For Cu/ZSM-5 catalysts, a prolonged hydrothermal aging process was also reported to cause an upward shift of TPR peak temperature due to some Cu-species on de-aluminated zeolite [5]. Therefore, the increase in the 330°C peak from aging at 800°C to 950°C in Figure 18 indicated that the extent of de-alumination increased. This observation agreed with the result in BET surface areas (Figure 17) that had a 15% decrease from 800°C to 950°C because of an increase in de-alumination or subsequent collapse of zeolite structure. However, it was noted that the three catalysts aged from 800°C to 950 °C for 1 hour still yielded good NH_3-SCR catalytic activities (Figure 12).

After aging at 1hr/1100°C, the catalyst had almost zero surface area (Figure 17). Since the zeolite was destroyed, no TPR peak around 330°C was observed (Figure 18). However, there was an elevated TPR curve above 400°C extending up to 600°C. This high-temperature TPR curve corresponds to the Cu species that strongly interacted with destroyed zeolite materials after 1hr/1100°C lean hydrothermal aging. Yan et al. experimentally showed that Cu-aluminate ($CuAl_2O_4$) yielded similar TPR features above 400°C [5]. It was likely that our observed Cu-species was reminiscent of $CuAl_2O_4$. The small TPR peaks between 200°C and 250°C are probably from discrete CuO particles or CuO/SiO_2 after the 1hr/1100°C aging. These Cu-species associated with materials from destroyed zeolite were not catalytically active for the NH_3-SCR reaction (Figure 12). In fact, the 1hr/1100°C aged sample had no NOx conversion below 500°C and negative NOx conversion above 500°C. This was the result of non-selective NH_3 oxidation with O_2 to yield additional net NOx.

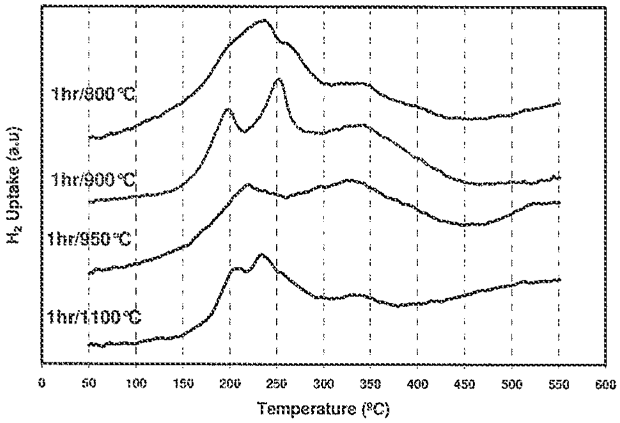

FIGURE 18. TPR results of 2007 SCR formulation aged for 1 hour and temperatures between 800°C – 1100°C.

At 900°C, an increase in aging time from 1 to 8 hours yielded an additional TPR peak at 400°C (Figure 19). This peak became more prominent after aging for 64 hours. As discussed above, the Cu-species responsible for the TPR peaks above 400°C were likely interacting strongly with materials from destroyed zeolite and not active for the desired NH_3-SCR reaction. As a result, for increasing aging time at 900°C, the growth of this 400°C TPR peak in Figure 19 corresponded to the decline in observed SCR activity in Figure 10. For the samples that were aged at 950°C, an increase in aging time also produced an extra TPR peak at 450°C. Apparently, the Cu-species interacting strongly with materials from destroyed zeolite became harder to reduce as the aging temperature became higher. After aging at 1hr/1100°C, the Cu-species likely would yield a TPR peak above 600°C as indicated in Figure 18.

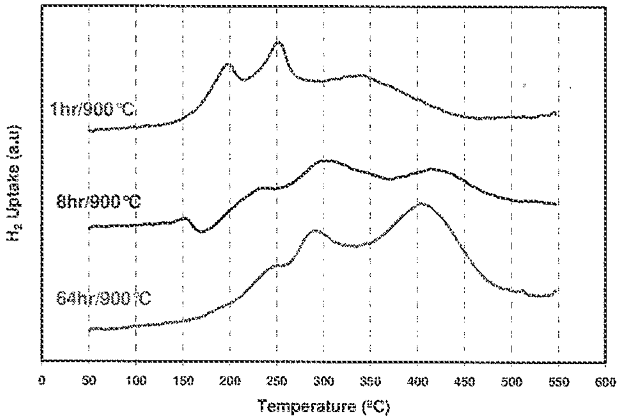

FIGURE 19. TPR results of 2007 SCR formulation aged at 900°C and durations from 1 hour – 64 hours.

CONCLUSIONS

The following conclusions emerge from this study:

- In past years, no reported Cu/zeolite SCR formulation was able to yield stable low temperature NOx performance after exposure to hydrothermal conditions consisting of 1 hour at 950°C. Within the last year, a remarkable Cu/zeolite SCR formulation was identified with high NOx conversion in the 200°C – 350°C temperature range. At the 950°C aging condition, the 2007 SCR formulation became more sensitivity as the duration was increased beyond 1 hour.
- Upon the completion of a full time-at-temperature durability study, the newly developed Cu/zeolite SCR formulation was confirmed to tolerate the following hydrothermal conditions:
  - > 256 hours at 700°C.
  - 64 hours at 800°C.
  - 4 hours at 900°C.
  - 1 hour at 950°C.
- The BET surface area results trended with the NOx conversion. The first 20% drop in surface area was associated with a marginal impact on the NOx conversion. Beyond the initial 20%, a further decline in the surface area was rapid and closely related to the negative impact on NOx performance.
- TPR of aged Cu/zeolite catalysts was used to correlate the change in Cu-species to the status of zeolite or to NH_3-SCR activity after aging. The observation of a TPR peak above 400°C indicated a strong interaction of Cu with destroyed zeolite and a decline in catalytic activity. Since the temperature of this TPR peak increased with increasing aging temperature, this feature may be used to diagnose the exposure temperature of a deactivated Cu/zeolite SCR catalyst.

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CONTACT

Giovanni Cavataio, Ph.D.
Ford Motor Company
Research and Innovation Center
2101 Village Road
P.O. Box 2053, MD3179, RIC
Dearborn, Michigan 48124
(313) 322-3357
jcavatai@ford.com

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In *Inter Partes* Reexamination of:	)	
	:	Examiner: DIAMOND, ALAN D
BULL ET AL.	)	
	:	Group Art Unit: 3991
Reexamination Control No. 95/001,453	)	
	:	Confirmation No: 2755
Patent No. 7,601,662	)	
	:	
Issued: October 13, 2009	)	
	:	
For: COPPER CHA ZEOLITE CATALYSTS	) :	

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Central Reexamination Unit
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION OF GARY L. HALLER, PH.D. UNDER 37 C.F.R. § 1.132

I, Gary L. Haller, do declare and say as follows:

1. I am the Henry Prentiss Becton Professor of Engineering and Applied Science at Yale University with joint appointments in the Departments of Chemical and Environmental Engineering and Chemistry. I received a B.S. in mathematics from the University of Nebraska at Kearney in 1962 and a Ph.D. in physical chemistry from Northwestern University in 1966. After a NATO Post-doctoral Fellowship at Oxford University, I joined the faculty of Yale where I have held a variety of administrative posts that include Chair of the Department of Chemical Engineering, Chair of the Council of Engineering, and Deputy Provost for Physical Sciences and Engineering. I have been the Chair of the American Chemical Society Division of Colloid and Surface Chemistry, President of the Catalysis Society of North America, co-Editor of the Journal of Catalysis, and served on the editorial boards of several journals that publish articles relevant to heterogeneous catalysis.

2. My research has involved the molecular understanding of heterogeneous catalysts and combines the inorganic chemistry of catalyst synthesis, physical chemistry of spectroscopic characterization of heterogeneous catalysts, and the kinetics and mechanism of simple organic probe reactions on heterogeneous catalysts. I am a co-author of about 220 publications, including one co-authored book and six patents. A copy of my curriculum vitae is attached as Exhibit A.

3. Since 1986, I have been a paid consultant with Engelhard Corporation, the predecessor in interest of the patent owner, BASF Catalysts LLC, in the areas of automotive catalysts, including treatment of diesel engine exhaust such as reduction of nitrogen oxides. I have been retained by the patent owner's counsel as a technical expert in this reexamination. I am being compensated hourly. I am not otherwise affiliated with the patent owner.

Scope of Declaration

4. The patent owner's counsel provided and I have reviewed United States Patent no. 7,601,662 ("the '662 patent"), the Office Action dated November 16, 2010 ("the Office Action"), and the references cited in the Office Action. I have also reviewed references cited in this Declaration.

5. I have been asked to provide my opinions on what would have been the view of a person of ordinary skill in the art as of February 2007. I believe that I can accurately describe the perspective of such a person. For the purpose of this declaration I have understood that a person skilled in this art would have had at least a Master's degree in chemistry or a related discipline, have knowledge of the structure and chemistry of molecular sieves, such as zeolites, factors that impact their hydrothermal stability and catalytic activity, including the reduction of oxides of nitrogen.

6. The opinions set forth in this declaration are based on my professional knowledge and expertise, as indicated in my curriculum vitae, my review of the '662 patent, the Office Action dated November 16, 2010, including the documents cited in the office action, as well as additional documents cited in this declaration.

Zeolite Materials and Hydrothermal Stability

7. Many factors can affect the hydrothermal stability of a zeolite. Zeolite structure (or framework) type, the nature of cations associated with tetrahedral aluminum in the zeolite structure, hydroxyl density, silica to alumina ratio, stabilizing thermal or chemical treatments, and other factors all have an impact on hydrothermal stability. Predicting hydrothermal stability based on one of these factors alone is nearly impossible, and the hydrothermal stability of a particular zeolite will ultimately depend more on the framework type and its overall composition than on silica to alumina ratio alone. This will be addressed in more detail below with respect to the rejection of claims 1-11 over Dedecek et al. in view of Chung. With respect to the nature of cations associated with tetrahedral aluminum in the zeolite structure, and the Office Action quote of the Request for Reexamination, that "the '662 Patent provides absolutely no guidance as to how one of ordinary skill in the art would measure the amount of non-exchanged copper present in the claimed CHA zeolite," the following response is provided. A person of ordinary skill in the art would be aware of the method of X-ray absorption spectroscopy (see C. Márquez-Alvarez, I. Rodríguez-Ramos, A. Guerrero-Ruiz, G. L. Haller, and M. Fernández-García, Selective Reduction of NOx with Propene under Oxidative Conditions: Nature of the Active Sites on Copper-Based Catalysts, J. Am. Chem. Soc., 1997, 119 (12), pp 2905–2914), that could be used to characterize both exchanged copper as well as non-exchanged copper, i.e., XANES and EXAFS analysis of X-ray absorption do not require long-range order and detect every atom at the X-ray absorption edge of copper.

Nitrogen Oxides Abatement in Exhaust Gas

8. The terminology "reduction of oxides of nitrogen" includes a variety of reactions, including adsorption, disproportionation, dissociation and/or oxidizing NO by oxygen, adsorption and/or dissociation of NO_2, reducing NO by the selective catalytic reduction (SCR) of NO with ammonia in the presence of oxygen, reducing NO by the selective catalytic reduction of NO with hydrocarbons with and without oxygen present, and reduction of NO with other reducing molecules present in exhaust gas such as hydrogen, methane, or CO. *See, e.g.*, Centi G. et al., Nature of Active Species in Copper-Based Catalysts and Their Chemistry of Transformation of Nitrogen Oxides, Applied Catalysis A 132 (1995) 179-259 at 185 (Exhibit B, at 185 (Table 1)). The mechanism and the reaction conditions of each of these reactions can vary widely, and to say that a particular material such as a specific Cu zeolite, such as ZSM-5, is useful for reduction of oxides of nitrogen does not

mean that the specific zeolite will be effective for each of these reaction types. For example, it is well known that three-way catalysts, which are effective for the abatement of hydrocarbons, carbon monoxide and NOx in traditional gasoline powered engines are not effective in lean burn engines such as diesel engines.

9. With respect to reduction of oxides of nitrogen in the presence of a reducing agent, in general, different reducing agents preferentially adsorb on different sites in different forms and lead to different mechanisms of action. In other words, the activity and mechanism of action of a particular reducing agent are not good predictors of the reactivity of different reducing agents on a particular zeolite catalyst. Alkenes, e.g., ethene or propene, are particularly effective reducing agents for NO on metal exchanged zeolites and it is generally agreed that these alkenes are preferentially adsorbed on acid sites. In contrast, while ammonia is a base that will adsorb on acid sites, "Ammonia readily reacts with copper ions especially in zeolite cavities forming copper-ammine complexes that have been characterized by several techniques such as adsorption measurements [24, 31], X-ray diffraction [313], ESR [38, 314-316], IR [38, 315, 317] and X-ray absorption [268] spectroscopies." *See* G. Centi and S. Perathoner, Applied Catalysis A: General 132, 1995, page 216, first sentence in section 4.3 (Exhibit C). It is for this reason that NO reduction by hydrocarbons and NO reduction by ammonia on Cu zeolites do not generally have parallel behavior and why using the results of hydrocarbon reduction of NO is not a good guide to NO reduction by ammonia on the same Cu zeolite, let alone for two different Cu zeolite catalysts when the structure type and/or composition of the zeolites are different.

The '662 Patent

10. The novel invention of the '662 patent is a catalyst comprising a zeolite having the CHA crystal structure, with a silica to alumina ratio greater than about 15 and a copper to aluminum atomic ratio greater than about 0.25. More specific claims of the '662 patent are directed to silica to alumina ratios in the range of 15 and 40, and/or Cu/Al ratios in the range of about 0.25 to 0.5. A review of the '662 patent, including the background, description, Examples and claims reveals that there was a longstanding need for catalyst material that had good low temperature conversion of NOx at 350 °C and below and that maintained NOx conversion without excessive loss of NOx conversion after hydrothermal aging at high temperatures exceeding 650 °C. As is evident from Figure 12 of the '662 patent, a novel aspect of the invention is not just hydrothermal stability with respect to silica to alumina ratio alone, but the particular hydrothermal stability exhibited by Cu-containing chabazite materials.

Rejection of Claim 1 of the '662 Patent Over Yuen/Ritscher

11. Claim 1 covers a catalyst comprising a zeolite having the CHA crystal structure and a mole ratio of silica to alumina greater than about 15 and an atomic ratio of copper to aluminum exceeding about 0.25. In the Office Action, claim 1 has been rejected as being unpatentable over Yuen, which incorporates by reference Ritscher. At paragraph 10, Yuen provides a process for the reduction of oxides of nitrogen, which involves contacting a gas stream with a molecular sieve having the CHA crystal structure having a mole ratio of 50 to 1500 of (1) an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to (2) an oxide selected from aluminum oxide, iron oxide, titanium oxide, gallium oxide or mixtures thereof. Taking into account the various combinations and without even considering varying weight percentages of oxide (1) and oxide (2), there are three possibilities for oxide (1) and fourteen possibilities of oxide (2). Yuen further says that the molecular sieve can contain a metal or metal ions such as cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof capable of catalyzing

reduction of oxides of nitrogen, which may be conducted in the presence of a stoichiometric excess of oxygen. This list includes eleven individual metals and taking into account the different combinations of these eleven metals together with the various combinations of oxide (1) and oxide (2), there are nearly three thousand possible materials, taking into account only binary metal combinations, having the CHA crystal structure described that may be capable of catalyzing the reduction of oxides of nitrogen.

12. Yuen appears to be more concerned with providing an improved method to manufacture chabazite materials than NOx reduction, as there are no examples in Yuen pertaining to reducing nitrogen oxides. In particular, paragraph 0012 makes note of the "advantage of the present invention that the reaction is conducted in the presence of hydroxide rather than fluoride" which distinguishes it over prior art cited in paragraph 0009. There is no discussion in Yuen of which CHA materials or catalyst properties such as which metal ions or amounts are important for the reduction of oxides of nitrogen to provide good low temperature conversion below 350 °C. The Office Action focuses on Example 3 (of 16 examples) of Yuen to combine with information in Ritscher. The selection of Example 3 appears to be random and no reasoning or information is provided as to why this example would provide a catalyst for the reduction of oxides of nitrogen oxides that is best among the 16 examples.

13. With regard to paragraph 0034 of Yuen, Yuen appears to be interested in the process for reducing oxides of nitrogen in the presence of a zeolite as discussed in Ritscher. In particular, Yuen specifies "the catalytic process in the combustion of carbon monoxide and hydrocarbons and the catalytic reduction of oxides of nitrogen contained in a gas stream," i.e., a three-way catalyst not involving SCR of oxides of nitrogen by ammonia. Yuen does not indicate that copper ions or the catalyst manufacturing techniques in Ritscher are of particular interest because Yuen lists eleven different metals/metal ions of interest. There is nothing stated in Yuen that chabazite structure zeolites would be better at NOx conversion than the zeolites in Ritscher. It could not be predicted which of the thousands of materials in Yuen would provide a material with improved properties with respect to reduction of oxides of nitrogen and hydrothermal stability and which metal or metal ion would provide such a catalyst.

14. According to the Office Action, paragraph 0034 of Yuen describes an example of a process for the reduction of oxides of nitrogen with reference to U.S. patent number 4,297,328 (Ritscher). Ritscher describes just one example of a process for reduction of oxides of nitrogen—a three-way catalytic process for removing carbon monoxide, hydrocarbons and nitrogen oxides from a gas stream. Ritscher appears to prefer ZSM-5 catalysts in his Examples and claims and lists other structure types such as ZSM-8, ZSM-11, ZSM-12, Hyper-Y, ultrastabilized Y, silacalite, Beta, mordenite, and erionite.

15. Selective catalytic reduction of oxides of nitrogen in the presence of oxygen or providing good low temperature conversion of NOx below 350 °C is not discussed in Ritscher. Ritscher provides no information with respect to providing improved NOx conversion of the zeolites or maintaining these properties or structure and surface area stability after hydrothermal aging. A person of skill in the art would not use the information in Ritscher in combination with Yuen because the zeolite framework types of interest in Ritscher and Yuen are dramatically different, and the properties of a ZSM-5 zeolite containing a certain amount of copper would not be expected to be the same for a zeolite having a different framework type such as chabazite.

16. Furthermore, the catalyst described in Ritscher Example at column 10, lines 28-29 contains 7.3% copper by weight, but the catalyst is a mixture of 80 parts of ZSM-5 zeolite and 20 parts

alumina (col. 10, lines 3-8). The amount of actual copper contained on the zeolite after ion exchanging the 80/20 zeolite/alumina pellets would be difficult to determine. To say that the catalyst is a zeolite that contains 7.3% copper by weight is speculative.

17. It must be noted again that the catalyst in Ritscher is a three-way catalyst, which is not designed to operate in a lean environment at low temperature, e.g., as low as 210 °C—the type of environment which the catalyst of the '662 patent was designed and demonstrated to be active. In fact, a close review of the Examples (Table V at column 7) shows that the aged (4 hours in 10% H_2O) samples that were run at stoichiometric redox ratio or in excess oxygen had **no** NOx conversion at all. This hardly provides a reason to a person of ordinary skill in the art to use the Example in Ritscher and to use a similar amount of copper in Yuen, who states that a catalyst for reducing nitrogen oxides in excess oxygen was desired. If anything, the skilled artisan would avoid using the information in Ritscher because the NOx conversion of the aged samples in excess oxygen was nonexistent.

The Rejection of Claims 1-11 Over Zones In View of Ishihara

18. The Office Action rejects claims 1-11 of the '662 patent, stating that one of ordinary skill in the art would have had a reasonable expectation that loading the chabazite zeolite described in Zones using the ion-exchange method described in Ishihara would have resulted in a copper chabazite that would be effective in the conversion of oxides of nitrogen to nitrogen. The Office Action states that a person of ordinary skill in the art at the time of priority filing of the '662 patent looking to make a copper exchanged zeolite for the reduction of oxides of nitrogen would have been motivated to use the ion exchange technique in Ishihara to add copper to the chabazite of Zones because Ishihara used and preferred SAPO-34, which is a very well-known silico-alumino phosphate molecular sieve having a structure of the chabazite type. I do not agree that this is the case.

United States Patent No. 6,709,644 (Zones)

19. Zones relates to a zeolite having the CHA crystal structure that can be used for numerous processes: separation of gasses including separating carbon dioxide from natural gas (col. 5, lines 66-67), as catalysts used for the reduction of oxides of nitrogen in a gas stream in the presence of oxygen (col. 1, lines 54-66) but the reducing agent is unspecified, converting lower alcohols and other oxygenated hydrocarbons to a gasoline boiling point hydrocarbon product (col. 5, lines 18-14), and for producing dimethylamine (col. 5, lines 36-40).

20. Zones does not present any data or examples pertaining to NOx reduction or suggest that the CHA material provides excellent nitrogen oxides reduction at low temperatures or has good hydrothermal stability compared to other zeolites. It appears that Zones pertains more to discovery of a new zeolite with a small crystal size and not to an improvement in catalytic reduction of nitrogen oxides. No particular significance can be attributed to the statement in Zones that the SSZ-62 zeolite was useful for reducing oxides of nitrogen nor what reducing agent might be used under any particular conditions, because generally speaking, many of the almost 200 framework types of zeolites will exhibit some NOx reduction capability. The important question is whether any particular properties or combination of properties would be expected by a person of skill in the art to be especially good based on the information in Zones—and that answer is no. The scientific literature and the '662 patent recognized that zeolites promoted with metals could be used for the reduction of oxides of nitrogen. The more important question is why would a person of skill in the art select one of the many zeolites available at the time of the '662 patent filing, and then choose the selected silica to alumina ratio and choose the amount of copper among the various other metal ions

(iron, cobalt, nickel, cerium, etc.) that promote the reduction of oxides of nitrogen? Zones provides no information on an amount of copper to be used—the passage relied on in the Office Action, namely column 5, lines 25-35, as teaching a copper percentage in the range of 0.05% to 5% does not pertain to a catalyst for reducing oxides of nitrogen, and it does not refer to copper metal. It refers to all metals in the Periodic Table (Groups I to VIII), with a preference for Group IA metals (not including copper), and this is in reference to a catalyst for the condensation of alcohols.

Ishihara

21. Ishihara et al. describe a copper ion exchanged SAPO-34 catalyst using propene to reduce nitrogen oxide. While SAPO-34 does have the CHA structure, it does not have the same chemical components, it is a silico-alumino phosphate of the chabazite type structure and not a alumino-silicate chabazite type structure having a silica to alumina ratio greater than 15 (see B. M. Lok et al., J. Am. Chem. Soc 1984, 106, 6092-6093 (cited in the Office Action and Request)). For the reaction of interest in Lok et al., n-butane cracking, SAPO-34 in this early comparison (see Table II), is inferior to chabazite by a factor of 2-70, indicating how different the reaction chemistries are for SAPO-34 and a alumino-silicate, both with the CHA structure. A more important aspect of the structure is the nature of the cation exchange capacity, critical for the ion exchange described in the '662 patent. In the alumino-silicate CHA described in the '662 patent having a silica to alumina ratio greater than 15, the cation exchange sites are created by isomorphous substitution of Si by Al, and thus, it is important to describe the ratio of copper to potential ion exchange sites resulting from Al substitution for Si (as Claim 1 does) as "an atomic ratio of copper to aluminum exceeding about 0.25." The same considerations apply to claims 3 to 9 of the '662 patent, which claim more specific ranges of silica to alumina and Cu/Al. However, the ion exchange sites of silico-alumino phosphates, discussed by Ishihara et al., create cation exchange sites by Si substitution for P. "Silicoaluminophosphates (SAPO-n) exhibit cation-exchange properties as a result of the isomorphous substitution of P in $AlPO_4$ by Si." (see line 8-10, first paragraph of the Introduction to Ishihara et al.) This point is repeated throughout Ishihara et al., (see lines 10-14, column 2, p. 97 of Ishihara et al.), "Consequently, all Si atoms added seem to substitute isomorphously at the lattice position of the P sites but not the Al sites. This is because only one kind of Si bonded with 4 Al atoms was recognized in ^{29}Si-MAS NMR spectra." Thus, the statement that "...Ishihara et al. teaches the use of an amount of copper in a CHA structure molecular sieve that would result in a copper to aluminum atomic ratio exceeding about 0.25 when used with the CHA zeolite of Zones et al." is not correct from a chemical standpoint because Ishihara et al. are discussing a different zeolite with a different chemistry, but more importantly, a minimum cation exchange ratio would now be stated in terms of copper to silicon atomic ratio, not in terms of copper to aluminum cation exchange ratio as claimed in '662 patent.

22. Furthermore, because the reaction chemistry is different in Ishihara et al. (hydrocarbon used as a reducing agent instead of ammonia), the zeolite chemistry is different, and the nature of the cation exchange sites are different (associated with Si instead of Al), it cannot be said that the SAPO-34, as described by Ishihara et al., would be useful for providing amount of copper in the alumino-silicate CHA discussed in the '662 patent. The statement in the Office Action that a person of ordinary skill "at the time of the priority filing of the Bull '662 patent looking to make a copper exchanged chabazite zeolite for the reduction of oxides of nitrogen with the chabazite of Zones '644 patent would have been motivated to use the ion exchange technique described in Ishihara to add copper to the chabazite of Zones '644 because Ishihara used and preferred SAPO-34, which is a very well known silico-aluminophosphate molecular sieve having a structure of the chabazite type." is equivalent to saying that MgO, SnAs, UC, LiH, and TiN are all chemically like NaCl because they all have the same rock salt (NaCl) crystallographic structure.

23. Putting aside the intent of the '662 patent and using the literal constraint of Claim 1, "...an atomic ratio of copper to aluminum exceeding about 0.25." it is also necessary to compare the actual copper to aluminum ratio used by Ishihara et al., which can be estimated from information provided

in section 2, Experimental: "SAPO-5, 11, and 34, (Si, Al, and P contents: 1.77, 12.09, and 10.03 mmol g^{-1}, respectively)" and "In the case of SAPO-n, this amount of Cu [3 wt%] corresponds to ca 75% of the formula ion-exchange capacity, which is estimated by assuming that all the Si forms ion-exchange sites." It should be noted that the Si:Al:P ratios given in Ishihara are presumably those in the synthesis solution, but they imply are also approximate compositions of the SAPO products. Thus, estimated from the information given above results in the atomic ratio of Cu/Al = (0.75 x 1.77)/12.0 = 0.10, well below the 0.25 prescribed by Claims 1-11. A second approach is to use the "Exchanged amounts of Cu^{2+} for each type of SAPO-n,... were estimated to be about 3 wt% from ICP analysis." Using the Al g^{-1} given above, and using the 3 wt% Cu to estimate the Cu/Al ratio as (0.03 g Cu per g catalyst)/63.546 g/mol Cu)/(0.01209 mol Al per g catalyst) = 0.04. Thus, Ishihara approximates a Cu/Al range of 0.04-0.1, the entire range being outside of Claims 1-11. Likewise, at 4 wt% Cu, where the NO conversion was maximum (see Fig. 4 of Ishihara et al.) would provide a Cu/Al atomic ratio of about 0.053-0.13, still outside of Claims 1-11 of the '662 patent.

24. One might also consider other aspects of Ishihara et al. that can be differentiated from claims 1-11 of the '662 patent, apart from the composition of the SAPO-34 catalysts (discussed above) and the nature or the reducing agent (propene instead of ammonia). Note also other differences in the testing relative to '662, particularly the 3 vol % H_2O, 2 hours aging (compared to 10 vol % H_2O, 50 hours aging in '662) and testing at a space velocity of 8,500 h^{-1} (compared to 80,000 h^{-1}). Both the less severe aging and the lower space velocity should have given the SAPO-34 a comparative advantage if SAPO-34 were catalytically similar to a alumino-silicate CHA, but low temperature NO conversion, e.g., around 250 °C, never exceeded 5% after the 800 °C (1073K) aging of SAPO-34 while for the '662 patent CHA catalysts conversion is of order 90% at the same temperature (see Fig. 2, 3, 4 and 7). Thus, even if the person of skill in the art ignored the differences between the materials and the reaction types (propene SCR versus ammonia SCR), that would provide little reason for a person of ordinary skill in the art to utilize the information in Ishihara et al. to modify the zeolite in Zones. If one were to consider crystal structure alone, the extremely poor conversion at low temperatures, particularly for the aged samples shown in Figure 5a of Ishihara et al., would lead a person skilled in the art that a chabazite structured material would not be a good candidate for reduction of oxides of nitrogen at low temperatures or as a material that maintained NOx conversion after hydrothermal aging.

25. In summary, the person of ordinary skill in the art would have no reason to modify the material in Zones as suggested in the Office Action to provide the catalysts in claims 1-11. The chemistry and ion exchange considerations of the materials in Ishihara and Zones are completely different, and there would be no expectation of success in using the techniques in Ishihara in the materials of Zones. In addition, the copper to aluminum ratios in Ishihara are outside the range of claims 1-11 of the '662 patent, and the Office Action fails to explain why one would modify the materials in Zones on the basis of weight percent copper based on the weight percent copper in the silico-alumino phosphate materials of Ishihara. Alternatively, if a person of ordinary skill in the art would consider the modification of the material in Zones based on crystal structure similarities (which they would not), they would be discouraged from making the modification because the low temperature performance of the materials in Ishihara is extremely poor, and the degradation of NOx conversion was quite high when exposed to moderate hydrothermal conditions.

The Rejection of Claims 1-11 Over Dedecek et al. in View of Chung

26. Dedecek et al. never state that chabazite zeolites are useful for the selective catalytic reduction of NOx. Dedececk et al. state: "[z]eolites containing Cu ions attract attention owing to their high catalytic activity in NO [1-5] and N_2O decomposition [6] and selective catalytic reduction (SCR) of NO with ammonia [7-9] and hydrocarbons [10-12]. The Cu^+ ions were suggested [13] to be catalytic centres in NO and N_2O decompositions." There is no further information in Dedecek about the properties of a chabazite containing copper that is useful or particularly good for reducing oxides of nitrogen at low temperatures.

27. It is further stated in the Office Action that "Dedecek et al. teaches a copper to aluminum ratio exceeding about 0.25..." and, in particular, "Dedecek et al. also discloses zeolites having a copper to aluminum atomic ratio of more than 0.25. In particular, Table 2 on p. 66 of Dedecek et al. shows natural zeolites of a copper to aluminum atomic ratio of 0.28, 0.34 and 0.38 and a synthetic zeolite having a copper to aluminum atomic ratio of 0.32. See the 4th-6th entries, respectively, and the 11th entry in Table 2 on p. 66. This statement ignores Table 3 which gives the chemical compositions of these Cu^{2+} chabasites. These are not the CuCHA zeolites as claimed and described in the '662 patent, but CuNa-CHA. Moreover, the examples of natural zeolite also have a Na/Al ratio of 0.08-0.17, a K/Al ratio of about 0.14 and a Fe/Al ratio of 0.31-0.35. That is, these CHA zeolites contain as much Fe as they do Cu. Also, the synthetic zeolite with a Cu/Al ratio of 0.32 has a Na/Al ratio 0.26. Moreover, none of these examples have a silica to alumina ratio of 15 or greater. The Requestor's Request states at page. 56, "Therefore, the mole ratio of silica (SiO_2) to alumina (Al_2O_3) of the synthetic zeolite is 5.4." A close reading of Dedecek et al., at page. 64, column 2 shows that this is the silica to alumina ratio of the starting material, "Zeolite Y (Si/Al = 2.7 [$SiO_2/Al_2O_3 = 5.4$]) in ammonium form was used as a source material...", so this was the silica to alumina ratio of the synthesis solution, not the product. No chemical analysis of the final zeolite is given apart from the Ca/Al ratio of 0.01 and Na/Al ratio of 0.94 (see Table 3, line 2); much of the Na remains after ion exchange with copper, i.e., Na/Al ratio is 0.26 after copper exchange, see Table 3, line 13. Thus, no example in Dedecek et al. with Cu/Al ratio great than 0.25 has a known silica to alumina ratio except for the natural chabasites (which have a silica to alumina ratio of 6.2 but contain cations such as Na^+, K^+ and Fe^{3+} in addition to copper that in all cases exceed the amount of Cu^{2+}. The statement "Thus, with respect to independent claim 1 of the '662 Patent, Dedecek et al. expressly discloses all of the claimed elements, except for the feature involving a silica to alumina mole ratio greater than about 15." seems an exaggeration in the light of the disclosure of the '662 patent that discloses CHA structures with only Cu^{2+} (and perhaps some unchanged protons) that are labeled CuCHA while Dedecek et al. CHA structures in all cases contain significant portions of the cations as Na (in the case of the natural version, K^+ and Fe^{3+}, as well) that are labeled CuNaCHAB to make that distinction in composition.

Chung et al.

28. One of the materials in Chung et al. was not a CHA structure but a MFI structure (see Fig. 1). After a hydrothermal aging at 800 °C for 6 h with 10% H_2O, the conversion of this catalyst dropped from about 70% (fresh) to about 5% at 350 °C (aged), see Fig. 1, hardly a demonstration of useful stability under hydrothermal aging that would be relevant to providing an improved zeolite material for reduction of oxides of nitrogen and having good hydrothermal stability.

29. The other structure in Chung et al. with variable silica to alumina ratio that was tested was of the MOR structure type, dealuminated by acid treatment and steaming to increase the Si/Al ratio and tested for NO removal activity. Compared to the CuZSM-5-2 (ZSM-5 structure), CuNZA2 (MOR structure) had comparable fresh activity (of order 70 % in the range of 350-400 °C, see Fig. 1) but all of the MOR structure catalysts (CuNZA2, CuNZA3, CuNZA4) had **zero** conversion (un-measureable activity) at and below 350 °C after aging at 800 °C with 10% H_2O for 24 hours, see Fig. 2, even though that aging was less severe, 24 h rather than 50 h, than in the Examples of the '662 patent.

30. Note that the catalysts of the MOR structure that had the highest silica to alumina ratio had zero activity at 400 °C after aging at 800 °C with 10% H_2O for 24 hours, while CuNZA3 had about 10% conversion at 400 °C, i.e., this example teaches away from high silica alumina ratios for low

temperature activity after aging. It should also be noted in Chung et al. that 1) the space velocity used for the NO activity is probably low compared to that required in auto engine applications, but is unknown (see section 2, Experimental, p 1512) and 2) that in any case the reducing agent is propene and not ammonia and thus none of these tests may be comparable to '662 because of the different reducing agent. A person skilled in the art would conclude, at most, after reading Dedecek et al. and Chung et al. that increasing the silica to alumina ratio of a zeolite would result in extremely poor conversion in the low temperature window below 350 °C, a key feature in the materials of claims 1-11 of the '662 patent. Thus, while the Requestor and the Office Action focus on "hydrothermal stability" in the literature references, the phrase "hydrothermal stability" is meaningless in heterogeneous catalysis if the catalyst has low or no catalytic activity.

31. It is questionable whether a person of skill in the art would utilize the teachings in Chung et al. with regard to silica to alumina ratio, because, as explained above, this is just one factor that impacts hydrothermal stability of a zeolite. In any event considering the vast differences in the structure types—MFI is a medium pore zeolite, MOR is a large pore zeolite and CHA is a small pore zeolite—and the fact that the CHA does not share any composite building units with either MFI or MOR, a person of skill in the art would limit the teachings in Chung et al. to the structure types studied.

32. In summary, a person of skill in the art would have no reason to modify the zeolitic materials in Dedecek et al. as suggested in the Office Action, because the study in Chung et al. of MFI and MOR structure zeolites would not be expected to be transferable to other structure types of zeolites, in particular CHA. In addition, the NOx conversion performance at low temperatures of the samples in Chung with high silica to alumina ratios was poor to nonexistent. Accordingly, a person of ordinary skill in the art would not modify the Dedecek et al. materials to provide materials in accordance claims 1-11 that have a silica/alumina ratio of 15 and a Cu/Al ratio greater than 0.25, or in specific claims the specific silica/alumina ratio of 25 to 40 (claim 3), 30 (claim 4) or the specific Cu/Al ratio of 0.30 to 0.50 (claim 5) or 0.40, or the specific catalysts claimed in claims 7 and 8.

<u>The '662 Patent Provides Unexpected Results</u>

33. Cavataio et al. (Exhibit D) have recognized the excellent results provided by the invention of the '662 patent. I have been informed that the materials tested in Cavataio et al. were prepared in accordance with the invention claimed in the '662 patent. Cavaito et al. said that the copper chabazite material was "remarkable." Cavaitao noted that no other Cu/zeolite SCR formulation was able to yield stable low temperature NOx performance after exposure to hydrothermal conditions, and that the Cu/zeolite formulation provided high NOx conversion in the 200 °C to 350 °C temperature range.

34. In conclusion, Yuen/Ritscher, Zones/Ishihara, Dedecek/Chung do not contain information leading one skilled in the art to expect a Cu chabazite having a silica to alumina ratio greater than 15 and a Cu/Al ratio greater than 0.25 would exhibit both excellent NOx conversion below 350 °C and maintenance of excellent NOx conversion at low temperatures after hydrothermal aging. There is nothing in Yuen, Zones or Dedecek indicating that chabazite materials would have properties any better than any of the other zeolites that have been used for NOx reduction, and Ritscher, Dedecek and Chung each show very poor NOx conversions at low temperatures and/or degradation of NOx conversions after aging, so there is nothing in any of these references that would lead a skilled artisan to modify the materials in accordance with the claims of the '662 patent.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made herein on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-identified patent.

Dated: February 8, 2011

By: Gary L. Haller
Gary L. Haller, Ph.D.

EXHIBIT A

GARY L. HALLER

Professor of Chemical & Environmental Engineering & Chemistry, Yale University

Department of Chemical and Environmental Engineering
9 Hillhouse Ave.
P.O. Box 208286
New Haven, CT 06520
Tel. (203) 432-4378

Professional Preparation

University of Nebraska, U.S.A.	Mathematics	B.S. 1962
Northwestern University, U.S.A	Physical Chemistry	Ph.D. 1966
Oxford University, U.K.	Chemistry	Postdoc 1966 – 1967

Appointments at Yale

1981-	Professor of Chemical & Environmental Eng. and Chemistry, Yale University
1997-2007	Master, Jonathan Edwards College
1996-1999	Chair, Department of Chemical Engineering, Yale University
1990-1994	Chair, Council of Engineering, Yale University
1985-present	Professor, Department of Chemical Engineering and Chemistry
1984-present	Henry Prentiss Becton Professor of Engineering and Applied Science
1984-1987	Chair, Council of Engineering, Yale University
July-Dec. 1983	Acting Chair, Department of Chemical Engineering
Jan.-June 1981	Acting Master, Jonathan Edwards College
1980-1981	Professor of Engineering and Applied Science, Yale University
1972-1980	Associate Professor of Engineering and Applied Science, Yale University
1971-1972	Yale University, Junior Faculty Fellowship
1967-1972	Assistant Professor of Engineering and Applied Science, Yale University

Awards:

Professeur Invité à l'Université Pierre et Marie Curie (Paris VI), 1996
NIOK (Netherlands Institute for Catalysis Research) Lecturer (Guest Teacher), 1996
Lacey Lecturer in Chemical Engineering; California Institute of Technology, 1996
Ipatieff Lectureship; Northwestern University, 1996
Harry Fair Lectureship; University of Oklahoma, 1995
Robert Burwell Lectureship; The Catalysis Society, sponsored by Amoco, 1995
Yale Science and Engineering Association Meritorious Service Award, 1995
Catalysis Society of Metropolitan New York Award for Excellence in Catalysis, sponsored by Exxon Research and Engineering Company, 1993
The George C. A. Schuit Lectureship, Center for Catalytic Science and Technology; University of Delaware, October 17, 1990.
Kearney State College Outstanding Alumni Award, 1988
Donald E. Fox Chemistry Lectureship; Kearney State College, NB, 1982

Professional Experience, Other than at Yale:

Sept. 1966- Sept. 1967	NATO Postdoctoral Fellow, Oxford University
Dec. 1971- July 1972	Universite Catholique de Louvain, Belgium
Summer 1974	U. N. Ind. Dev. Org., Consultant, Bahia Blanca, Argentina
Summer 1975	Chair, Gordon Research Conference on Catalysis

Jan. 1977- Dec. 1979 Jan. 1989- Dec. 1991	Council of the Gordon Research Conferences
Sept. 1977- Sept. 1981	International Union of Pure and Applied Chemistry, Associate Member, Commission on Colloid and Surface Chemistry
Mar. 1978 - Aug. 1978	Science Research Council, Senior Visiting Fellow, University of Edinburgh
Jan. 1982 - Dec. 1982	Chair, Division of Colloid and Surface Chemistry, American Chemical Society
July 1981 - Dec. 1981	Visiting Scholar, National Bureau of Standards
Aug. 1986 -	Member, Connecticut Academy of Science and Engineering
July 1992 -July 1996	General Chairman, 11th Intern. Congr. on Catalysis
Jan.-June 2010	Visit Scholar, New York University

Consulting Experience:

Jan. 1969 - July 1969	Dept. of Health, City of New Haven, CT
Sept. 1971- Dec. 1975	Monsanto Co. (Univ. Research Inst. of Conn., Inc.)
Oct. 1974 - July 1975	Olin Corp. (Univ. Research Inst. of Conn., Inc.)
Dec. 1974 - July 1975	Commerce Technical Advisory Board, U. S. Dept. of Commerce
Dec. 1975 - Jan. 1977	Environment, Inc., Branford, CT
Jan. 1975 - Dec. 1979	Warner-Lambert Co., Milford, CT
Jan. 1978 - Dec. 1980 Oct. 1992 - Sept. 1993	U. S. Department of Energy
Summer, 1982	Union Camp Corporation
July 1982 - Dec. 1982	EXXON Research & Engineering Co.
Nov. 1982 - Nov. 1983	Olin Corp., Metals Division
April 1982- June 1984	National Science Foundation
April 1982 - 2001	CYTEC, Inc., Stamford, CT
Jan. 1986 - Jan. 1998	Sun Refining and Marketing Co.
Jan. 1986 -present	Engelhard Corp. (now BASF Corporation)

Editorial Boards

1982 - 1990	Board of Editors, **American Scientist**
1984 -	Board of Editors, **Catal. Rev. - Sci. & Eng.**
1985 - 2003	Board of Editors, **J. Catal.**
1988 - 1993	Co-Editor, **Journal of Catalysis**
1988 - 1998	Advisory Board, **Catalysis Letters**
1989 -2001	International Editorial Board, **Reaction Kinetics and Catalysis Letters**
July 1998	Board of Editors, **Journal of Molecular Catalysis A: Chemical**

Catalysis Society

July 1989 - June 1993	President, The Catalysis Society
Jan. 1977 - June 1989	Board of Directors, The Catalysis Society
Aug. 1985 -June 1989	Vice President, The Catalysis Society
Aug. 1983 -July 1989	Foreign Secretary, The Catalysis Society

Publications

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10. "The Structure and Activity of Chromium Oxide Catalysts. II. Influence of Catalyst Structure on Activity for Reactions of Cyclopropane," J. Catal. 25, 391 (1972); with S.R. Dyne and J.B. Butt.
11. "Adsorbed Water on Single Crystal Oxides", Proc. of Fifth Intern. Congr. on Catal. (J.W. Hightower, ed.) Vol. 1, pp. 17-317, North-Holland (Amsterdam) 1973; with R.W. Rice.
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15. "Recycling Molecular Beam Reactor," Proc. Fourth Intern. Symp. on Molecular Beams (F.M. Devienne, ed.) Cannes, France, July 1973; with G. Prada Silva and J.B. Fenn.
16. "Resource Utilization and Environmental Impact of Alternative Beverage Containers," Proc. Environmental Impact of Nitrile Barrier Containers LOPAC: A Case Study (F.D. Wharton, Jr., ed.) published by Monsanto (St. Louis) 1973, p. 77.
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72. "Comparison of Hydrogenation and Hydrogenolysis on Unsupported and Silica-Supported Rh-V2O3 and Pt-V2O3", Faraday Symposium No. 21, Faraday Transactions I, J. Chem. Soc.; 83, 2091, (1987); with Y.J. Lin and D.E. Resasco.
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EXHIBIT B

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APPLIED CATALYSIS
A: GENERAL

Review

Nature of active species in copper-based catalysts and their chemistry of transformation of nitrogen oxides

Gabriele Centi *, Siglinda Perathoner

Department of Industrial Chemistry and Materials, Viale Risorgimento 4, 40136 Bologna, Italy

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Abstract

Copper-based catalysts are active in a wide range reactions of transformation of nitrogen oxides and represent an useful model system to better understand the fundamental aspects of the chemistry and mechanism of reaction of catalytic transformation of these pollutants. After an introduction on the reactivity of copper-based catalysts (supported and unsupported copper oxide, Cu-zeolites, cuprates and other copper compounds) in various reactions of conversion of nitrogen oxides, four main sub-topics are discussed in detail: (i) nature of copper species, (ii) chemisorption and surface transformations of NO, (iii) relationship between copper species and activity in the conversion of nitrogen oxides and (iv) mechanism of reduction of nitrogen oxides to N_2. Five reactions of transformation of nitrogen oxides are discussed in detail: (i) decomposition of NO, (ii) reduction of NO with ammonia in the presence or not of oxygen, (iii) reduction of NO with hydrocarbons in the presence of oxygen, (iv) reduction of NO with CO and (v) decomposition of N_2O. The mechanism of reduction of nitrite and N_2O by copper enzymes is also discussed, with a view to provide some useful insights on the chemistry of transformation. In this review particular attention is directed towards controversial points in the literature, underestimated questions, and hypothesis and theories which do not allow interpretation of all sets of experimental data. Discussion is also focused on the presence of multiple and competitive pathways of transformation, the relative roles of which depend on reaction conditions.

Keywords: Nitrogen oxides; NO_x; N_2O; NO reduction; Copper-based catalysts; Cu-zeolites; Cu/ZSM-5; Reaction mechanism; Chemisorption

Contents

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* Corresponding author. E-mail cicatal@boifcc.cineca.it, fax. (+39-51) 6443679.

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1. Introduction

The general term nitrogen oxides indicates the class of compounds of nitrogen and oxygen which includes N_2O, NO/N_2O_2, NO_2/N_2O_4, N_2O_3, N_2O_5 and NO_3 (unstable), where the/symbol shows compounds in reversible equilibrium. NO emissions in the lower atmosphere are caused principally by combustion processes in stationary or mobile sources. Especially in industrialized countries, the latter is responsible for up to 60% of global atmospheric NO emissions. In contact with air and light, NO readily transforms to NO_2. Both nitrogen oxides then give rise to a series of complex chemical/photochemical reactions in the upper atmosphere which result in the formation on the one hand of nitric/nitrous acid, which significantly contributes to *acid rain*, and on the other hand in the formation of *photo-*

chemical smog. NO itself is not an irritant, but can react with haemoglobin to form methaemoglobin [1]. In respect to its toxicity, the TLV-TWA value for NO is 25 ppm. NO_2, on the contrary, is an irritant gas and causes pulmonary edema and exudative inflammation [1]. Chronic exposure to low doses results in coughing, headache and gastrointestinal disorder. The TLV-TWA value for NO_2 is 3 ppm.

N_2O forms mainly via microbial action in soil, but significantly high N_2O emissions occur in several chemical processes (for example, up to 30–50% in adipic acid production) [2]. N_2O does not play a significant role in the troposphere, but contributes substantially to ozone depletion in the stratosphere as well as to the greenhouse effect [2–4]. N_2O does not irritate the mucous membrane and has a powerful analgesic action; however chronic exposure may cause polyneuropathy and myelopathy [1]. The TLV-TWA value for N_2O is 50 ppm.

Several approaches are possible to reduce nitrogen oxides emissions into the atmosphere from stationary or mobile sources, but the catalytic approach is the most effective to meet current and future requirements. An early patent on this topic goes back to 1924 by Fauser, but it is from the beginning of the 1960's that a great deal of research interest has been centred on the problem of the catalytic removal of nitrogen oxides. Current commercial catalytic systems are principally noble-metal based three-way catalysts for the purification of car emissions (gasoline engines) and vanadium-on-titania based catalysts for the control of stationary-source NO emissions by selective catalytic reduction (SCR) in the presence of ammonia [5–7].

In recent years, a great deal of research has also been centred on the study of copper-based catalysts for the conversion of nitrogen oxides, principally for the possibility of developing new technologies of direct decomposition of NO to $N_2 + O_2$ or of selective NO reduction with hydrocarbons in an oxygen-rich atmosphere [8–12]. Copper-containing catalysts (zeolite- and oxide-based samples) are active in a wider range of reactions of transformation of nitrogen oxides with respect to other catalytic systems. Copper is also the key component in the enzymes involved in the nitrogen cycle. Copper-based catalysts are thus an ideal model to understand the mechanism of transformation of nitrogen oxides because they give the opportunity to approach the problem from a multiplicity of points of view and to verify the validity of hypotheses and theories on analogous reactions and/or catalysts.

The scope of this review is to discuss and analyze critically the literature data on (i) the nature of copper species in supported copper oxides and copper ion-exchanged zeolites and (ii) the mechanistic aspects of the chemistry of interaction and transformation of nitrogen oxides over these catalysts. A comparison with the mechanism of action of copper-based enzymes in the transformations of nitrogen oxides is also given to evidence the several analogies between these enzymes and solid catalysts. Scope of the review is not to compare the reactivity of the various catalysts to indicate which samples show superior performances, but instead to discuss the properties of all copper-based catalysts in the transformation of nitrogen oxides. In fact, a significative limit of several of the hypotheses present in literature is that they cannot be generalized to explain the behaviour of other samples. The possibility offered by copper-based catalysts to analyze the chemistry of transformation of nitrogen oxides from various perspectives (different, but homogeneous series of samples; reactions involving different nitrogen oxides or reducing agents; reactivity in the presence or not oxygen; comparison with the behaviour of analogous enzymes) is thus unique and may be very fruitful for the fundamental aim of a better understanding of the relationship between surface properties, reactivity and reaction mechanism.

2. Overview of the reactions of transformation of nitrogen oxides in which copper-based catalysts are active

2.1. Reduction of NO with or without reducing agents: background and overview

Interest in the activity of copper-based catalysts for the conversion of NO began around the end of the sixties [13–17]. At that time attention was focused on investigating possible alternative catalytic systems to those based on the use of noble metals for the purification of exhaust gas from gasoline engines. Supported copper oxides were found to have the highest activity among the tested transition metal oxides for the reduction of NO in the presence of CO [14]. Later, copper-exchanged zeolites (Y and X types) were also shown to have high activity in this reaction [18,19]. Several studies have been reported on the characterization of these copper-exchanged zeolite catalysts [18–31], but these studies were focused especially on the investigation of the redox changes in the reaction with CO, hydrocarbons, ammonia and H_2 and not on the activity in the conversion of NO.

The high activity of copper oxide in the reduction of NO with NH_3 in the presence of O_2 was also recognized early [32]. Later, copper-zeolites were also found to be highly active in this reaction. Partially Cu^{II}-exchanged Y-type zeolites [$Cu^{II}NaY$], in particular, were shown to exhibit excellent as well as unique catalytic activities [33–39]. The key feature of these catalysts is the presence of a reversible maximum in the activity at very low temperature (about 110°C) due to a reversible change in oxidation state of the copper. The low-temperature activity of this catalyst in the reduction of NO with NH_3 in the presence of O_2 is comparable to that of Pt-based catalysts [40], but for practical applications V_2O_5/TiO_2-based catalysts are preferable for the treatment of emissions from stationary sources due to their reduced sensitivity to poisoning and higher stability [7], albeit they are active at higher temperatures (usually in the 300–400°C range). It should be noted, however, that zeolite catalysts are commercialized for the reduction of NO with NH_3/O_2 [40,41] for particular high-temperature applications (above 400–450°C). Centi et al. [42] showed that Cu/ZSM-5 has a distinct advantage over V_2O_5/TiO_2 catalysts in terms of a reduced rate of the side reaction of ammonia oxidation.

The interest in copper-zeolites and especially Cu/ZSM-5 increased considerably as a result of the finding of Iwamoto et al. [43,44] of the superior activity of Cu/ZSM-5 in the direct decomposition of NO to N_2+O_2 [43–48] in comparison with other copper ion-exchanged zeolites [49,50] or catalysts. Cu/ZSM-5 was found to be sensitive to poisoning by SO_2, H_2O and oxygen, decreasing the prospects for possible application. However, soon was discovered that the addition of hydrocarbons to the oxygen-rich feed leads to a drastic increase in the rate of the selective reduction of NO to N_2 [48,51,52]. This discovery opened the field of applications for these catalysts to the treatment of oxygen-rich exhaust gas from mobile sources such as those deriving from two-stroke or lean-burn gasoline engines or diesel engines. The presence of excess oxygen in these emissions limits the efficiency of current three-way noble-metal catalysts for the reduction of NO to N_2. Alternative catalytic systems thus appear to be attractive [8,9]. Noble metal-based, in fact, are active in the selective reduction of NO in the presence of excess oxygen [53–55], but show a very sharp maximum in the conversion of NO increasing the reaction temperature. Indeed, several unresolved problems limit the outlook for successful use of zeolites in automotive converters: (i) hydrothermal stability, (ii) sensitivity to poisoning, (iii) possibility of manufacturing suitable shapes with sufficient mechanical resistance to thermal stress and vibrations, (iv) high light-off temperature and limited temperature window, (v) possible formation of harmful byproducts, and (vi) necessity of post-engine hydrocarbon additions to reach the optimum hydrocarbon/NO ratio required to meet current and future legislative regulations on NO emissions. A low hydrothermal stability, in particular, is the more critical weakness of copper-containing zeolites.

Interesting possibilities are also offered by a combination of noble metals and copper. Pd–Cu have been shown to be able to combine both advantages [56], eliminating the necessity for the use of Rh in automotive converters. Copper-based catalysts were proposed for automotive exhaust purification [57], when a low level of sulphur in gasoline is present. Recent developments from the Toyota research group [58,59] have also indicated the fruitful combination of a nitrogen oxide storage component to a noble metal component ('NO_x storage–reduction catalysts'). These catalysts store NO_x under oxidized conditions and then reduce the stored NO_x to nitrogen under stoichiometric and reduced conditions. The new catalyst is claimed to have higher NO_x reduction activity in a wide temperature range. The NO_x storage capacity of alumina may be promoted by a component such as copper which forms stable nitrates and enhances their rate of formation. Pt/Cu on alumina catalysts thus are potential catalysts for this application. A Pt/Cu catalyst also was found to have superior activity at room temperature in the reduction of NO with CO in an aqueous acid solution [60], even though the practical relevance is questionable.

Various other metal-exchanged zeolites have been found to be active in the NO selective reduction by hydrocarbons/O_2 such as Ga/ZSM-5 [61,62], Co/ZSM-5 [63], Ce/ZSM-5 [64], Ga/ferrierite [65], Co/ferrierite [66] as well as the zeolite itself in the acid form [67], albeit at higher temperatures. Their activity, however, depends considerably on the nature of the hydrocarbon used and on the experimental conditions [9–12], differently from copper-zeolites which show good performances in a wider range of reaction conditions and using different kinds of hydrocarbons. Metal oxides such as alumina have also been found to be active at high temperature in the selective reduction of NO with hydrocarbons/O_2 [68–70], but in general the addition of copper promotes the catalytic behaviour. The results, however, depend considerably on the oxygen concentration [70–72]. The presence of other co-cations such as Cs [73] or Ga [70] may further promote the activity. Copper-based catalysts are thus a reference catalyst family for the investigation of the mechanism of selective reduction of NO, albeit for practical applications their low hydrothermal stability may prevent a commercial use.

The selective reduction of NO with hydrocarbons/O_2 (HC-SCR) over metal-exchanged zeolites is interesting not only for the purification of car emissions, but also for the possibility of substituting ammonia as the selective reducing agent for the elimination of nitrogen oxides in emissions from stationary sources (flue gas, nitric acid plants, etc.). This would reduce risks and safety problems connected to the transport and handling of large amounts of ammonia, the secondary pollution derived from ammonia slip and equipment corrosion. Li and Armor [63,74] showed that using methane as the reducing agent under net oxidizing conditions, Cu/ZSM-5 is ineffective, whereas other catalysts such as Co/ZSM-5 show a good activity. Ga/ZSM-5 is also active with methane [62]. Recent results indicate a dissociative chemisorption of methane without O_2 chemisorption over Ga/ZSM-5 and the opposite behaviour over Cu/ZSM-5 [75]. This difference is probably responsible for the inactivity of Cu/ZSM-5 with methane, whereas using higher alkanes (propane) the hydrocarbon activation is easier and Cu/ZSM-5 shows superior catalytic performances with respect to Co/ZSM-5. It should be noted that significantly lower performances are obtained in the CH_4-SCR reaction over Ga/ZSM-5 (maximum NO conversion about 40% [62]; similar results were observed using Co/ZSM-5 [74]) as compared to those observed in C_3H_8-SCR reaction over Cu/ZSM-5 (NO conversion higher than 95%) [76]. The worse performances using methane in comparison to those using higher alkanes is a significative drawback for CH_4-SCR technology for stationary sources.

Summarized in Table 1 is an overview of the different reactions of nitrogen oxides conversions in which copper-based catalysts are active.

2.2. *Other applications of copper-based catalysts for conversion of nitrogen oxides*

Supported copper oxides, and copper oxide on alumina [77–80] or silica [81] in particular, are used for the combined removal of SO_2 and NO_x from flue gas. SO_2 reacts with supported copper oxide to form sulphate species easily reduced in a separate stage by treatment with H_2 or CH_4 [82–86], and at the same time

Table 1
Examples of uses and applications of copper-based catalysts in transformation of nitrogen oxides

Reaction or application	Catalyst	Reference
$2NO + 2CO \rightarrow N_2 + 2CO_2$	CuO	[13,16]
	CuO on TiO_2	[113,114]
	CuO on Al_2O_3	[115]
	supported Cu/Cr oxides	[57]
	Cu/Y	[18]
	Cu/ZSM-5	[116]
	cuprates	[117]
$2NO + 2NH_3 + 0.5O_2 \rightarrow 2N_2 + 3\,H_2O$	CuO	[32]
	CuO on various oxides	[118]
	Cu/Y	[34]
	Cu/ZSM-5	[42]
	Cu-mordenite	[119]
$2NO \rightarrow N_2 + O_2$	Cu/Y	[50]
	Cu/ZSM-5	[43,48]
	cuprates	[120]
NO + hydrocarbons → N_2, CO_2, H_2O	Cu/ZSM-5	[9,47]
	CuO on alumina	[70,71]
$NO + 0.5O_2 \rightarrow NO_2$	Cu/Y	[105]
Combined SO_2 and NO_x removal	CuO on alumina	[78–80]
	CuO on silica	[81]
	CuO on active carbon	[87]
NO_x reduction in tail gas of nitric acid plants	CuO–NiO on alumina	[90,91]
NO_x and CO elimination in off gas of nuclear waste processing plants	Cu/ZSM-5	[96]
Photocatalytic NO decomposition	CuO on silica	[97]
	Cu/ZSM-5	[98]
Photocatalytic N_2O decomposition	Cu/ZSM-5	[99]
N_2O decomposition	Cu/ZSM-5	[103]
	cuprates	[121]
NO removal by selective adsorption	BaO-CuO	[107]
Catalytic sensors for NO_2	CuO–NiO–Sc_2O_3	[108]
Enzymatic denitrification	N_2O reductase	[111]
	nitrite reductase	[112]

catalyzes the reduction of NO with NH_3/O_2. The activity in the reduction of NO is influenced little by the progressive sulphation of supported copper species [84,85] differently from the V_2O_5/TiO_2 catalysts [7]. The technology was tested in pilot plant facilities and technico-economical estimations indicate the promising outlook for the process.

Similar technology for the combined removal of SO_2 and NO_x is based on the use of copper oxide supported on carbon, but operates at lower temperatures (about 150°C) as compared to about 350°C for the systems based on copper oxide supported on oxides. SO_2 is oxidized and adsorbed on carbon in the form of sulphuric acid/ammonium bisulphate or sulphate instead of copper sulphate, whereas NO is converted to N_2 in the presence of ammonia/oxygen [87]. The addition of copper considerably enhances the activity of carbon for the latter reaction [88]. Demonstration plants of this technology exist [87], but the critical aspects for wider application are the cost of active carbon, rapid degradation of carbon by gasification, sample regeneration and by-product formation during regeneration. Carbon-supported copper-based catalysts also have been shown to have high activity in the reduction of NO with CO and simultaneous oxidation of CO and have been proposed as alternative catalysts for the removal of NO and CO from exhaust gas [89].

A copper/nickel oxide on alumina catalyst is used for the abatement of NO_x emissions in several nitric acid plants [90,91]. These emissions are characterized by a NO_2/NO ratio nearly unitary due to the low temperature of the gas and by the absence of SO_2. In the Cu/Ni oxide on alumina catalysts, the promotion effect of nickel is mainly that of increasing the number of Cu^{2+} ions in tetrahedral positions owing to the displacement in the defective spinel-type surface of γ-Al_2O_3 of Cu^{2+} from the octahedral positions by Ni^{2+} [92,93]. Blanco et al. [94] have also shown that the NO_2/NO ratio in the feed has a considerable influence on the rate of reaction. Optimal performances were found for a 1:1 ratio due to the higher rate of reoxidation of reduced Cu^+ ions to Cu^{2+} shown by NO_2 as compared to O_2.

Cu/ZSM-5 has been successfully applied for the control of both NO_x and CO emissions from nuclear waste processing plants [95,96] the off-gas of which contains concentrations of about 1–3% of these pollutants. The original process uses two fixed-bed reactors for the selective catalytic reduction of NO_k with ammonia and oxidation of CO over a H-mordenite catalyst and a third reactor containing Pt and/or Cu-based catalysts for clean-up of the ammonia slip and unconverted CO, but the use of Cu/ZSM-5 catalysts allows an increase in the overall performance of the technology.

The photocatalytic decomposition of NO over copper oxide supported on SiO_2 [97] and Cu/ZSM-5 [98] has also been demonstrated, but present results do not allow predictions regarding possible practical applications. The essence of the reaction is the reduction of isolated Cu^{2+} ions to Cu^+. The formation of the latter is a maximum for evacuation temperatures of about 800–900°C. The Cu^+ species react at room temperature with NO forming nitrosyl adducts which under UV irradiation give rise to an electron transfer reaction from an excited Cu^+ ion to the π-antibonding orbital of NO with back-donation to the vacant orbital of the Cu^+ ion. The local charge separation and weakening of the N–O bond is the driving force for the decomposition of NO. The photocatalytic decomposition of N_2O into N_2 and O_2 over Cu/ZSM-5 has also recently been reported [99,100], but the authors suggest that the reaction was related to the quenching of the excited state of the dimer of a monovalent copper ion (Cu^+–Cu^+) by N_2O molecules.

The outlook for practical applications is much better for the catalytic decomposition of N_2O. Due to the greenhouse effect of N_2O (over two orders of magnitude greater than CO_2) and its role in stratospheric ozone depletion, it was estimated that N_2O emissions should be considerably reduced [2–4]. In E.U. countries, for example, anthropogenic N_2O emissions should be reduced from about 1200 kton N_2O-N/year to about 200 kton N_2O-N/year in order to arrive to a climate goal of limiting future global warming to 0.1°C/decade [2]. Two are the main sources which can be reasonably controlled by catalytic treatments: (i) emissions from fluidized bed combustion (especially from municipal waste and sewage sludge incineration) and (ii) emissions from chemical processes using or producing nitric acid [4]. Various papers have been published on the catalytic decomposition of N_2O [101], but few studies have addressed the question of the analysis of the behaviour of the catalyst under real conditions for the possible applications [102]. Most of the catalysts reported in the literature either have reaction rates which are too low or deactivate very quickly. Copper-exchanged zeolites have been suggested to be promising catalysts [103,104], even though sensitive to poisoning by water and other components.

Copper ion-exchanged zeolites have been reported to be the most active for the oxidation of NO to NO_2 [105], a necessary step for the development of a process for removal of nitrogen oxide by adsorption on a solid adsorbent, since NO_2 is much more reactive and less difficult to remove. Indeed, the homogeneous gas phase oxidation of NO usually occurs with a too low rate under the temperature and NO concentration conditions necessary for practical applications. More recently, Arai and coworkers [106,107] have also proposed a process of nitrogen oxides removal using BaO–CuO binary oxides. Adsorbed NO is present in the final form as Ba nitrate, but probably the mechanism involves the NO oxidation over copper ions to form a copper nitrate species. The nitrate ion then shifts to Ba since the Ba compound is more stable.

Copper oxide is also a key component for the preparation of catalytic sensors for nitrogen oxides. Imanaka et al. [108] have recently reported the good sensitivity properties of copper oxide and scandium oxide mixed with p-type semiconducting NiO for NO_2 detection especially in low concentrations. The role of copper is to enhance the NO_2 sensing characteristics.

Finally, copper is the active element in the enzymatic processes of interconversion of nitrogen compounds [109–112]. NO is produced and consumed via processes mediated by metalloproteins that contain iron or copper and it is a key intermediate in the global biological nitrogen cycle. Copper-containing enzymes play a central role in denitrification, whereby bacteria (nitrite and nitrous reductases) use nitrate and nitrite ions as terminal electron acceptors ultimately to produce gaseous nitrogenous products (NO, N_2O, and/or N_2). Other useful Refs. [113–121] of reactions of nitrogen oxides over copper-based catalysts are listed in Table 1.

3. Nature of copper species in copper-based catalysts

3.1. Supported copper oxides

3.1.1. Copper-on-alumina catalysts

Alumina supported copper catalysts have been extensively characterized in the past for their wide range of applications in oxidation and hydrogenation reactions. Recently, renewed interest in these catalyst has derived from their activity in the catalytic combustion of hydrocarbons [122,123] and alcohols [124] and their performance in the combined removal of NO_x and SO_2 [78–80]. The alumina supported copper samples have been studied by a variety of techniques for the characterization of their bulk and surface properties [92,93,122,125–138]. The papers of Friedman et al. [126], Knözinger and co-workers [92,93], Strohmeier et al. [133] and Lo Jacono and co-workers [128,134] are those in which the problem of the identification of the surface copper species has been studied in more detail. The nature of the copper species depends clearly on the specific kind of alumina used, but almost all studies dealt with γ-Al_2O_3 supported copper. γ-Al_2O_3 has a spinel-type structure in which the oxygens are cubic close-packed similar to the packing in $MgAl_2O_4$. The unit cell consists of 32 oxygens, 21 1/3 aluminiums and 2 2/3 cation vacancies distributed between the tetrahedral and octahedral sites. γ-Al_2O_3 has a fairly well ordered oxygen lattice with considerable disorder in the tetrahedral Al lattice. Further details can be found in the classical review of Knözinger and Ratnasamy [139] and in that of Locke et al. [140]. The possibility of filling surface defect sites of alumina with copper ions to form a $CuAl_2O_4$ surface spinel-type compound was recognized earlier by Wolberg and Roth [125] in their study of these catalysts by X-ray adsorption edge spectroscopy. These authors identified three phases: isolated Cu_{2+} ions, a copper aluminate surface phase and crystalline CuO. Friedman et al. [126,127] confirmed these results and added further evidence (i) on the threshold limit for copper loading necessary to result in the appearance of crystalline CuO (4 wt.-% Cu per 100 m^2/g alumina) and (ii) on the predominant presence of Cu^{2+} ions in tetragonally distorted octahedral coordination. About 10% of the copper ions are in tetrahedral coordination, but the octahedral/tetrahedral ratio depends on the calcination conditions. Longer calcination at 600°C results in the final formation of bulk-like $CuAl_2O_4$ in which 60% of the copper ions are in tetrahedral coordination and the remaining in octahedral coordination. The surface copper aluminate phase therefore is different from bulk copper aluminate. Knözinger and co-workers [92,93] further added the concept of the possibility of modification of the prevalent copper coordination by doping with Ni^{2+} ions which preferentially occupy the octahedral sites in subsurface layers and in the bulk. The presence of Ni^{2+} leads to a Cu^{2+} redistribution with an increased tetrahedral site population by Cu^{2+} and an enhanced segregation of copper on the surface, reasonably in form of paracrystalline copper oxide particles. Ni-modified copper-on-alumina samples show superior performances in NO_x elimination from the tail gas in nitric acid plants [90,91,94].

Increasing the copper loading on γ-Al_2O_3 there is thus a change from isolated copper ions to a defect surface copper aluminate to paracrystalline and crystalline CuO. However, recent results [137] suggested that in the sub-monolayer region are not present discrete, isolated copper ions, but instead rows of copper ions. The model of these sub-monolayer species is shown in Fig. 1 together with a schematic drawing of the change in copper species as a function of the copper loading.

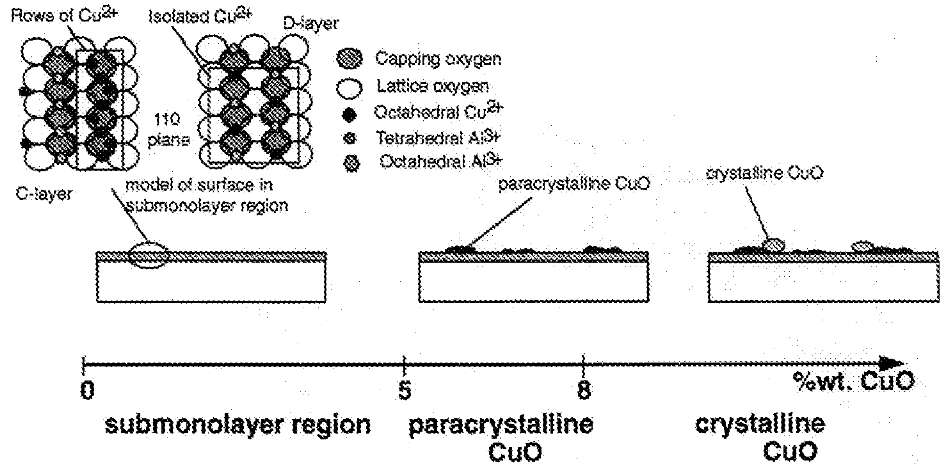


Fig. 1. Surface model showing the incorporation of Cu^{2+} ions in the (110) plane of γ-Al_2O_3 [137]. C- and D-layer nomenclature as given by Knözinger and Ratnasamy [139].

Differences in the reactivity of the various copper species exist, but results are contradictory. Electron spin resonance (ESR) data [137] suggest that rows of copper ions reduce easier than isolated copper ions, but the data are only indicative. Hierl et al. [93] have suggested that the Cu^{2+} ions in tetrahedral sites are more easily reduced than those in octahedral sites, whereas Strohmeier et al. [133] have reported the absence of influence of the site symmetry on the reducibility and also the absence of any special differences between the surface copper aluminate phase and supported copper oxide. Hierl et al. [93] also have reported that the reduction with H_2 leads to the formation of small metallic particles only, whereas only Cu^+ ions are found after a similar treatment in vacuum. Lo Jacono et al. [128] have suggested, on the other hand, a thermodynamic distribution of Cu^{2+}, Cu^+ and Cu^0 as a function of the degree of reduction. The problem of the reactivity of the different surface copper species requires further studies, especially for a better identification of the structure/activity relationships in these samples. Unclear is also the problem of the nature of surface changes during the catalytic reaction or after redox cycles and the effect of these modification on surface reactivity. Laine et al. [132] observed the following order of activity in alumina supported copper samples for CO oxidation: prereduction with CO $>$ prereduction with H_2 $\gg$ fresh calcined sample.

The interpretation is the formation of small copper crystallites after prereduction; smaller copper clusters form in the first case due probably to the formation of Cu-carbonyl species. During the catalytic runs, however, the catalyst progressively deactivates due to the reaction of surface CuO crystallites with alumina to form the copper aluminate phase. A similar interpretation has been suggested by Marion et al. [122] to explain the deactivation observed in methane combustion. Choi and Vannice [56] have suggested that the activity in CO oxidation of prereduced alumina supported copper is due to a thin overlayer of Cu_2O with O vacancies or to Cu_2O/Cu interface sites. A similar mechanism of surface stabilization of Cu_2O particles through oxygen vacancies in the support has been proposed by Dow and Huang [141]. On sulphated copper-on-alumina samples, on the other hand, redispersion of copper was observed after an initial reduction/reoxidation cycle with an increase in the specific activity [84]. Pepe et al. [134] observed that a reduction/reoxidation cycle produces a redispersion of the $CuAl_2O_4$ phase with a change in the surface reactivity in isopropanol conversion. Huang et al. [115,136] observed that the temperature of the reduction with H_2 and the copper loading have a considerable effect on the activity in CO oxidation and NO reduction with ammonia, even though their explanation based on the SMSI effect does not seem appropriate for the discussion of the data. Probably, the change in activity is due to a change in the distribution of copper species as a consequence of the heat treatment.

3.1.2. Copper-on-silica catalysts

Silica-supported copper samples show good activity in several catalytic reactions such as steam reforming, water-gas shift, ester hydrogenolysis, liquid phase hydrolysis, and oxidation of CO and hydrocarbons and thus these catalysts have been studied extensively.

Copper on silica samples prepared by ion exchange with tetramine copper ions were first reported by Kobayashi and co-workers [142,143] and then used by several other groups [143]. It has been observed that the nature of the surface copper species depends on the copper loading and calcination temperature. In samples calcined in the 400–600°C range isolated copper ions and highly dispersed Cu^{2+} clusters were observed. The latter crystallize to bulk CuO above 700°C, whereas bulk CuO forms already by calcination at 500°C when copper is impregnated on silica in an amount exceeding saturation by the ion-exchange method. Isolated species remain as such even with high temperature calcination, but their amount is limited to less than 1 wt.-% Cu. Two different mechanisms of copper deposition can be identified: (i) ion exchange of $[Cu(NH_3)_4]^{2+}$ ions with pairs of silanol groups on the silica surface to form a well-dispersed network of single Cu^{2+}-diamine ions attached to the silica surface, and (ii) precipitation of Cu^{2+} as copper hydroxide from the preparation solution. Similar indications on a double mechanism of copper deposition were observed on a copper-on-alumina catalyst prepared by impregnation with $CuCl_2$ [144]. Kohler et al. [145,146] further extended the investigation on the characteristics of samples prepared using ion exchange of $[Cu(NH_3)_4]^{2+}$ with silanol sites. The authors agree on the above indications, but further add that isolated copper ions reduce to Cu^+ only and not to metallic copper, differently from the small copper oxide particles easily reducible to Cu^0 derived from the $Cu(OH)_2$ precursor. The precipitated species is concentrated in very small clusters ($\ll 5$ mm), but no further indication is given about the possible structure of these small copper clusters. The authors report that with increasing copper loading on the silica, isolated copper ions are found for loadings less than 0.5 wt.-%, well dispersed copper in the form of very small crystallites is

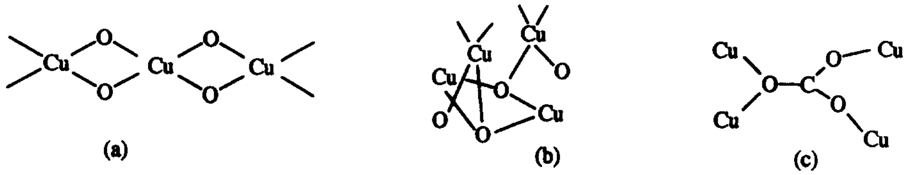


Fig. 2. (a) and (b) Model of surface polynuclear copper species present on silica surface depending on method of preparation according to Nomura et al. [151]. (c) Surface malachite-type species formed on silica according to Millar et al. [159].

found for loadings in the 0.5 to 6 wt.-% range and larger copper crystallites are found for loadings above 6%. In comparison with alumina, the dispersion of copper sites on silica is much lower.

The same ion-exchange procedure also has been used for the preparation of copper-on-silica catalysts photoactive in the decomposition of NO [97]. Characterization of a low loading (1 wt.-%) copper on silica sample by photoluminescence spectroscopy [147] indicates the presence of a main band at 520 nm which can be attributed to the electronic transition in Cu^+–Cu^+ dimer or multinuclear species [97,98,148]. In contrast, in copper ion-exchanged ZSM-5 prepared by the same procedure a main photoluminescence band at around 430 nm is present which can be attributed to isolated Cu^+ species. Results of photoluminescence studies thus contrast with the other results cited.

Kakuta and co-workers [149–155] extensively characterized silica supported copper catalysts prepared by impregnation with the binuclear copper complex $[Cu_2(CH_3COO)_4–2H_2O]$ and compared results with those obtained using ion exchange with the Cu^{2+}-tetramine complex. The preparation from the acetate complex leads to higher activity in CO oxidation by N_2O or O_2 than that from the amine complex. ESR and IR data [149,150] indicate that in the former catalyst the binuclear structure of the starting copper complex is retained, whereas the preparation from the amine complex leads to isolated Cu^{2+} ions, in partial agreement with the above discussion (multinuclear copper species were not considered, but probably are present since the copper loading was about 3 wt.-%). In the calcined sample prepared from the acetate XPS [153] and X-ray absorption spectroscopy studies [151,154,155] in contrast indicate the presence of one-dimensional chains formed of parallelogram-shaped CuO units (average coordination number 1.6) and in the sample prepared from the amine complex of imperfect microcrystalline CuO. Reported in Fig. 2 are the proposed structures of multinuclear copper species on silica [151]. Two aspects characterize the differences between the two samples: (i) in the case of one-dimensional chains on silica (acetate preparation) all the copper atoms are available at the surface for adsorbate interaction, whereas a lower fraction is available in the three-dimensional paracrystalline CuO (amino complex preparation), and (ii) the local structure of the multicentre oxygen bridged copper sites, is different. The authors propose that in CO oxidation by N_2O and reasonably also in N_2O decomposition binuclear copper sites are needed and thus the acetate sample is more active than that prepared from the amine complex.

It also should be noted that in both proposed surface structures of supported copper oxide the local coordination of the copper sites is different from that of bulk crystalline CuO [156] which is characterized by oxygen coordination parallelograms which form chains by sharing edges. Such chains traverse the structure in the (110) and ($\bar{1}$10) directions, the two types of chain alternating in the (001) direction. Therefore, there are three kinds of nearest copper atoms around a copper atom in crystalline CuO: four at 2.90 Å, four at 3.08 Å and two at 3.17 Å. In the paracrystalline species of copper oxide the coordination environment for Cu, on the contrary, is significantly different (see Fig. 2).

The stability of these proposed surface multinuclear copper species is not clear. X-ray photoelectron spectroscopy (XPS) [153,157] and X-ray absorption near edge structure/extended X-ray absorption fine structure (XANES/EXAFS) data [151] suggest that reduction with CO leads to small clusters of metallic copper plus limited Cu^+ ions (acetate preparation) or to Cu^+ primarily (amine complex preparation) [158]. However, the reversible formation of initial copper oxide species was not investigated. It was shown, on the contrary, that the interaction with acetic acid vapours leads to considerable changes: CuO chain units are cleaved by acetic acid to form binuclear Cu^{2+} species and metallic copper (acetate preparation), whereas the CuO network is cleaved to form the mononuclear Cu^{2+} complex (amine complex preparation). Reversibility of the reaction, however, is not indicated.

The surface properties of samples prepared by the acetate method have also been studied by Millar et al. [159], without providing however further significant insight on the surface composition of the copper species, apart from the possibility of the formation of a malachite-type copper species [$Cu_2CO_3(OH)_2$] after exposure to CO of a reduced sample reoxidized with N_2O. Their model of surface copper species is shown in Fig. 2c and further evidences the role of adsorbate in surface reconstruction mechanisms during the catalytic reaction.

The various surface species are characterized by different reducibility characteristics. An easier reducibility of supported multinuclear copper oxide species with respect to the copper ions directly interacting with the silica surface was indicated by Gentry and Walsh [160] who used the temperature-programmed reduction (TPR) method to study the properties of silica and alumina supported samples, but detailed data on the relationship between reducibility and type of surface copper species (controlled by the preparation method) are not given. Bond et al. [161] have recently reported the results of another study on the reducibility characteristics of supported copper samples using the TPR method, but the above problem was not addressed. These authors observed that copper oxide particles supported on TiO_2 were easier to reduce, but did not explain the reasons for the enhanced reducibility. Van der Grift et al. [162] noted, on the other hand, that silica supported reduced copper particles of identical geometric size may exhibit widely different oxygen uptake rates per unit surface area depending on the crystallographic habit (density of packed copper surface). They also observed that upon increasing the

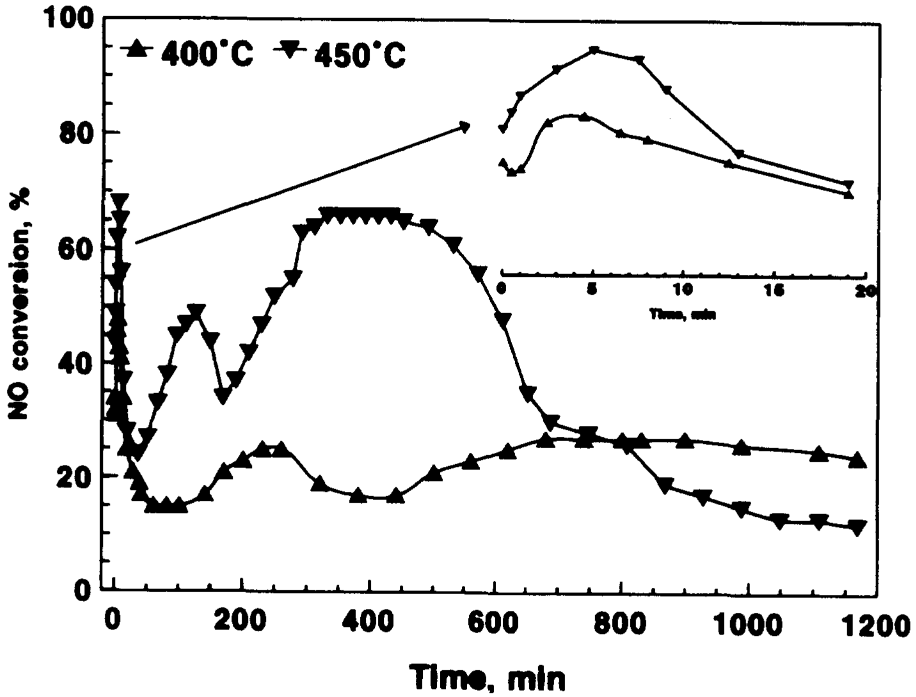


Fig. 3. Change in the conversion of NO over a 7.5 wt.-% CuO on silica catalyst as a function of time-on-stream at 400°C and 450°C during the reduction of 800 ppm NO with an equimolar amount of NH_3.

severity of the reduction treatment, the structure of the copper particles on silica changes from an atomically rough surface (exposing a large number of coordinatively unsaturated surface atoms) to a stepped surface (exposing small terraces) to a densely packed surface (exposing larger flat terraces). As long as the copper particle size is not increased, the change in surface is reversible. De Jong et al. [163] also observed that the particle sizes and shapes of copper on silica can be modified by repeated redox cycles. The problem of the metastability of supported copper particles during catalytic tests or redox cycles should thus be studied in more detail. An example of the interesting behaviour during in situ transformations of copper oxide supported on silica is reported in Fig. 3 showing the time-on-stream change in the catalytic behaviour during $NO + NH_3$ anaerobic reaction. The presence of minima and maxima in the activity is due to a progressive reduction of the catalyst accomplished with reconstruction of surface supported copper species.

Pretreatment of the catalyst also influences the surface properties. Higgs and Pritchard [164] showed that when reduction takes place before complete decomposition of the nitrate, a nitrited copper surface may form which completely alters CO chemisorption experiments. Kenvin and White [165] characterized samples prepared by non-aqueous adsorption of Cu^{2+}-acetylacetonate on silica and observed that a partially decomposed Cu^{2+} complex (bonded to an acetylacetonate ligand and a surface siloxide) gives rise to a different spectrum of chemisorbed

NO as compared to a totally decomposed sample. The advantage in using the acetylacetonate, according to these authors, is to maximize the dispersion of isolated copper ions. They claim that nearly 100% dispersion of copper in the form of isolated ions on silica could be obtained for a 3.8 wt.-% Cu sample prepared with this method, in comparison with around 0.5 wt.-% Cu using other preparations (see above). In addition, isolated copper ions prepared from the acetylacetonate complex show different reducibility characteristics. For these surface copper sites quantitative removal and addition of one oxygen per Cu atom is reported [165], where for preparation with the amine complex, for example, reduction up to Cu^+ only was suggested [145,151]. A more direct comparison of the reducibility behaviour under the same conditions, however, would be preferable to further support this statement. A stable dispersion of isolated copper ions prepared from acetylacetonate is also indicated [165]. The authors also observed that Cu atoms in the 3.8 wt.-% Cu sample are separated by about 5 Å. They call this sample 'monolayer', but clearly the surface coverage is much lower than that expected on the basis of the formation of a real monolayer of copper oxide on the silica surface (about 26.6 wt.-% Cu taking into account that a silica of 200 m^2/g was used by Kenvin and White [165] and that a square-pyramidal or tetrahedral $Cu^{2+}O_4$ unit has an area of about 7 $Å^2$ [156]). In addition, assuming an homogeneous dispersion of silanol groups on the silica surface, for a 3.8 wt.-% Cu loading the estimated copper to copper distance is about 7 Å and thus slightly higher than that indicated by the authors on the basis of their surface model. Kenvin and White [165] also report that the copper to copper distance is larger than that necessary for multiple site demanding reactions such as N_2O decomposition, but the interesting question is not demonstrated.

Several studies also exist on the characterization of silica-supported copper oxide prepared by deposition–precipitation [166–169]. A specific observation worth noting made in these works is the possible formation of a copper hydrosilicate precursor phase [168] with structural characteristics analogous to those of chrysocolla $Cu_8(OH)_{12}\cdot(Si_4O_{10})_2\cdot nH_2O$. After reduction, this precursor phase gives rise to small metal particles in the 3–8 nm diameter range. The possible presence of this precursor phase in samples prepared from the Cu^{2+} amine complex is also suggested [168] in contrast to the findings discussed above. Amara et al. [170] have also suggested a different model of surface copper species on silica in their study of the characteristics of SiO_2-supported copper(I) species obtained by reduction of samples prepared from the Cu^{2+}-amine complex grafted on silica. On the basis of characterization data using various techniques, they conclude that for samples with copper loadings below 1–2 wt.-% Cu, copper(II) ions can be selectively reduced to Cu^I ions in agreement with previous findings [145,151], but they suggest that the reactive sites for Cu^I formation are $(Cu^{II}–O–Cu^{II})^{2+}$ pairs. Differently from other authors, they also suggest that isolated Cu^{II} species reduce to Cu^0 at temperatures above 300°C. Supported Cu^I species could also be prepared directly by exchange of ammonia treated silica with the $Cu^I(NH_3)_2$ complex [170]. Differently from the more stable species obtained by reduction of the Cu^{2+} pair, the

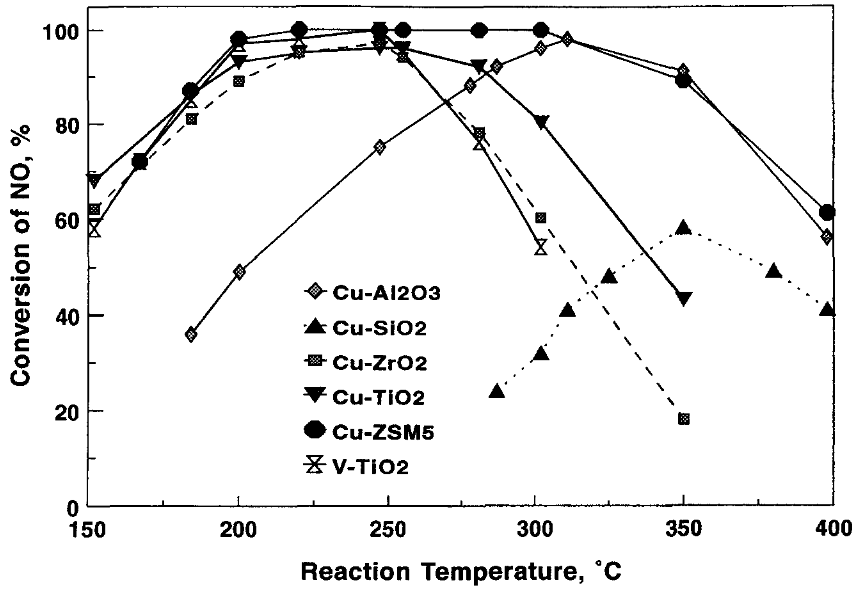


Fig. 4. Comparison of the conversion of NO over various copper-supported samples and a V–TiO_2 catalyst [42].

Cu^+ ions obtained by direct exchange easily reduce to Cu^0 even under vacuum at 200°C. These results constitute further evidence of the necessity for further studies in the area of silica supported copper catalysts, notwithstanding the great deal of work already done in this area.

3.1.3. Copper on titania and zirconia

Much more limited data exist on the characterization of the surface species present on other oxide supports such as ZrO_2 and TiO_2, even though the interesting properties of zirconia supported copper catalysts in methanol synthesis and hydrogenation reactions has stimulated research interest in this catalytic system in recent years [171]. Well defined indications on the nature of the copper species on these supports are thus missing, especially concerning the relationship between specific nature of the support and type of surface copper species. The results of Iizuka et al. [118], however, indicate that the reduction of nitric oxide with H_2 or NH_3 over copper oxide catalysts supported on ZrO_2 or TiO_2 is very sensitive to the type of support. The comparison of the conversion of NO in the presence of NH_3/O_2 (SCR) on a 5 wt.-% copper oxide sample (preparation by ion exchange) on various kinds of oxide supports (Al_2O_3, SiO_2, ZrO_2, TiO_2, ZSM-5) also shows the considerable effect of the support. Results summarized in Fig. 4 clearly show the superior performances of zirconia and titania supported copper oxide samples in this reaction [42]. Using these supports the results are analogous to those obtained with a highly reactive copper ion-exchanged ZSM-5 sample where all the copper ions are well dispersed and anchored to Brønsted zeolitic sites, as discussed in Section 3.1.4 and to those obtained using vanadium-on-titania catalysts (well known SCR catalyst

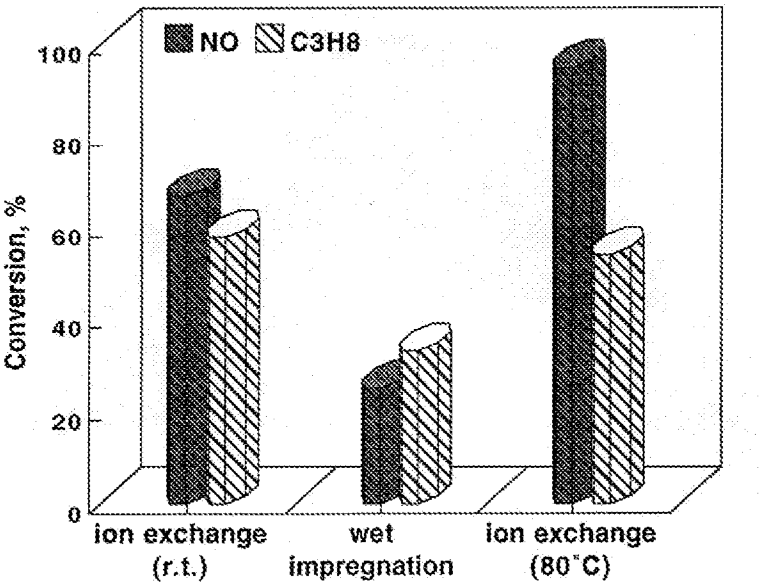


Fig. 5. Comparison of the activity in NO reduction with propane/O_2 of Cu/ZSM-5 catalysts containing 4 wt.-% CuO, but prepared by ion exchange with a copper acetate solution at 25°C or at 80°C, and by incipient wet impregnation [191].

[7]). The data reported in Fig. 4 suggest a very good copper dispersion over ZrO_2 and TiO_2 supports.

Shimokawabe et al. [172,173] have characterized zirconia supported copper catalysts using the same method of impregnation with an aqueous solution of tetramine copper(II) nitrate used by the same authors for copper/silica catalysts [143,174]. Results indicate that Cu^{2+} with an octahedral environment is predominantly present for copper loadings below 3 wt.-% and bulk CuO above 8 wt.-%. They also noted that highly dispersed CuO on zirconia is readily crystallized to bulk CuO in TPR experiments when compared to silica, but reasonably this is due to zirconia sintering only. These results thus suggest a better dispersion of isolated copper ions over zirconia as compared to silica and alumina, but further data on the exact surface structure of the copper species are lacking. Koeppel et al. [175] have studied copper/zirconia catalysts prepared using various procedures including ion exchange with a Cu^{II} tetramine solution, but without providing any clear indications about the nature of the surface copper species and the influence of the preparation method. The role of the amorphous zirconia matrix in the stabilization of microcrystalline copper particles, however, is pointed out. Limited additional data on the structure of copper species supported on zirconia are available in the literature. Sun and Sermon [176], for example, report data on copper-doped zirconia aerogels, but the results do not provide further insight on the structural characteristics of the copper species.

Information in the literature on the nature of the copper species in TiO_2 is limited. It should be noted that in this case in the reduced samples strong metal–support interaction phenomena are also possible [177]. Using high-resolution transmission electron microscopy and IR spectroscopy, Bocuzzi et al. [113,178] have characterized titania supported copper samples with specific reference to their activity behaviour in NO and CO interaction. They suggest the presence in the reduced sample of small metal particles exposing almost isolated and partially positive copper sites in close contact with a reduced defect titania. In oxidized samples, an amorphous copper oxide layer is present. Amores et al. [179] indicate that CuO–TiO_2 samples produced by impregnation with copper nitrate are composed of dispersed surface complexes of both divalent and monovalent copper linked to the titania support. CuO, as a separate phase, appears only for loadings greater than monolayer capacity (see Section 3.1.2 for the estimation of the monolayer capacity). These authors also observed that Cu^{2+} centres are easily reducible and small clusters of Cu can be formed even by mild reduction.

3.1.4. Open problems on the nature of copper species in supported catalysts

The following main open questions about the nature of supported copper species are unsolved or need further in-depth studies:

1. Nature (form and dimension characteristics, nuclearity, local copper coordination and structure, surface characteristics, defective properties, etc.) of small paracrystalline copper oxide particles (briefly referred to as defective CuO) on oxide supports and role of the support and preparation method on the formation of these species.
2. Stability and species interconversion in redox cycles or during catalytic tests of supported defective CuO.
3. Reactivity and redox characteristics of defective CuO in relation to the properties of copper species (mono- or multi-nuclear) which interact directly with the support oxide through oxygen bonds.
4. Nature (coordination, presence of unsaturations, changes in coordination upon adsorption of reactants or products, number of direct bonds with the oxide support, etc.) of isolated copper sites and role of the nature of the support on it; relationship between the characteristics of the support (acid–base properties, crystalline structure and faces exposed, impurities, etc.), preparation method and dispersion of copper species.
5. Presence of additional specific copper sites (copper dimers, for example), their stability and role of the preparation method in their formation.

3.2. Unsupported copper samples

There is little information in the literature on the surface properties of unsupported copper oxide. Busca [180] has used IR spectroscopy to characterize a CuO sample prepared by thermal decomposition of $Cu(OH)_2 \cdot CuCO_3$, and found that after activation in vacuum both weak Cu^{2+} and Cu^+ Lewis acid sites are present. However, the general problem of the relationship between surface properties of copper oxide and crystalline habit or faces exposed, and nuclearity is not considered. A comparative study on the structural and surface properties of unsupported copper oxide samples obtained from different controlled preparations therefore may be very valuable, especially for a more clear identification of the nature and properties of supported paracrystalline copper oxide particles and their transformation during the catalytic reaction. Comparative studies with the characteristics of well defined reference copper species are also needed. Jernigan and Somorjai [181] recently studied the properties and reactivity in CO oxidation of thin films of metallic copper, copper(I) and copper(II) oxide grown onto graphite, and found that the rate of CO oxidation decreases and the activation energy increases with increasing copper oxidation. Balkenende et al. [182,183] have studied the NO and CO interaction with low-index, stepped single-crystal copper surfaces [Cu(111), Cu(100), Cu(110), Cu(710) and Cu(711)] in comparison with copper/silica catalysts. The results suggest the role of nuclearity of supported copper particles on the catalytic behaviour in the NO/CO reaction. The same authors have also studied the surface properties of Cu/SiO_2 catalysts oxidized by NO or O_2 [184]. The properties of copper monocrystal surfaces have also been studied by Raval et al. [185] and Wee et al. [186], whereas Xu et al. [187] have analyzed the surface chemisorption properties of model silica supported copper.

3.3. Zeolite-based copper catalysts

The presence of an ordered and known crystalline lattice with defined exchangeable sites makes transition metal ion-exchanged zeolitic materials well suited for spectroscopic studies on the nature of the surface bonding of ions to the zeolite framework and on the coordination chemistry of these surface-bound ions. Therefore, transition metal ions in zeolites have been extensively studied in the past [188–190].

3.3.1. Different copper species present in copper-containing zeolites

Copper ions are introduced into the zeolite as exchangeable cations on extralattice positions and thus only well dispersed and isolated copper ions interacting with the zeolite framework via one or two oxygen-bridging bonds may be expected. However, due to hydrolytic/thermal transformations (Section 3.3.3) and a local precipitation of copper hydroxide due to local changes in pH (Section 3.1) the formation of higher nuclearity multinuclear copper complexes inside the zeolitic channels is possible. In general, the formation of such a species is limited by exchange in dilute, slightly acidic solutions (typically 0.01 N and pH in the 5–6 range, as at lower pH values dealumination of the zeolite may be possible) and low temperatures of the ion-exchange solution. The dimensions of the ion-exchange copper complex (acetate versus amine copper complex for example) is also important, especially for the zeolite with the smaller cavities. The modality of preparation of copper ion-exchanged samples thus plays a significant role in the formation of isolated versus multinuclear copper species in the zeolitic cavities. This problem however it not well recognized in the literature. Most of the characterization studies, in fact, have been focused on the identification of characteristics and properties of isolated copper species interacting with the zeolitic framework, since these species are easier to characterize by common spectroscopic techniques (for details on their ESR and UV-VIS diffuse reflectance spectra see the review of Schoonheydt [189]).

The identification of defective multinuclear copper oxide species that are X-ray diffraction (XRD) amorphous requires less common techniques such as X-ray absorption spectroscopy and the possible level of identification of their structural/surface features is definitively less precise. Nevertheless, there are several catalytic results which indicate that their presence enhances the catalytic performances of Cu-zeolite in nitrogen oxide conversion. Reported in Fig. 5 is an example of the catalytic activity in NO reduction with propane/O_2 of two analogous Cu/ZSM-5 samples prepared by the ion-exchange procedure, but in one the exchange is carried out at room temperature and in the second at 80°C [191]. The amount of copper is the same in the two samples, but in the latter sample there is an increase in the relative ratio between multinuclear and isolated copper species. The results of Fig. 5 show that this increase is beneficial for the activity of the zeolite in NO oxidative reduction with propane. Similar conclusions were drawn by Valyon and Hall [192] who compared the activity in NO decomposition of Cu/ZSM-5 samples prepared by ion exchange at two pH values.

Various other evidences exist on the presence and catalytic role of bi- or multinuclear copper species Lei et al. [193] suggested that $[\mathrm{Cu{-}O{-}Cu}]^{2+}$ pair are instrumental in the catalytic decomposition of NO. The presence of polymeric amorphous $(\mathrm{-Cu{-}O})_n$ species was shown using photoluminescence spectroscopy [98,147,148,194], XANES and EXAFS techniques [195] and temperature-programmed reduction/temperature-programmed desorption (TPR/TPD) and FT-IR techniques [196]. Shpiro et al. [197,198] indicated that the co-existence of isolated and multinuclear (called small copper/oxygen aggregates) species is necessary for NO reduction with hydrocarbons. Ebitani et al. [99,100] have suggested that a dimeric species of copper was the active species in photocatalytic decomposition of N_2O over Cu-containing ZSM-5 zeolite. Parrillo et al. [199] also noted that a considerable fraction of the copper was not associated with framework Al sites in Cu/ZSM-5 even at low exchange levels. In all cases, however, detailed data on the possible structure of the multinuclear copper species do not exist. It should be noted, however, that in analogous Cr-silicalite Spoto et al. [200] showed by time-resolved IR spectra the presence, together with isolated species, of polymeric chains formed inside the silicalite channels. The latter are shorter, with distinct spectroscopic features as compared to amorphous species formed on the external surface of the zeolite crystallites, and characterized by a zigzag one-dimensional type structures extending in several zeolitic cages.

Different isolated copper ions interacting with framework Al and characterized by a different reactivity may also exist. Wichterlova et al. [201–204] used photoluminescence spectroscopy in combination with ESR and IR to characterize copper ion-exchange ZSM-5, Y and erionite zeolites. They found two types of copper species, one without an extra-framework ligand and one with an extra-framework oxygen or hydroxyl ligand. The relative amounts of these species depend on the Si/Al ratio and copper loading. Type (I) sites, characterized by a pyramidal ligand field symmetry and in vicinity of two framework Al were suggested to be active for the reduction of NO with NH_3. Type (II) sites, characterized by a ligand field symmetry close to planar and in vicinity to one Al framework atom were suggested to be the more active for NO decomposition. Both types of copper sites were instead suggested to be necessary for the reduction of NO with hydrocarbons [204].

Finally, in addition to copper species inside the zeolitic channels, copper species on the external surface of zeolite crystals may also form. Shpiro et al. [197] have shown by XPS studies that in Cu/ZSM-5 prepared by impregnation there are large, aggregated copper species on the external surface which are not present in the samples prepared by ion exchange. The presence of these copper aggregated on the surface has a negative influence on the activity according to Shpiro et al. [197], a positive influence according to Lee et al. [205] and a negligible role according to Zhang et al. [206].

During the catalytic reaction redispersion and change of copper species due to ion mobility especially under hydrothermal conditions was also noted. Various authors have observed migration of Cu^{2+} ions inside the zeolite channels during the solid-state reaction between cupric compounds such as CuO and zeolite [207–212]. The driving force of the process is the reaction of copper ions with the zeolite Brønsted groups. The process is enhanced by increasing the temperature and in the presence of water or ammonia in the gas phase which help the mobility of copper ions. For this reason, significant reconstruction effects of copper species during the catalytic reaction may be expected. However, the opposite effect has also been observed in catalytically or hydrothermally deactivated Cu/ZSM-5 catalysts, namely the growing of large CuO crystallites which can lead to local destruction of the zeolite crystallinity [213,214]. The formation of these large crystallites of CuO deactivates the catalyst in NO reduction by HC/O_2 [215], but clearly these CuO crystallites differ significantly from the defective multinuclear copper species stabilized inside the zeolite channels. The stability of isolated Cu^{2+} ions interacting with the framework was shown to depend on zeolite structure. Parrillo et al. [215] observed that Cu migrates easier when in Y zeolite structure than in ZSM-5.

3.3.2. Localization and stability of copper ions which interact with the zeolite framework

The crystallographic sites of the exchangeable cations are briefly summarized in Fig. 6 for faujasite, mordenite and MFI zeolite. The various sites differ in regard to ideal point symmetry and thus the copper ions located at the various sites have distinct spectroscopic features. Schoonheydt [189] has summarized the EPR and UV-VIS diffuse reflectance features of the Cu^{2+} ions in the various coordination

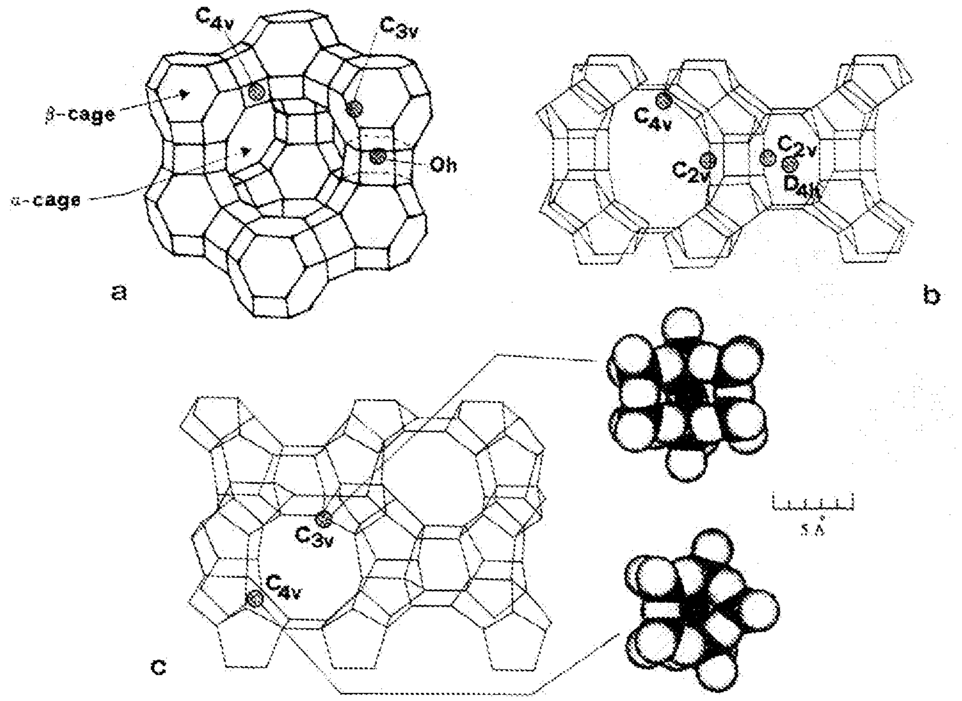


Fig. 6. Schematic drawing of the structure of faujasite (a), mordenite (b) and MFI (ZSM-5) (c) showing the exchangeable cation sites and their ideal point symmetry. Molecular models of the hexagonal and pentagonal rings facing the ZSM-5 channels [227] (white spheres: oxygens; grey spheres: Si or Al) and localization of copper inside these sites (black spheres: copper ions) are also shown.

sites of mordenite and faujasite. In MFI (ZSM-5), on the contrary, ion-exchange sites are located on the walls of the channels (Fig. 6c). Four-, five- or six-coordinated Cu^{2+} can be formed, but the various locations are not significantly different in terms of the energy of the interaction, in contrast to the cases of faujasite and mordenite [189]. Therefore, in MFI no single preferential site is observed. Apparently the local coordination of Cu^{2+} in ZSM-5 does not differ significantly from analogous situations in mordenite and faujasite, but there are two main significant differences. The first is that in mordenite and faujasite part of the copper ions are located in *hidden sites* (for example, in hexagonal rings in faujasite; site I in Fig. 6a) where the shielding effects of lattice oxygen prevent or greatly limit the possibility of their interaction with gaseous molecules. In faujasite and mordenite, for example, the reducibility of the copper ions depends on their localization [216–219] which is a function of the Si/Al ratio, copper loading, nature and amount of cocations (alkaline metals, in particular). The second significant difference is the local softness of the oxygen which decreases in the MFI $\gg$ mordenite $\gg$ faujasite series and thus the covalency of the coordinative bond decreases. The local charge seen by molecules coordinating the copper ions and the shielding effect of oxygen coordinating the copper ions thus differ considerably from zeolite to zeolite. This explains the differences observed in terms of NO coordination, for example (see

Section 4), but also the small differences observed in the Cu^{2+} ions coordinated at equivalent sites in MFI [207–209,220–222], faujasite and mordenite [189] or zeolite such as SAPO-5 and SAPO-11 [209,223,224]. The softness characteristics of lattice oxygen depend not only on the structure of zeolite, but also on the Me/Si ratio and the properties of heteroatom [225,226]. The substitution (completely or partially) of Al ions with B, In, Ga etc. or Si with Ge is thus a key to modify these properties.

A further interesting observation in relation to the shielding effect of framework zeolite oxygen on the reactivity and properties of isolated copper species has been made by Spoto et al. [227]. They noted by computer modelling that copper ions in the hexagonal and pentagonal rings facing the ZSM-5 channels are located in an inner position with respect to the facing oxygen and that, depending on the oxidation state (due to different ionic radii) they can move toward more internal positions of the framework (where they would be shielded by oxygen) or more facing positions (where they are prone to interact with ligands). More extensive computer modelling studies of local copper site environments, as well as the dynamics of molecular motion and adsorption would certainly be a key factor to improve our knowledge about these catalysts. Some attempts in this direction are already found in the literature [228,229].

Thermal migration from one site to another and the inhibition effect of monovalent cocations has been noted by several authors. These effects are a key aspect of the understanding of catalytic behaviour of copper-containing zeolites, for example why partially Na^+ exchanged Cu-Na/Y zeolite is more active in NO conversion with NH_3 (see Section 2). However, migration of copper ions may be accelerated by bonding with gaseous molecules. Maxwell et al. [27] have observed migration of copper cations in faujasite to sites located at the entrance of supercages. Strome and Klier [230] demonstrated the movement of Cu^I ions induced by CO chemisorption from less accessible to more accessible positions in Cu^+/Y samples. It is also known that ammonia promotes Diels–Alder synthesis over Cu^I/Y for the same reason and Itho et al. [231] recently showed that various kinds of alcohols cause relocation in Cu-Na/ZSM-5 of Cu ions from recessed sites to more open spaces (channel intersections). The relocation of copper ions during the catalytic reaction over long or short distances induced by chemisorption is thus a quite general phenomenon and all observations agree in indicating that a metastable position for catalytically active copper ions is usually observed. The copper complex in ion-exchanged zeolite should thus be considered in a heterogenized homogeneous state [231] which is metastably created in situ during the catalytic reaction.

3.3.3. Valence state of copper during the catalytic reaction

Redox properties of copper-zeolite have been extensively studied in the past. For example, Maxwell and Drent [22] have studied the reducibility by butadiene and ammonia of Cu/faujasite, whereas Naccache and Ben Taarit [21] and Huang [24] analyzed it by CO. The self-reduction of Cu^{2+} ions to Cu^+ upon prolonged evacuation has also been recognized [30]. Several subsequent studies on the same topics do not add significant further information, but a recent study on the effect of H_2, CO and vacuum treatments on the Cu^I photoluminescence signal can be cited [201]. The different copper species identified in Cu/ZSM-5 were reduced with a different rate due to the presence or absence of extra-lattice oxygen (ELO). This observation raises the question of the nature of the reactive oxygen released during the reduction process as O_2 or incorporated in the reaction products (H_2O, CO_2). Reactive oxygen may be either zeolitic or extraframework (ELO). In the first case, the reaction would produce Lewis acid sites that effectively have been detected after long evacuations [30]. Results of isotope exchange experiments using $C^{18}O_2$ [232] over NaY and NaCaY zeolites show that the presence of bivalent cations enhances the amount of lattice oxygen taking part in exchange. Exchange reactions using $^{18}O_2$ [233] suggest that the introduction of Cu^{2+} ions into NaY increases the rate of exchange. Similar conclusions were obtained from the study of the exchange of oxygen between water and zeolite oxygen [234]. Therefore, zeolitic lattice oxygen may take part in the process of reduction.

Due to the strong electrostatic field in zeolite cavities $Cu(OH_2)^+$ species may give rise to hydrolytic reactions forming $Cu(OH)^+$ Brønsted sites as shown over 20 years ago [21,30,234,235]. Further dehydration forms bridged Cu^{2+} pairs:

$$2Cu(OH)^+ \rightarrow Cu^{(2+)}\text{–O–}Cu^{(2+)} + H_2O \qquad (3.1)$$

Similar conclusions can be drawn from ESR studies on Na-Cu/Y by Chao and Lunsford [236]. They also showed that only a small fraction of the total copper content is represented by isolated Cu^{2+} ions. These bridging oxygens or those present in the other possible multinuclear copper species (polymeric chains, for example; see Section 3.3.2 (these extra-lattice oxygens are usually called ELO without any distinction on the specific type of multinuclear copper species present inside zeolite cavities) are easier to reduce than zeolite framework oxygen. Benn et al. [20] have shown in their study on the nature of reactive oxygen in Na-Cu/X zeolite that ELO species are those responsible for anaerobic oxidation of CO. They suggest that only at the higher temperatures does the further reduction to form Cu^0 involve zeolite framework oxygen. Using H_2 instead of CO Benn et al. [20] obtained different results and this can explain why different results have also been found by other authors [193]. Oxygen bridging two copper sites is easier to abstract. In a study of the redox chemistry of *excessively exchanged* Cu-Na/ZSM-5 samples Sarkany et al. [196] confirmed that CuO and $(Cu\text{–O–}Cu)^{2+}$ species reduce easier than isolated copper species. The latter can also spontaneously reduce upon high-temperature vacuum treatment. They also noticed that Cu^0 may be oxidized at high temperatures by the action of zeolite protons and that CO favours this oxidation, probably due to the formation of a stable Cu^I–CO complex.

The redox chemistry of copper species in zeolite, even though complex, has been well established, but more questionable is the relevance of these observations for the catalytic behaviour. The problem can be viewed with reference to the anaerobic decomposition of NO. The obvious approach is to consider that there is a spontaneous desorption of oxygen with formation of oxygen vacancies and two Cu^+ ions. NO dissociatively chemisorbs on these sites; NO oxygen replenishes the vacancy and reoxidizes the copper ions while the $N^\cdot$ migrates to another site to combine with another $N^\cdot$ to form N_2. The rate of NO dissociation is controlled by the rate of oxygen desorption. In a study of the reaction kinetics Li and Hall [237] found a first order dependence of the rate of NO decomposition on the NO concentration and a half negative order for the effect of oxygen. These kinetic results agree well with the simple model of a reaction controlled by oxygen desorption. However, several other consecutive results showed that the mechanism is probably more complex. Results from spectroscopic studies also by the same authors (see Section 4 and Section 6) were not consistent with the proposed model, but especially other kinetic data have shown that the order of reaction with respect to NO is higher than 1.0. Iwamoto et al. [238], for example, have reported for an analogous sample a reaction order between 1.2 and 1.5. Centi et al. [239,240] found a reaction order of 1.8 and fitted the data using a rate equation derived from the following assumptions: (i) the reversible formation of a dinitrosyl intermediate and (ii) a synergetic cooperation between two active sites in the rate limiting step based on the conversion of a N_2O_3-like intermediate. IR evidence supports these assumptions. Over Cu-Na/Y, Iwamoto et al. [50] also found a reaction order of 1.6. The role of Cu^+ ions in the mechanism of decomposition of NO is thus not demonstrated by the kinetic data.

Shelef and co-workers [241,242] have argued that a mechanism of NO decomposition involving coordinatively unsaturated Cu^{2+} ions may be proposed without the necessity of invoking a cyclical oxi-reduction of the surface sites. Yasuda et al. [243] on valence controlled La_2CuO_4-based mixed oxides found that the active sites for NO decomposition over these catalysts are coordinatively unsaturated Cu^{2+} ions on the surface that can be easily oxidized to Cu^{3+} upon NO adsorption. Spoto et al. [227,244] have carried out spectroscopic studies of Cu^I/ZSM-5 zeolites, and suggested that NO interaction with Cu^I ions gives rise to a Cu^{2+}–$O^{(-)}$ species (a Cu^{2+} species containing extra-lattice oxygen formed during the reaction itself) which is the real active species in NO decomposition via a $Cu^{2+}(NO)(NO_2)^-$ intermediate. Giamello et al. [245] have suggested a similar reaction mechanism and showed that Cu^+ is unstable under NO pressure and undergoes oxidation to Cu^{2+} at room temperature. The mechanisms of NO decomposition which consider NO chemisorption only on Cu^+ ions [246,247] should therefore be reconsidered.

It is also worth noting that all authors that have carried out IR studies of the interaction of NO with Cu/ZSM-5 have observed the formation of nitrite/nitrate species (a series of bands below 1600 cm^{-1}), but some of them have simply neglected their catalytic importance [246]. Apart from the possible role of these oxidized NO species in the decomposition of NO (see Section 6), their formation in the absence of gaseous oxygen implies that copper ions should be reduced.

Therefore, the simple observation of Cu^+ ions during the interaction with NO does not necessarily imply that Cu^+ ions are those active in NO decomposition, because they can derive from a side reaction such as the oxidation of chemisorbed NO to nitrite/nitrate species.

Liu and Robota [248] have studied the reaction using XANES spectroscopy. They found the formation of Cu^I in large amounts after activation at 500°C in an inert flow. The amount of Cu^I decreases considerably after admission of NO, but does not completely disappear. They also observed a relationship between amount of Cu^I detected using their method and rate of NO decomposition and therefore concluded that the role of Cu^I ions in the reaction is demonstrated. However, a closer inspection of their data shows that the amount of Cu^I ions increases above 500°C, whereas the rate of NO decomposition decreases. Other authors using in situ ESR studies have found that there is no spontaneous thermal reduction of Cu^{2+} ions up to 500°C or in any case it is limited to less than 10–20% of the copper ions [249]. Similar conclusions were obtained by XPS spectroscopy [250].

Recent results from isotopic experiments of Valyon and Hall [251,252] indicate that (i) Cu^{2+} promotes the rate of exchange, in analogy to older results [232,233], and (ii) lattice oxygen is involved in the decomposition mechanism and desorption of O_2. However, the identity of the oxygen atoms introduced into the solid is not conserved. Oxygen atoms may be introduced at one place and O_2 may be formed and released from elsewhere on the solid. ^{18}O atoms formed by decomposition enter the solid through portholes (at reduced sites), mix with nearby lattice oxygens and at the same time an equivalent number of the latter diffuse to positions where they can be stabilized as ELO. No clear evidences support this mechanism of lattice oxygen scrambling, because the possible role of adsorbed oxygen species and disproportionation reactions of adsorbed NO was not taken into account. The disproportionation reaction of 4 NO molecules to $N_2O + N_2O_3$ ($NO_2 + NO$) over zeolites is well documented in the literature [253,254]. Earlier observations were made over 40 years ago [255] and also recently the formation of N_2O_3 by reaction of NO and NO_2 over Cu/ZSM-5 was reported [256]. The key feature of the reaction mechanism is the reversible formation of a surface nitrate–nitrosyl complex which can give rise to products of disproportionation or reversibly to starting chemisorbed NO species [253]. This chemistry should be considered in the analysis of isotopic effects.

The problem of the real active state of copper during catalytic reaction is even more complex when reducing agents (hydrocarbons, ammonia) and oxygen are present together with NO. XPS/XAES and EXAFS/XANES studies of Cu/ZSM-5 catalysts after various treatments or interactions with propene, O_2 and NO have been carried out by Shpiro et al. [197,198] who concluded that copper is predominantly in the 2+ oxidation state under conditions relevant for selective reduction of NO in lean-burn engine exhaust gas [197]. In situ ESR monitoring of the state of copper ions during interaction of propene, NO and O_2 with Cu/ZSM-5 leads to the same conclusion [257], but the possibility of reduction of copper ions at low temperature was observed. Grunert et al. [258] observed that the predominant oxidation state for copper was 2+, but the presence of Cu^+ was also detected depending on the reaction conditions. Shpiro et al. [198] also suggested that isolated Cu^{2+} ions are responsible for propene activation and in particular the formation of a Cu allyl radical intermediate. Early studies on Cu/Y zeolites using UV and IR spectroscopies [259] indicated that Cu^{II} can be easily reduced to Cu^{I} upon adsorption of propene to form a Cu^{I} π-allylic intermediate. Liu and Robota [248,260] have suggested that this cuprous complex reacts with NO and O_2 to give N_2 and CO_2, but also noted that the same complex is an intermediate for carbon formation. Propene conversion with Cu/Y catalysts has been thoroughly studied by Yu and Kevan [261–265] and Mochida et al. [266,267]. Their research was focused on the partial oxidation of propene to acrolein, but it is possible to conclude that unselective oxidation to CO_2 (aimed at the reaction in the treatment of lean-burn engine emissions) is correlated to the Cu^{2+} ions. Yu and Kevan [262] also noted that water vapour (a significant reaction product in hydrocarbon oxidation) alters both the mechanism of carbon deposit formation and that of hydrocarbon oxidation. Cu^{2+} ions have also been suggested as being responsible for the activity of Cu-Na/ZSM-5 catalysts in alcohol conversion [231]. Finally, Choi et al. [268] using X-ray absorption spectroscopy found evidence that Cu^{2+}-amine complexes are those responsible for the activity of these samples in NO reduction with ammonia/O_2.

The active state of copper during nitrogen oxides transformations is thus controversial. In situ time-resolved spectroscopic experiments with a simultaneous recording of the catalytic behaviour, possibly using also labelled compounds, are necessary to clarify this important question.

3.3.4 Open problems in the characterization of the properties of Cu-zeolite samples

The following area of research need in-depth studies for a better correlation between the nature of copper sites in Cu-zeolites and their reactivity in nitrogen oxides conversion:

1. Presence, structural characteristics, and stability during reaction and role in the conversion of nitrogen oxides of oxygen-bridging multinuclear (binuclear or with a higher nuclearity) copper species stabilized inside the zeolite channels; role of zeolite structure and preparation method in their formation; differences in the properties between multinuclear species inside the zeolite cavities and on the outer surface of zeolite crystallites; development of suitable spectroscopic methods for their identification and characterization.
2. Identification of the dynamic situation of copper species during the catalytic reaction; phenomena of redispersion, migration and interconversion between copper species; effect of co-adsorbent on the displacement and mobility of copper species; formation of metastable copper species (homogeneous versus heterogeneous behaviour of copper ions); dependence of siting and accessibility of isolated copper ions from gaseous molecules on the valence state of copper; development of in situ techniques to investigate the metastable nature of copper species during the catalytic reaction.

3. Shielding effect of zeolite lattice oxygen on Cu^{2+} and Cu^{+} mono- or multi-coordination of gaseous reactants; role of zeolite oxygen softness on isolated copper ion reactivity; tuning of the properties of copper ions (spectroscopic, chemisorption and reactivity) by partial or total substitution of Al ions with B, In, Ga, etc. or Si with Ge in MFI zeolite; use of computer simulation to determine the local environment of isolated copper ions and estimate their chemisorption characteristics; computer simulation of the dynamics of molecular motion.
4. Relevance of the redox chemistry of copper ions on the chemisorption and surface transformations of nitrogen oxides; effect of gas phase or solid state modifiers on the copper redox reactivity.

3.4. Cuprates and other copper compounds active in conversion of nitrogen oxide

Several oxocuprates or copper-containing compounds have been tested in the past and found to show interesting activities in NO conversion with CO, NO and N_2O decomposition (see Section 2 and Table 1). However, a detailed discussion of the structural characteristics of these compounds is beyond the scope of this review. Reference is made to the comprehensive review of Müller–Buschbaum [269] who has reported the structural characteristics of several oxocuprates and compounds containing Cu^{2+} ions in closed polyhedra. Several of these compounds have been found to show interesting behaviour in the conversion of nitrogen oxides [see, for example, the special issue of Catal. Rev.-Sci. Eng. [270] devoted to catalysis by perovskite oxides].

4. Chemisorption and surface transformations of NO

NO is a widely used probe molecule for the study by infrared (IR) spectroscopy of the surface properties of transition metal ions in oxide matrices [138,271,272]. The coordination and activation of NO by transition metal ions in coordination complexes was instead widely discussed in Refs. [273–275].

4.1. Nature and role of nitrogen oxide adspecies in the decomposition of NO

The predominant mode of chemisorption of NO on isolated copper ions is a linear linkage through the nitrogen end with an electron transfer from the π^* level of NO to the *d*-orbital of the metal atom, followed by back-donation from the occupied *d*-orbitals of the metal to the empty π^* antibonding orbital of NO. The net electron transfer may thus vary from a $NO^{\delta+}$–$M^{\delta-}$ to a $NO^{\delta-}$–$M^{\delta+}$ situation depending on the entity of back-donation which is proportional to the local charge density on the metal ions. The NO stretching frequency of NO in the gas-phase falls at 1876 cm^{-1}; this band shifts to higher frequencies when net electron transfer is from NO to metal and in the opposite direction when net transfer is from metal to NO, because back-donation occurs through antibonding orbitals and thus determines a weakening of the N–O bond. Taking into account that Cu^{2+} has a d^9 and Cu^+ a d^{10} configuration, it is expected that the stretching frequency of NO chemisorbed on Cu^{2+} gives rise to a shift to higher frequencies with respect to the gas phase frequency, and to lower frequencies for chemisorption on Cu^+. Giamello et al. [245] found, in agreement, a mononitrosyl band at 1912 cm^{-1} over Cu^{2+}/ZSM-5 and at 1811 cm^{-1} over Cu^+/ZSM-5. The frequency, however, depends on the coordination environment of the copper ions. On CuO/Al_2O_3, a mononitrosyl species on Cu^{2+} ions is found in the 1881–1910 cm^{-1} range and that on Cu^+ ions in the 1772–1786 cm^{-1} range depending on copper loading [137]. In particular, both bands were found to move to lower frequencies with increasing copper loading due probably to an increase in the lateral copper-to-copper interaction which in turn increases the local charge on the metal and thus back-donation to NO. The shift in the NO stretching frequencies in partially positive or negatively charged mononitrosyl species coordinated to copper ions in zeolites with respect to free NO molecules is always low in comparison with limiting cases for NO^+ (2354 cm^{-1}) and NO^- (1100 cm^{-1}) ions [245], showing that charge separation in copper–nitrosyl complexes in zeolites is limited anyway.

In the negatively charged mononitrosyl species ($NO^{\delta-}$) weakening of the N–O bond can suggest that this species is an intermediate in NO decomposition. Several years ago Van der Bleek et al. [276] proposed that requirements for the reduction of NO in the presence of oxygen include the coordination of NO over transition metals as NO^- together with reversible or no adsorption of O_2. More recently Iwamoto et al. [246] proposed that NO reacts with Cu^+ to form Cu^{2+}–NO^- (single, twin). Adjacent pairs are then supposed to react yielding N_2, O_2 and Cu^{2+}. Hall and Valyon [247,277] also indicated that this species is the first step of the reaction, but suggested that the extra electron density present in the Cu–$NO^{\delta-}$ species allows the addition of a second NO molecule to form a dinitrosyl species. This intermediate is responsible for N–N bond formation and decomposition activity.

In the mechanism of NO decomposition over metallic Pt discussed [278] the first step is the formation of a $M^{\delta+}$–$NO^{\delta-}$ complex, but bond breaking occurs only when a positive contribution to the overlap integral between the antisymmetric π^* acceptor orbital of NO and unpaired antisymmetric orbitals of active sites is present. In Cu/ZSM-5 this positive contribution to the overlap integral cannot occur and thus the coordinated NO do not dissociate. However, when a potential surface hole is present due to a lattice oxygen vacancy, NO is trapped in the potential hole and dissociates due the local crystal field which gives the extra energy required for N–O breakage. This process of NO dissociation is fast and observed in a variety of cases on prereduced samples [279]. Furthermore, it is expected not to give rise to IR detectable transient adspecies. This mechanism of N–O bond breakage is basically different from that involving the formation of a $M^{\delta+}$–$NO^{\delta-}$ intermediate complex such as over metallic Pt. For example, NO interacts from the oxygen side and does not require chemisorption on the transition metal. It is thus not correct to suppose a relationship between the nitrogen oxide adspecies detected by IR and the mechanism of NO dissociation over oxygen vacancies. Copper, however, may stabilize oxygen vacancies created by spontaneous reduction in Cu/ZSM-5 due to electron transfer, but it is expected that various other transition metals have the same function. The Cu/ZSM-5 is instead a very specific catalyst for the decomposition of NO. There is thus confusion in the literature about the relationship between nitrogen oxide adspecies observed by IR and the mechanism of the decomposition of NO. A reanalysis is thus helpful.

Gandhi and Shelef [16] observed in adsorption isotherm studies a faster and stronger adsorption of NO on Cu^{2+} than on Cu^{+} ions. Giamello et al. [245] observed the formation of a Cu^{+}–$(NO)_2$ dinitrosyl species with increasing NO pressure. At 77 K, when the NO pressure over Cu^{+}/ZSM-5 is increased an isosbestic point is observed in the reversible interconversion from mononitrosyl (IR band at 1812 cm^{-1}) and dinitrosyl species (two IR bands at 1827 and 1734 cm^{-1}) [244] which clearly indicates that the two species interconverted. At room temperature, the situation is more complex since a mononitrosyl species over Cu^{2+} and Cu^{+} ions [244,245] is present at the same time. This is due to the fact that already at room temperature Cu^{+} ions are easily oxidized to Cu^{2+} by NO [244,245]. Earlier EPR studies [280] are in agreement with this indication. Reported in Fig. 7 is an example of the spectra obtained upon room temperature NO chemisorption on oxidized Cu^{2+}/ZSM-5. It can be noted that in the spectrum recorded after the short contact, the dinitrosyl species (two bands at 1827 and 1734 cm^{-1}) is clearly present. The presence of the band at 1812 cm^{-1} does not allow one to say whether or not the dinitrosyl may form over both Cu^{+} and Cu^{2+} ions, but clearly shows that the IR results are not significantly different in the case of the predominant presence of Cu^{+} or Cu^{2+}. The IR results of Valyon and Hall [277,281] are in general agreement with those discussed above, but the quality of the spectra is significantly lower, several additional bands not observed by other authors are present and a variable position of some bands is observed. The IR frequency of the Cu^{2+}–NO species, for example, varies from 1895 to 1911 cm^{-1} in the various spectra. The IR results of Sepulveda-Escribano et al. [282], even though limited, are also consistent with the above indications.

Due to the higher ionic radius, Cu^{+} ions isolated at room temperature are located in a more open position in the hexagonal or pentagonal rings facing the ZSM-5 channels as compared with Cu^{2+} ions [227]. At room temperature, the mobility of copper ions is limited and thus it is reasonable to expect that dinitrosyl species form from Cu^{+} and not from Cu^{2+}, but due to the steric hindrance of facing lattice oxygen and not for electronic reasons. In fact, it may be expected from orbital overlap and electrostatic repulsion considerations that the coordination of a second NO molecule is easier on a $(Cu^{2+})^{\delta-}$–$NO^{\delta+}$ complex than on a $(Cu^{+})^{\delta+}$–$NO^{\delta-}$ complex. Detailed quantum-mechanical calculations, however, are necessary to

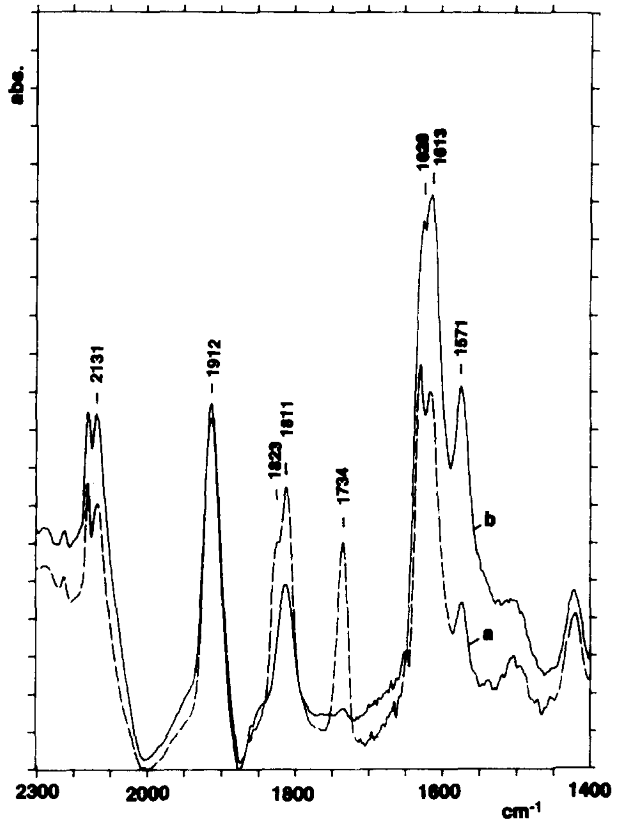


Fig. 7. Infrared spectra of a Cu/ZSM-5 catalyst ($SiO_2/Al_2O_3 = 49$, $2Cu/Al = 115$ molar ratios) in contact with NO at room temperature for 10 min (a) and 30 min (b) [239].

solve this question. At higher temperatures the copper ions tend to be displaced to more open positions during the catalytic reaction. During reaction, therefore, the situation may be significantly different than at room temperature. Valyon and Hall [277] also have reported spectra recorded at high temperature, but due to the absence of studies by dosing NO pressure limited conclusions from their data can be derived. The formation of dinitrosyl species over Cu^{2+} ions is thus an open problem.

The possible role of dinitrosyl species in the mechanism of NO decomposition is also unclear. Shown in Fig. 7 is the comparison of the IR spectra of nitrogen oxides adspecies recorded after 10 and 30 min of contact of the preoxidized Cu^{2+}/ZSM-5 catalyst with gaseous NO at room temperature. Two significant changes occur as a function of time-on-stream: (i) the dinitrosyl species disappear and (ii) simultaneously the intensity of a series of bands in the 1500–1650 cm^{-1} region increases. These bands are due to nitrite/nitrate species bridged or linearly bonded to surface ions. Giamello et al. [245] obtained analogous IR results and they observed that these bands are comparably less intense over Cu^{2+}/ZSM-5 than over Cu^{+}/ZSM-5, similarly to that found for the relative intensity of the dinitrosyl species. Spoto et al. [244] also found comparable results, even though they observed only a single broad absorption band in the 1400–1500 cm^{-1} region, probably due in their case to the presence of a single type of nitrite species. However, their time-resolved results also suggest a correlation between disappearance of the bands of dinitrosyl species and formation of nitrite/nitrate species. The results of Valyon and Hall [277,281] are consistent with these indications, but they also observed the presence of chemisorbed NO_2. Iwamoto et al. [238], on the contrary, did not analyze these bands.

Other small IR bands in the 2000–2300 cm^{-1} region have been observed by all authors, even though also in this case some small differences are present. These bands can be attributed to chemisorbed NO_2 (a small band at 2130 cm^{-1}, correlated to intensity of bands at around 1600 cm^{-1}; see Fig. 7) and possibly to chemisorbed N_2O (2249 cm^{-1}). The latter, however, do not vary significantly with time-on-stream [244] (see also Fig. 7). In addition, bands in this region may also be due to copper nitride (Cu_3N) species [283–285]. Copper nitride was detected by XPS/FT-IR characterization in $YBa_2Cu_3O_7$ after decomposition of NO [286]. A further more detailed analysis of these bands may be necessary.

In summary IR data give useful indications about the reaction mechanism, even though some additional specific studies may be necessary. In particular, IR data indicate that the disappearance of the dinitrosyl complex leads to the formation of chemisorbed NO_2 or nitrite/nitrate species. Oxygen released in the transformation of dinitrosyl species remains bound to the surface and does not desorb, but preferentially reacts with a NO molecule to form nitrite/nitrate species which are relatively stable. Further NO molecules therefore do not react with isolated copper ions, but rather with Cu–(NO_x) like complexes. This is the basis of the mechanism proposed by Spoto et al. [244] and Giamello et al. [245] in contrast with the hypotheses suggested by (i) Iwamoto et al. [238] that single, twin negatively charged mononitrosyl species react together to give $N_2 + O_2$, (ii) Valyon and Hall [277,281] that the dinitrosyl is the direct intermediate to $N_2 + O_2$ and (iii) Sarkany and Sachtler [193,287] that NO adsorbs on $[Cu–O–Cu]^{2+}$ complexes forming $Cu^{+}–NO^{-}$ type species which decompose regenerating the initial complex. The question must be viewed in terms of the stability of nitrite/nitrate copper species and relative rate of oxygen desorption or reaction with NO at the temperatures of the catalytic tests [288]. Data on these topics are limited, but some useful indications exist in the literature. Li and Armor [289] have observed in temperature-programmed experiments that at room temperature N_2O and N_2 form during NO adsorption, but the activity rapidly disappears. During consecutive thermodesorption, several desorption peaks for NO were observed, the highest of which is also associated with oxygen desorption. Hierl et al. [290] observed over a CuO/Al_2O_3 catalyst that reduced copper ions are initially active for NO decomposition, but oxygen adatoms are retained on the surface and react with NO to form nitrite/nitrate species. They also observed that nitrite species may disproportionate to NO and nitrate and that the thermal stability increases with increasing oxidation state of nitrogen in nitrogen oxides adspecies. In transient catalytic experiments over Cu/ZSM-5 Centi et al. [291] concluded that the order of stability increases in the following order: NO or $(NO)_2 \ll NO_2 \ll NO_3$.

They found, in particular, that copper nitrate is particularly stable and gives rise to inhibition of the catalytic activity during NO reduction with propane/O_2. Schay and Guczi [292] used transient catalytic tests to study the decomposition of NO over Cu/ZSM-5 and observed (i) an initial overshoot in N_2 formation and (ii) NO poisoning the catalyst activity.

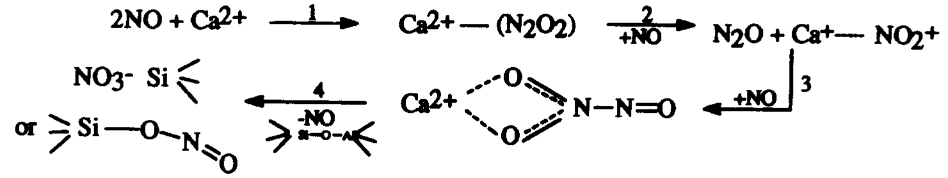
Combining these indications with IR data it is possible to suggest the following sequence of surface modifications which occur during the catalytic decomposition of NO over Cu/ZSM-5:

1. Initially on the sample activated in He flow, Cu^+ sites are present due to the spontaneous reduction of zeolite copper sites.
2. NO interacts with these reduced copper sites forming reasonably a dinitrosyl intermediate complex which decomposes forming N_2 or N_2O (depending on reaction temperature), but leaving oxygen adatoms on copper ions.
3. NO reacts with these oxygen adatoms forming nitrito species or by further conversion, nitrato species.
4. Nitrate species are relatively inactive and reduce the surface reactivity. The magnitude of the poisoning effect depends on the relative rate of decomposition of the nitrate species versus its rate of formation which in turn depends on oxygen concentration. Oxygen thus inhibits decomposition because it enhances the formation of less active species more than inhibiting the spontaneous desorption of oxygen.

In this surface model, copper-nitrito complexes are those responsible for catalytic activity by further NO chemisorption in analogy with mechanisms proposed by Spoto et al. [244] and Giamello et al. [245]. This mechanism is that prevailing under stationary conditions, whereas that involving a dinitrosylic intermediate is effective only under transient conditions (initial overshoot in N_2 formation [292]). The thermal stability of the nitrito complex and its rate of transformation to less active nitrate species explain the presence of a maximum in activity as a function of the reaction temperature. However, several aspects of this model of surface reactions of nitrogen oxide adspecies (their thermal stability and surface reactivity in the presence of increasing partial pressures of NO, the formation of copper nitride species, the modification of the nature of adspecies at high temperature, etc.) need further more detailed studies for their confirmation. Temperature-programmed surface reaction experiments in the presence of O_2 and NO appear to be useful together with spectroscopic studies and possibly theoretical modelling using a quantum-mechanical approach. It should be observed, however, that the suggested reaction mechanism is in agreement with kinetic evidence [239,240].

4.2. *Effect of O_2 on nitrogen oxide adspecies*

The discussion in Section 4.1 of the mechanism of NO decomposition over Cu/ZSM-5 showed the central role of oxidized nitrogen oxide adspecies on the surface



Scheme 1. Reaction mechanism proposed by Chao and Lunsford [253] for the disproportionation of NO over CaY.

reactivity of zeolites. When gaseous oxygen is fed together with NO, the oxidation of NO as a key step in the reaction mechanism is more evident. In the reduction of NO with hydrocarbons in excess oxygen, several authors agree in suggesting that the oxidation of NO to NO_2 is the first step in the reduction of NO to N_2 [293–300]. Blanco et al. [94] and Centi et al. [137] have suggested that NO_2 is also involved in the mechanism of reduction of NO in the presence of ammonia/oxygen over alumina-supported copper catalysts. In contrast, direct evidence regarding the role of oxidized nitrogen oxide adspecies in the high temperature reduction of NO with NH_3/O_2 over zeolites has not been reported, but recent results [301,302] strongly support this statement. Furthermore, Mizumoto et al. [36] proposed in the past that in the low-temperature (about 100°C) anaerobic reduction of NO with ammonia over Cu^{2+}-Na/Y, the key reaction is as follows:

$$Cu^{2+}(NH_3)_m(NO_2)^- + (NH_4)^+ \rightarrow Cu^{2+}(NH_3)_m + N_2 + 2H_2O \qquad (4.1)$$

Since oxygen is absent, the copper-amino nitrite complex derives from the disproportionation of 3 NO molecules to give $N_2O + NO_2$ in the presence of the copper-amino complex anchored to the zeolite framework. The disproportionation of NO over zeolites has been known for several years [255] and its mechanism has also been studied in detail using infrared [253] and electron spin resonance [254] spectroscopies. The reaction mechanism proposed is outlined in Scheme 1. NO reacts with a stabilized surface N_2O_2 dimer to form N_2O and $(NO_2)^+$. Due to the electrostatic field of zeolite, the further reaction with a NO molecule forms a N_2O_3 surface complex which is stabilized by the zeolite field in comparison to the gas phase. At higher temperatures this N_2O_3 adspecies may transform to a nitrate or covalent nitrite species by reaction with lattice oxygen. When a transition metal ion is present (Ni^{2+}) [254], electron transfer reactions are accelerated, but the above adspecies are also better stabilized due to the modification of the Madelung energy of the crystal. It should be noted that the Madelung site potential is not only important as regards the possible influence on stability and pathways of surface transformations of chemisorbed species, but also as regards the reactivity characteristics of transition metal ions, as suggested by Moretti [303] when discussing the Auger parameters of Pd and Cu intrazeolite ions or entrapped clusters.

Recently, the disproportionation reaction of NO over MFI zeolites (H-, Na-ZSM-5 and silicalite) was also studied using ^{15}N-NMR spectroscopy [304]. Even though using this spectroscopy some of the species detected by IR or ESR were not observed due to their large line broadening, it was possible to show the formation of N_2 and N_2O, probably through the decomposition of N_2O_3. The technique, however, made it possible to analyze the reactivity of surface nitrogen oxide adspecies upon addition of O_2 and/or NH_3 [304]. Oxygen considerably modifies the nature of adsorbed species, leading to the formation of a not well identified N_xO_y ($y>x$) adspecies, different from a nitrate. Upon NH_3 adsorption, a $NO \cdot NH_3$ complex forms as shown by the presence of an ^{15}N isotopic exchange from NO and NH_3. This complex gives rise to the formation of N_2, but when oxygen is also co-adsorbed the rate of N_2 formation is enhanced considerably due to the formation of a $N_xO_y \cdot NH_3$ complex. This complex is different from ammonium nitrate, the presence of which is also detected, but which plays a less important or negligible role for N_2 formation. It is interesting to note that these conclusions are analogous to those obtained using different techniques (IR and ESR coupled to non-stationary catalytic tests) in the study of the mechanism of reduction of NO to N_2 with NH_3/O_2 over copper-on-alumina catalysts [137,305].

The results of the study of the disproportionation reaction and surface transformations in the presence of oxygen illustrates that products of the reduction of NO (N_2O, N_2) may form as a consequence of surface reactions involving higher nitrogen oxides [306]. It is known that oxygen promotes the chemisorption of NO and its conversion over oxides and zeolites [279,291,306–409] with a maximum conversion of NO at about 350°C as expected on the basis of the equilibrium reaction [297,309,310]. Centi et al. [279,291] have observed, however, that the NO oxidation over Cu/ZSM-5 in a continuous flow reactor leads to the formation of small, but not negligible, amounts of N_2 and N_2O together with NO_2. The reaction occurs at 250°C in the absence of ammonia, hydrocarbons, etc. or reducing pretreatment of the catalyst and must be attributed to surface transformations (probably disproportionation/decomposition) involving higher nitrogen oxide adspecies, since their formation in the absence of oxygen at the same reaction temperature is negligible. The results obtained are summarized in Fig. 8a which reports the response observed at 250°C when a step change in the concentration of NO is made in an O_2/helium flow. The dotted lines represent the response obtained without the catalyst and the solid lines that with the catalyst. It is shown that apart from the two initial peaks in N_2 and N_2O formation, the amount of N_2 and N_2O increases after about 2 min of time-on-stream in coincidence with initial detection of NO_2 in the gas phase. The comparison of the response curves for NO with or without the catalyst (Fig. 8a) shows, furthermore, that high amounts of NO remain chemisorbed on the catalyst at 250°C, as also seen from desorption experiments after these catalytic tests [291]. This is in agreement with results of Arai et al. [105] suggesting a co-operative adsorption of NO and O_2 as a key step for NO_2 formation over Cu^{2+}-zeolites. In the reverse experiment of a step change of O_2 concentration over the catalyst maintained in a flow of NO in helium (Fig. 8b), an initially larger activity in the conversion of NO to N_2 and N_2O is observed, which clearly derives from the promotion effect of oxygen on surface transformations. However, the activity later decreases even though it remains higher than in the absence of oxygen. This result

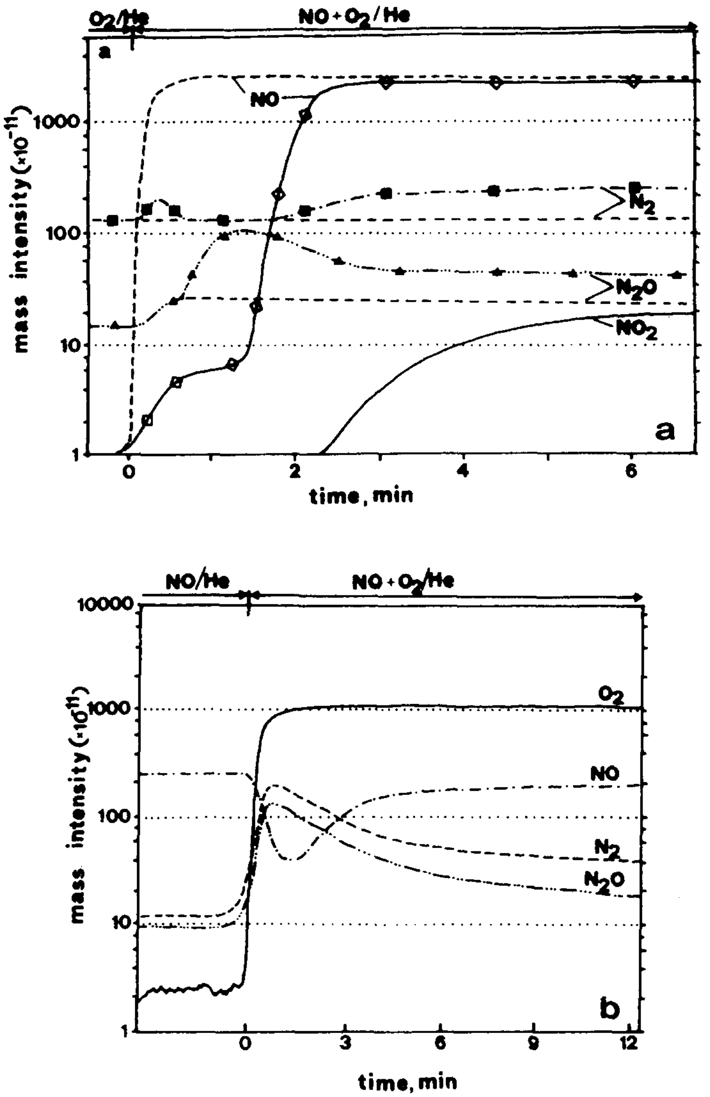


Fig. 8. (a) NO step-change experiments at 250°C over Cu/ZSM-5 in a flow of oxygen in helium [291]. Solid lines: mass intensity response during experiments in the presence of the catalyst. Dotted line: response when the catalyst is substituted with quartz pellets. (b) O_2 step-change experiments at 250°C over Cu/ZSM-5 in a flow of NO in helium [291].

indicates that initially oxidized nitrogen oxide adspecies are more reactive in the presence of NO towards the formation of N_2 and N_2O, but their transformation, probably to surface nitrate, leads to a decrease in the surface reactivity. It should be pointed out that the reaction temperature for these experiments (250°C) is significant in regard to the NO reduction with hydrocarbons/O_2, since Cu/ZSM-5 is already active above 200°C [291].

Higher nitrogen oxides such as N_2O_3 may thus play a significant role in the pairing reaction of the nitrogens, as suggested by Adelman et al. [256]. Shelef et al. [295], in agreement, showed that at short residence times, with excess reductant and in the absence of oxygen, the NO_2 itself is reduced only back to NO, just as various other oxides [311]. For the selective reduction of NO_2 to N_2 (N-pairing), instead, strongly oxidizing conditions are required, just as for the complete reduction of NO. Burch and Millington [312] have also proposed that $NO \cdot Cu^{2+} \cdot NO_2$ is the active intermediate over Cu/ZSM-5 in the reduction of NO with hydrocarbon and O_2.

4.3. Influence of co-adsorbents on the nature and reactivity of surface copper complexes with nitrogen oxides

Ammonia readily reacts with copper ions especially in zeolite cavities forming copper–ammine complexes that have been characterized by several techniques such as adsorption measurements [24,31], X-ray diffraction [313], ESR [38,314–316], IR [38,315,317] and X-ray absorption [268] spectroscopies. At room temperature a tetra-amino Cu^{2+} complex with a square planar symmetry forms. At higher temperatures, this complex may release part of the NH_3 coordinated molecules forming a distorted tetrahedron. Over Cu^+ ions, ammine complexes of $[Cu(NH_3)_2]^+$ stoichiometry have been identified [24]. All copper–ammine complexes are thermally unstable upon evacuation. Choi et al. [268] have suggested their presence in Cu-mordenite catalysts after tests at 250°C in the $NO + NH_3 + O_2$ reaction, but in situ evidence was not given. In Cu/ZSM-5 [302] copper dimers coordinating ammonia and NO_2 have been instead suggested.

Coordinated ammonia changes the chemisorption characteristics of the copper ion. Huang [24] has observed that oxidation by oxygen of a Cu^+-Y zeolite is much faster in the presence of ammonia. Adsorption of carbon monoxide may result in the displacement of one ammonia molecule, but the CO vibration frequency is different than in the complete absence of ammonia, because the higher electron density of copper due to ammonia ligands increases the amount of π back-bonding to CO [317,318].

NO coordinates in an analogous way to carbon monoxide. Tri- and tetra-ammine copper complexes with a NO molecule as a ligand were proposed by Williamson and Lunsford [38] on the basis of IR and ESR data. X-ray absorption experiments [268] indicate, even though they do not constitute proof, the existence of these complexes also in Cu-zeolites after catalytic tests in the $NH_3 + NO + O_2$ reaction.

Oxygen greatly promotes the NO conversion over Cu-Na/Y for temperatures above 120°C [37], but no spectroscopic evidence was reported to demonstrate the possible change or lack of change in the copper–ammine–mononitrosyl complex. Mizumoto et al. [36,37] have proposed the formation of a $Cu^{2+}(NH_3)_m(NO_2)$ complex, whereas Lunsford and co-workers [38,39] have suggested that this complex does not form or in any case does not play a role in the reduction of NO. Definitive conclusions from these studies on the role of oxygen co-adsorption, however, cannot be derived.

The formation of these complexes is influenced by various other co-adsorbents, but the effect depends on reaction conditions. Water vapour considerably inhibits conversion of NO due to both competitive adsorption on copper ions [37] and an induced reconstruction of copper coordination. The two effects depend differently on temperature. Recent data [301] on the effect of the pretreatment of Cu-Y zeolites in the reduction of NO with ammonia lead to analogous conclusions. SO_2 inhibition also depends on the reaction temperature and is less above 300°C, due to the volatilization of the ammonium sulphate or bisulphate formed [119,319,320]. In the presence of SO_2 other species may also form such as a copper species surrounded by various sulphate anions [268] and, due to zeolite dealumination, a Cu–Al sulphate [37]. The former was also proposed by Hamada et al. [195] to be present in SO_2-deactivated Cu/ZSM-5 catalysts for decomposition of NO. Iwamoto et al. [321] noted, however, that the catalytic activity of Cu/ZSM-5 is inhibited slightly by SO_2 during the reduction of NO with propene/O_2, but inhibited considerably during NO decomposition. Therefore, the two reactions are influenced differently by the change in the coordination environment of copper, showing the limitation of possible generalizations.

The relationship between modification of copper chemisorption characteristics in the presence of co-adsorbate forming stable species, however, may be more complex. In Section 3.3.2 it was shown that in the presence of water or ammonia in the gas phase, copper ions may relocate to more open positions in the zeolite where they are more prone to coordinating molecules [209,261–265,317,322]. The formation of more stable complexes such as in the case of sulphate probably may limit this relocalization process. Therefore, not only the electronic characteristics of the coordinating copper ion may be influenced by the formation of these complexes, but also its mobility and possibility of coordination with multiple molecules. On the other hand, the easier mobility of the copper ions inside the zeolite should have a negative influence on the long term stability. Various data show deactivation of Cu/ZSM-5 during reaction [323,324] and the possibility to form large CuO crystallites [213,214]. An inhibition of copper mobility therefore may have a negative effect in short term experiments, but may be positive in longer term experiments limiting the growth of copper particles. In copper-on-alumina catalysts for the simultaneous removal of SO_2 and NO_x, for example, it has been shown that surface sulphate species on alumina limit the rate of copper sintering, maintaining the catalyst in a highly dispersed state even after severe reaction conditions [84,86].

The study of the influence of co-adsorbate on the deactivation behaviour, however, is very complicated due to the presence of several simultaneous and interrelated effects. Water, for example, causes zeolite dealumination due to a steaming effect [325] and destruction of the zeolite framework due to the growth of CuO crystallites [213,214]. The presence of water also leads to modifications in the chemisorption of the reagents and may have an effect on the reoxidation of reduced copper [157,265] and the increase in chemically adsorbed oxygen [326]. Catalytic studies alone therefore do not make it possible to discriminate between the various factors, even when coupled with an extensive characterization of the deactivated catalysts. In situ studies with simultaneous recording of the change in catalytic activity are necessary not only for an understanding of the reaction mechanism, but also of the deactivation mechanism. Especially when complex feedstocks are used such as in direct tests of the performances of metal exchanged zeolites in the treatment of real motor vehicle emissions, the complexity of the phenomena prevent detailed conclusions on the deactivation phenomena. For example, CO is a significant component of vehicle emissions, but has multiple effects due to the fact that it: (i) participates in the mechanism of NO reaction, (ii) changes the nature of the copper complexes, (iii) displaces adsorbed NO [327], and (iv) may form volatile transition metal–carbonyl complexes. These effects overlap those previously mentioned, but it is reasonable to expect synergetic negative effects in several cases, which in some cases can lead to very rapid deactivation [328].

Little information can be found in the literature regarding the effect of co-adsorption phenomena on the surface reactivity of copper-based catalysts for nitrogen oxides transformation. There are several possibilities to be considered, such as (i) enhanced chemisorption in the presence of co-adsorbates (for example, the previously cited higher O_2 chemisorption of copper–ammine complexes with respect to copper ions in Cu-Y [24]), (ii) co-adsorbate induced surface reconstruction (for example, the change in coordination and zeolite localization of copper ions during reaction — see above), and (iii) the specific depressing of side reactions (water assists the partial oxidation of propene due to the inhibition of side reaction of oligomerization [265] and the inhibition of the rate of ammonia oxidation to N_2 over copper-on-alumina upon NO chemisorption [137]). In zeolites, other additional co-adsorption related effects may also play a role, such as the kinetic antagonism suggested by Cho [329] to explain the inhibition by C_2H_4 on the diffusion–adsorption of C_3H_6 during NO reduction tests by hydrocarbons/O_2 over Cu/ZSM-5, in contrast to the behaviour observed in the absence of ethylene. Much more attention should be given to the study and understanding of co-adsorption phenomena, especially under reaction conditions close to those of the catalytic tests.

5. Transformations of nitrogen oxides with enzymes

The bioinorganic chemistry of copper plays an essential role in several human life activities and in the global nitrogen cycle [330–335]. Denitrification, the dissimilatory transformation of nitrate or nitrite to gaseous products (N_2O and/or N_2), is a central process in the biological nitrogen cycle responsible for depleting the soil of nitrogen necessary for plant growth and for production of N_2O. Important enzymes involved in denitrification include nitrite and nitrous reductases that have copper in their active sites [109–112,336–351] and their analogies with solid copper-based catalysts have been suggested recently [109].

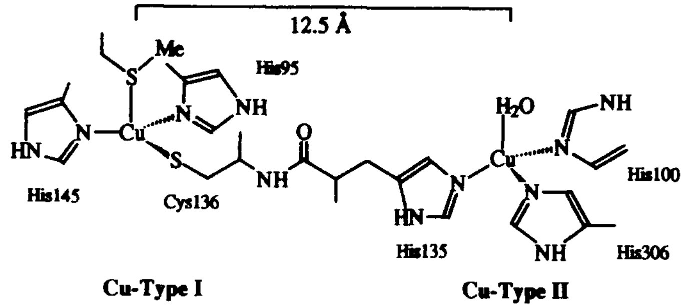
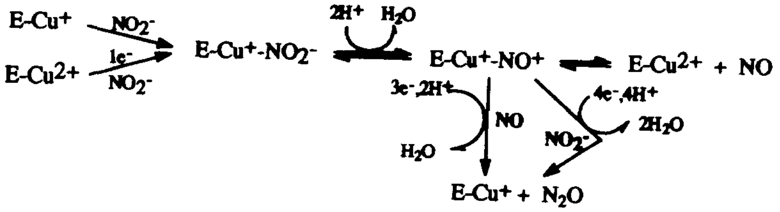


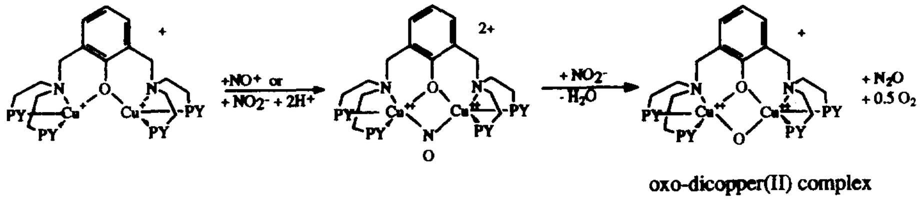
Fig. 9. Schematic representation of copper sites in nitrite reductase from *Achromobacter cyclastes* [336].

Copper enzymes have been isolated in several denitrifying bacteria (see Suzuki et al. [337] and Libby and Averill [344] and references therein). However, the copper enzyme nitrite reductase from *Achromobacter cycloclastes* is studied in more detail [112,336,337,343,344,347,351]. A schematic representation of the copper sites in the enzyme is shown in Fig. 9. The enzyme contains two well separated copper ions (Cu···Cu = 12.5 Å), one copper being bound to ligands typical for type 1 centres (blue copper with a trigonal–planar ligand set) and the other (type 2 centre, non-blue copper with the four coordinated ligands in a tetragonal array) being coordinated by three histidines and a labile aquo moiety. The two copper ions are connected by a His–Cys (Histidine–Cysteine) sequence, where His is coordinated to the type 2 Cu and Cys to the type 1 Cu. The environment of the type 1 Cu is found in several other copper containing electron-transfer proteins, whereas more debate exists about the presence of type 2 Cu in the various copper enzymes [344]. The two types of copper sites have distinct spectroscopic features. For example, an EPR hyperfine splitting with small $A_{\parallel}$ values of $30–70 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ defining type 1 Cu and larger $A_{\parallel}$ values of $130–180 \cdot 10^{-4}\ \mathrm{cm}^{-1}$ defining type 2 Cu [347]. The two copper sites play different roles in the mechanism of nitrite reduction. Type 1 Cu has the function of transferring electrons to type 2 Cu, whereas type 2 Cu is responsible for the binding and reduction of nitrite to NO or N_2O [336,340,344,352].

Shown in Scheme 2 is the mechanism of reduction of nitrite at type 2 Cu sites in nitrite reductase from *Achromobacter cycloclastes* [109,343,344]. The copper–nitrite complex formed either from reduced or oxidized forms of the enzyme [348] is transformed to a labile cuprous–nitrosyl complex (Cu^+–NO^+) [109,112,337,343] by direct reaction or in the presence of $2H^+$ and an electron,



Scheme 2. Mechanism of reduction of nitrite anions on type II copper sites in nitrite reductase from *Achromobacter cyclastes* [109].



Scheme 3. Mechanism of reduction of nitrite in a biomimetic di-copper complex [345].

the latter case for the oxidized enzyme. The copper–nitrosyl intermediate is the key compound of the reaction, but its direct characterization in the enzyme is difficult. Several studies have been done to synthesize mimetic compounds of the enzyme [110] or of the copper–mononitrosyl intermediate [109,349] and compounds that mimic some steps in the reaction pathway [345]. The copper–mononitrosyl intermediate may also form directly by reaction of NO with the oxidized form of type 2 Cu (Cu^{2+}), besides that through reduction of nitrite. This double pathway of formation explains the presence of a 'NO-rebound mechanism' [343], i.e., that the reaction of the enzyme with nitrite in the presence of NO increases the N-pairing reaction (N_2O formation), whereas the rapid removal of NO (reduction product of nitrite) avoids the production of N_2O. Isotopic experiments with $^{15}NO_2^-$ in the presence of ^{14}NO clearly demonstrate the above mechanism [343]. The copper–mononitrosyl intermediate may thus decompose or react with a second NO or $(NO_2)^-$ molecule to give the product of N-pairing (N_2O). The role of the second copper site (type 1) is to shuttle electrons to type 2 Cu via a dipeptide bridge during catalysis [353,354].

These results indicate some main concepts which may be relevant for an understanding of the catalytic behaviour of copper sites on solid surfaces:

(a) The intermediate in the formation of the product of N-pairing (N_2O) is a Cu^+–NO^+ complex which may form either by reaction of NO with Cu^{2+} or by reduction of a Cu^+–$(NO_2)^-$ adduct.

(b) Attack of a second NO or nitrite molecule (especially the latter [343]) on the partially positive mononitrosyl intermediate yields the product of N-pairing (N_2O), whereas in the absence of rapid reaction with these other molecules, the intermediate complex decomposes. The mechanism of reaction of a metal–nitrosyl compound with nitrite has been shown to occur in biomimetic copper complexes [345] that also mediate N–N coupling reactions starting both with nitrite or NO. In the latter case Paul and Karlin [345] have suggested an alternative possible pathway via a dinitrosyl intermediate.

(c) A cooperative mechanism occurs between two copper sites, the first with the function of nitrite binding and reduction and the second with the function of shuttling electrons to the first. Apart from the electron transfer, the nitrite reduction occurs on a single copper ion. Oxygen bridged dinuclear copper complexes have also been shown to reduce nitrite (Scheme 3). The dicopper(I) complex reacts with a nitrosonium cation (NO^+) or a nitrite to give a stable $(Cu^{II})_2$–NO^- complex that reacts with another nitrite to give N_2O and an oxo-dicopper(II) complex. A significant difference with respect to the mechanism on a single copper site (Scheme 2) is that Cu^{2+} ions rather than H^+ help drive the oxo-transfer, trapping O^{2-} and producing Cu–O–Cu complexes. The reaction of the dicopper(II) complex with NO, on the other hand, gives directly the oxo-dicopper complex and N_2O, probably via a $Cu^{II}–(NO)_2–Cu^{II}$ dinitrosyl intermediate [345]. The reaction of $(NO_2)^-$ with the $(Cu^{II})_2–NO^-$ complex generates $Cu^{II}–(N_2O_3)^{2-}–Cu^{II}$ or $(NO^-)–Cu^{II}...Cu^{II}–(NO_2)^-$ complexes depending on which species, NO^- or Cu^{II}, is present [345,355].

The ν_{NO} in the $(Cu^{II})_2–NO^-$ complex is found at 1536 cm^{-1} and at 1460 cm^{-1} in the dinitrosyl $Cu^{2+}–(NO^-)_2–Cu^{2+}$ complex [345] and therefore at considerably lower frequencies than in analogous species over copper ions in zeolites (see Section 4.1). In analogous mononuclear copper nitrosyl complexes [109,349] the ν_{NO} band is found at higher frequencies (about 1710–1720 cm^{-1}) depending on the coordination environment for copper, indicating that a considerable shift to lower frequencies is expected when NO coordinates as a bridging ligand on a binuclear copper site rather than on a single copper ion. The problem of NO coordination in mononuclear versus binuclear copper centres in solid copper-based catalysts, however, has not been analyzed in the literature, even though several authors have proposed the presence of such binuclear copper sites, oxygen bridged, in zeolite or supported catalysts (see Section 3).

The second step of N_2O reduction to N_2 in biological systems is made by a different type of enzyme, N_2O reductase, the terminal enzyme in a complete denitrification pathway. All N_2O reductases isolated to date are complex multicopper enzymes; those from *Pseudomonas stutzeri* and *Paracoccus denitrificans* are the most studied [111]. The native enzyme may be isolated in various forms and contains a maximum of eight copper ions per protein molecule. The high-activity form of N_2O reductase from *P. stutzeri* (purple; called N_2OR-I) [111,350] contains Cu_A-type sites [111] and is characterized by the presence of $Cu^{II}...Cu^{I}$ centres [356]. EPR and ENDOR data also indicate that at least one cysteine and one histidine are ligands of Cu_A and that substantial spin density is delocalized in the cysteine sulphur $[Cu^I–S^-]$ [357]. The role of the purple Cu_A site is not clear, but Riester et al. [350] have suggested that its function is to flow electrons to a second copper site (a Cu^{2+} site which interacts magnetically with Cu_A) binding the N_2O molecule, and determining the cleavage of the N–O bond.

Analogously to nitrite reductase (NiR) the role of binuclear copper sites is not that of determining a cooperative activation of the nitrogen oxide (for example, as a bridging ligand), but instead one copper has the function of binding the molecule and the second that of shuttling electrons to cause cleavage of the N–O bond. NO, however, has a different effect on the activity of the two NiR and N_2OR enzymes. In the first case, NO promotes nitrite reduction via a N-pairing pathway (N_2O formation, see the above discussion regarding the 'NO-rebound mechanism'), whereas in the second case NO inhibits the reduction of N_2O [350], probably coordinating at the Cu_A centre and inhibiting electron transfer. In both enzymes, CO inhibits the reaction, because it displaces coordinated NO [350] and reduces charge density at the copper site responsible for electron transfer [350]. NO or CO coordination to electron-transfer copper sites [Cu^I sites linked to a sulphur atom or a cysteine unit which stabilizes by resonance the charge on copper] reduces their electron-transfer activity due to backdonation to coordinated molecules. In the case of the N-pairing reaction, this negative effect on the rate of nitrite reduction due to NO coordination is compensated by the positive effect on the rate of the N-pairing reaction. NO increases the concentration of the labile copper–nitrosyl complex, the intermediate step to the formation of the active (NO^+)–Cu–$(NO_2)^-$ complex. In N_2O reductase on the other hand, only the negative effect of inhibition of the electron-transfer function is present, the same effect shown by CO coordination.

In conclusion, data on the copper enzyme activity in nitrite and nitrous oxide reduction indicate the role of multiple copper sites in the mechanism of transformation, but a two-function synergetic mechanism is involved rather than a cooperative mechanism. Copper–nitrosyl species form, but over Cu^{II} ions from NO and over both Cu^{II} and Cu^I from nitrite. Cu^{II} centres are also those suggested to be responsible for coordination of N_2O molecules, whereas a second copper centre (linked to a sulphur atom that stabilizes the charge on copper by resonance) has the function of shuttling electrons to the first copper site in order to cause cleavage of the N–O bond. The active copper complex responsible for the N-pairing reaction to N_2O has strong analogies with that suggested as being responsible for N_2 formation from NO over Cu-zeolites which involves coordination of both a nitrite anion and a nitrosonium cation at the same copper centre. The nitrosyl–copper complex, precursor of the active complex, may form via different reaction pathways, but is rather labile. Various coordinating molecules such as CO may displace NO inhibiting the reaction rate, but have the additional negative effect of coordination at copper sites responsible for the electron transfer function, thus reducing the ability of these copper sites to transfer the electrons necessary for cleavage of the N–O bond.

6. Relationship between copper species and activity in conversion of nitrogen oxides

6.1. *Synergetic cooperation between active sites in the direct decomposition of NO*

It is widely accepted that copper ion-exchanged MFI zeolites show enhanced catalytic properties in the decomposition of NO as compared to other copper-zeolites and copper-supported oxides [9–12,44,48]. However, in zeolites like faujasite and mordenite there is a partial localization of copper ions in cavities with restricted access to gaseous reactants (see Section 3.3.2), and usually these samples were utilized with a SiO_2/Al_2O_3 ratio considerably lower than that present in

Cu/ZSM-5 zeolites. The specific activity per copper ion depends on the SiO_2/Al_2O_3 ratio, notwithstanding some contrasting results in the literature [44,358]. Therefore, is necessary to re-evaluate the performances of samples (i) with different zeolite structure, but the same SiO_2/Al_2O_3 ratio (using, for example, dealuminated faujasite and mordenite and taking care to avoid the presence of extralattice Al), (ii) with the same crystallite size and defect characteristics (factors usually not taken into account), and (iii) with the same number of copper ions at accessible sites. Tests also should be extended to Cu-zeolites with analogous pore sizes, but different structural characteristics, and to other Cu-zeolites with the MFI structure, but having the Al substituted isomorphically with other trivalent elements such as B^{3+}, In^{3+} and Ga^{3+} that do not vary the total number of Brønsted sites, but influence their acid strength. Some attempts in the literature follow this direction [215], but data are not enough for conclusive evidence on the role of the structure of zeolite in the modification of the reactivity characteristics of copper ions.

Unclear is also the relationship between copper species and reactivity in NO decomposition. Larsen et al. [359] found by ESR the presence of two kinds of Cu^{2+} ions with square-pyramidal and square-planar coordination, confirming older results of Sass and Kevan [360]. Similar observations were made by Wichterlova and co-workers [201–204] using photoluminescence spectroscopy combined with ESR and IR investigations. These authors also indicate that only planar copper ions in close vicinity to one Al framework are active in NO decomposition (see also Section 3.3.1 and Section 4.1). Other authors [98,147,246] assigned instead the same species detected by Wichterlova and co-workers [201–204] to $Cu^{+}\cdots Cu^{+}$ dimers and suggested that the activity in NO decomposition is connected to the presence of these sites. Analogous results were indicated by Lei et al. [193] on the basis of IR and ESR studies.

Coordination characteristics of copper ions may be modified also by adding co-cations. Several attempts in this direction have been made by adding other co-cations such as Mg^{2+}, Ce^{3+}, La^{3+}, Co^{3+}, Ni^{2+} to Cu-zeolites [361–364]. It has been suggested that the role of Mg^{2+} is to stabilize copper ions in ZSM-5 by occupying hidden sites [362,363], even though it is not clear what these hidden sites are in ZSM-5. Rare earth co-cations behave in a different way. They promote copper activity, but it is not clear through which type of mechanism [362]. Probably, the mechanism of these co-cations is more complex. Factors such as (i) direct participation of the co-cation in the reaction mechanism (promoting some reaction steps such as electron or oxygen transfer from Ce^{3+} to Cu^{2+}, or stabilizing some reaction intermediates/products such as shifting nitrate from Cu^{2+} to Mg^{2+} because it is more stable on the latter), (ii) modification of the electrostatic field and surface potential within pores/cavities of the zeolite, (iii) change of local softness around copper ions, (iv) modification of copper coordination and/or mobility and (v) change in diffusional properties of NO, etc., cannot be reasonably excluded. The identification of the main effect is therefore very difficult, but clearly the absence of a more general theory prevents a better understanding.

The same reasoning applies to very recent data on the decomposition of NO on Cu/ZSM-5 in which copper was introduced both at exchangeable sites and during the hydrothermal synthesis of the zeolite itself [365]. Better catalytic results were claimed for samples where copper was introduced both at the synthesis stage and later by ion exchange, although the low maximum NO conversion (about 50%) and the limited differences in activity between the various samples do not allow these results to be considered conclusive. The authors suggested that in the more active sample a higher number of active sites are present, but did not explain the reasons for this. Copper cannot be introduced directly into the zeolite framework for structural reasons, but rather only at defect sites (hydroxyl nests). The presence of copper during the template hydrothermal synthesis of zeolite reasonably modifies crystallization, creating more defective crystallites as well as influencing crystallite size. This problem was not recognized by Eränen et al. [365] and thus it is not possible to conclude on the basis of their data that specific more active sites were created by their preparation method. Furthermore, Kubelkova et al. [366] have shown various additional possible effects which may influence copper properties in Cu-zeolites prepared by adding copper directly at the zeolite synthesis stage. The absence of systematic and careful studies on the problem of the relationship between the nature of the copper sites and activity in NO decomposition thus prevents clear conclusions to be drawn on this problem from literature data.

The exchange level of copper-zeolite is another important factor which determines the performance in NO decomposition. There is general agreement in the literature that better performances are obtained with 'overexchanged' Cu/ZSM-5 samples [9–12,44–48]. The exchange level is considered 'stoichiometric' when $Cu/Al = 0.5$, i.e., when one Cu^{2+} ion has replaced two Na^{+} ions. With increasing exchange level, a typical 'S-shaped' curve of activity is found [44,45]. Hall and co-workers [192,237] found that not only activity, but also the turnover frequency (NO molecules converted to N_2 per Cu ion per second; TOF) increases up to an exchange level of about 130–140% and then remains constant. Their data were obtained under pseudo-differential reactor conditions, but using data up to a conversion of 20% for which the differential approximation is no longer valid. Furthermore, experimental error in these conditions is significantly high. Campa et al. [367] and Moretti [368] found comparable results, even though their data, also obtained under pseudo-differential conditions, showed a roughly 100-fold increase in turnover frequency when the exchange with copper increases from 80 to 100% and then remained constant. Valyon and Hall [192], on the other hand, have reported a nearly linear increase from 20% to 140% in TOF which passes from about $0.1 \cdot 10^{-2}$ to $1.2 \cdot 10^{-2}$. Centi et al. [239,240], in contrast, studied the change in the specific rate of NO depletion per mole of Cu at high conversion (40–80% range). They determined the specific rate constant using the appropriate rate equation (determined in specific kinetic tests) and integral reactor model. This procedure makes it possible to determine more correctly the value of specific rate constants. Their results [240] showed that the specific rate constant passes through a maximum for an exchange level of about 120–140%; the increase in the rate constant is about 10-fold with respect to values for samples with an exchange level below 30%. Analogous results (maximum in the rate of NO depletion) have been reported by Iwamoto and Mizuno [9], but in the presence of C_2H_4/O_2.

Notwithstanding some differences, all authors thus agree that the specific rate of reaction per copper site is higher for samples near or above the 100% exchange level than in samples with exchange levels below 50%. The interpretation of this effect, however, is questionable, as discussed above about the relationship between nature of copper species and activity.

Hall et al. [19,192] considered the problem of higher activity of overexchanged samples from a different point of view. They suggested the formation of species containing extra-lattice oxygen (ELO). ELO originates from the preparation of the catalyst and is closely associated with the Cu^{2+} ions introduced by base exchange [192,369]. ELO is not necessarily held as bridged oxygen between two cations (Cu^{2+}–O–Cu^{2+}), but does sit somewhere on the lattice. Transition metal cations simply act as source or sinks for electrons [277]. This conclusion is supported by isotopic trace element experiments [247,251] which suggest that the activity cannot be assigned to identifiable ELO-copper ion ensembles, but is rather a collective property of the copper-zeolite itself. ELO desorbs spontaneously as O_2 above 400°C upon evacuation [237] and thus can be responsible for reduction of the copper. On the other hand, IR data [277] indicate that ELO is responsible for oxidation of NO to NO_2 and higher oxides. The role of ELO is thus not clearly defined, but Valyon and Hall [251] have proposed (i) a function of furnishing electrons to the copper site where NO is chemisorbed, in order to break the N–O bond and provide a path to N–N bond formation, and (ii) a function of allowing a faster pathway for O_2 desorption. A kinetic model based on a transformation occurring on a single copper ion, but with a second site synergically cooperates with the first in the rate determining step fitted correctly the data from low to high conversions [239,240] and explain the maximum in the specific activity as a function of exchange level and reaction temperature found experimentally.

Co-cations such as Ce^{3+} may also promote the electron transfer leading to the decomposition of NO over Cu/ZSM-5 (see above). Recently Klier et al. [370] have reported an analogous effect showing that the decomposition of NO over Co/A zeolite may be considerably promoted by addition of Ce^{3+} as a co-cation. They also suggested a role of Co as a NO binder and of Ce^{3+} as a redox element to promote dissociation of NO.

Less data exist, on the contrary, on the role of copper species in the decomposition of NO over cuprate catalysts [243,286,371–374]. Lin et al. [286] have suggested that on $YBa_2Cu_3O_7$ each Cu atom in the CuO plane (the unit cell is composed of a series of planes stacked in the sequence –CuO/BaO/CuO_2/Y/CuO_2/BaO–) has an oxygen vacancy which is also coordinated to the Ba atom in the BaO plane. NO dissociatively chemisorbs on this oxygen vacancy (□) forming a nitride ion bonded to both copper and barium atoms:

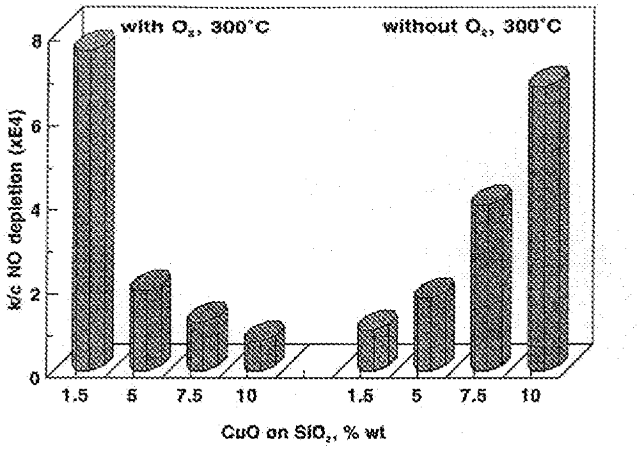


Fig. 10. Specific rate of NO depletion per mole of Cu (l h^{-1} mol Cu^{-1}) at 300°C in the presence or absence of O_2 over copper-on-silica samples with increasing copper loading [42].

ion [36]. The amide-like species reacts with coordinated NO to give $N_2 + H_2O$ and Cu^+, reoxidized by NO itself (forming a copper–amino–nitrate complex and N_2O) or by oxygen (especially at temperatures above the maximum in NO + NH_3 activity at about 120°C) [36,37]. Cu^+ may also coordinate ammonia and NO (see Section 4.3), but the complexes formed are more labile and the Cu^+ itself is less prone to reduction than Cu^{2+}. Oxygen, however, may have a further effect, that of reoxidizing Cu^+ only at the end of the catalytic cycle. In fact, the Cu^+–NH_2 adduct is rather labile as shown by quantum-mechanical calculations (only a weak dative bond may form [383]), whereas Cu^{2+}–NH_2 is a more stable species since back-donation and formation of a covalent bond is possible. The presence of oxygen or of an electron-donor centre thus stabilizes the intermediates, favouring the pathway via the nitrosoamide intermediate with respect to other competitive pathways (amide complex decomposition, further H abstraction from amide, etc.). A reaction mechanism via a nitroamine intermediate has been proposed by Busca [384] to occur over copper-on-titania catalysts, in analogy to comparable IR results obtained over vanadium-on-titania catalysts [385]. The above chemistry explains recent results of Wang and Hwang [301] on the effect of the pretreatment on the activity of Cu-Y zeolite and the kinetic behaviour observed by Komatsu et al. [302] over Cu/ZSM-5.

Over metallic copper, the mechanism should be different for three main reasons: (i) the copper–ammine complex may not form, (ii) dissociative chemisorption of ammonia and progressive further H-abstraction is faster and (iii) dissociative chemisorption of NO is also faster. The main pathway thus occurs through dissociatively chemisorbed N species and not nitrosoamide-like species (or a copper template reaction between NH_2 and NO). In agreement, isotopic labelled experiments with $^{14}NO + {}^{15}NH_3$ mixtures show an increase in the formation of unlabelled N_2 and N_2O molecules over metallic Cu with respect to CuO [32].

$$\mathrm{OBa\square CuO + NO \rightarrow 0.5\ OBaNCuO + 0.5\ OBaOCuO} \qquad (6.1)$$

The nitride species further reacts with NO forming a nitrito group:

$$\mathrm{OBaNCuO + NO \rightarrow OBaNCuONO} \qquad (6.2)$$

The nitrito complex may undergo further transformations leading to the formation also of nitrate, N_2 and N_2O, but details of the mechanism are not given. The above mechanism also suggests that the catalyst rapidly deactivates. The analogy between this catalyst and the BaO–CuO system proposed by Arai and co-workers [106,107] as a new catalyst able to adsorb NO at low temperature forming stable nitrates which then decompose at higher temperature should be noted.

In a study on La_2CuO_4-based catalysts Yasuda et al. [243,374] suggested, on the other hand, that NO adsorbed on Cu^{2+} ions forms either Cu^{+}–NO^{+} or Cu^{3+}–NO^{-}, but especially the latter. Adsorption of NO on a second near-lying copper forms a second Cu^{3+}–NO^{-} complex which reacts with the first to form N_2 and starting $\square$–Cu^{2+}–$\square$–Cu^{2+}– site after O_2 desorption. Teraoka et al. [371] have suggested differently that over perovskite-type oxides NO decomposition occurs at a pair of adjacent oxide ion vacancies, reasonably implying rapid catalyst deactivation. Indeed, Halasz et al. [372,373] demonstrate that under stationary conditions the activity of these catalysts for NO decomposition is negligible and that their activity can be observed only under non-stationary conditions, reasonably due to surface vacancies. Very limited data also exist on the mechanism of decomposition of N_2O over these catalysts. Swamy and Christopher [121] have suggested the necessity of having a mixed-valence Cu^{2+}–Cu^{3+} multicenter for N_2O to have high activity, but the data do not allow generalization of the results.

6.2. Active sites in the reaction of NO with hydrocarbons and O_2

Analogously to the case of NO decomposition, the catalytic activity of Cu/ZSM-5 in the reduction of NO with hydrocarbons (ethylene) and O_2 has been reported to have a maximum for an exchange level of about 100–120% [8,375], suggesting a basic analogy between the active sites for this reaction and those for NO decomposition. However, the considerable influence of the nature and concentration of hydrocarbon on the reactivity of the zeolite (see below) makes this statement very questionable. Copper also promotes the catalytic activity of SiO_2–Al_2O_3 in the same reaction [376] with a maximum in NO reduction at an intermediate copper loading. The ethylene oxidation instead depends linearly on copper content (up to 13 wt.-% CuO at least). The authors suggest that the activity for the conversion into N_2 is related to the ability of the catalyst for oxidation of C_2H_4 by oxygen or NO and that too much oxidation ability results in low conversions in N_2. This indicates, on the other hand, that the scale of activity of a series of samples with increasing copper content is very dependent on the reaction conditions. In agreement, Chajar et al. [377] found that in the same series of homogeneous samples different relative orders of activity are found depending on the specific conditions chosen for the comparison. Jen et al. [378] also showed that the evaluation of a Cu/ZSM-5 catalyst for the reduction of NO with C_3H_6/O_2 should incorporate a broad range of conditions, and not only a single condition.

A further problem was evidenced in the work of Shpiro et al. [197,198]. On the basis of electron and X-ray absorption spectroscopies they concluded that three types of copper species are present (isolated copper species, small copper/oxygen aggregates, larger copper oxide-like aggregates). The turnover number for NO reduction increases with copper dispersion, but Shpiro et al. [197,198] also observed rapid interconversion of the various copper species during the catalytic reaction. They noted that the interconversion promotes the reaction, since an enhanced interaction of copper ions with the acidic centres of zeolite is possible. Bethke et al. [379] also suggested that the activity in NO reduction with propene/O_2 depends on copper dispersion over ZrO_2. These conclusions are in clear contrast with those of Jen et al. [378] and Wichterlova et al. [204] indicating that two different types of active species cooperate in the reaction. Kucherov et al. [257] instead proposed that square-pyramidal isolated cupric ions were the most active, but they studied samples in which other types of copper species were absent.

It may be concluded that various types of copper species are active in the NO reduction with hydrocarbons/O_2, although probably with a different turnover number, and possibly a synergic cooperation between the sites is required as suggested by Wichterlova et al. [204]. However, data are too limited for a conclusive statement. Furthermore, the interconversion between the copper species makes identification difficult of a specific copper species with higher activity in the reaction. Grunet et al. [258] observed, in fact, that the nature of copper species was dependent on the atmosphere and reaction temperature. The greater mobility of the copper species in the reaction with hydrocarbons/O_2, especially when compared with the higher stability observed in NO decomposition, is probably due to the formation of water as a reaction product and/or feed together with hydrocarbon/O_2 (Section 3.3.2). On the other hand, this mobility of the copper species is negative for the application of these samples. Armor and Farris [380] noted, in fact, the lower hydrothermal stability of Cu/ZSM-5 in comparison with Co/ZSM-5. Mabilon and Durand [381] noted the rapid deactivation of a Cu/mordenite sample under hydrothermal conditions, and Kharas et al. [213,214] the formation of large CuO particles (responsible for sample deactivation) during catalytic tests.

Therefore, contrary to the case of NO decomposition where a specific type of active copper sites is required, the conversion of NO with hydrocarbons/O_2 is much less sensitive to the nature of copper species, even though the modality of preparation plays an important role [377]. In agreement, it was observed that Cu-zeolites having considerably different activity in NO decomposition show nearly equivalent or much smaller differences in activity when O_2 and/or hydrocarbon are present [279].

6.3. Influence of copper species on the competitive reactions during NO reduction with NH_3/O_2

Literature data on the reduction of NO with ammonia have especially evidenced the formation of copper-ammine species (see Section 4.3) and their role in the mechanism of NO reduction. Oxygen, when present, was usually considered to play the role only of reoxidizing agent for reduced copper instead of NO, but not to have a direct role in the mechanism of NO reduction. A more critical analysis of the literature data, however, shows that this is not true and that both the reaction mechanism and the nature of the active copper species change, depending on the presence of oxygen.

Iizuka et al. [118] have compared the activities of samples prepared by supporting copper oxide over TiO_2 or ZrO_2 and have found that the latter samples were more active than TiO_2 samples in the $NO+NH_3$ reaction. They suggested that copper on zirconia reduces more easily to metallic copper than on titania where mainly Cu^+ forms. Metallic Cu shows a higher activity for the $NO+NH_3$ reaction, due to a faster NH_3 dissociative chemisorption [32,382], and thus copper-on-zirconia should be more active than copper-on-titania [118]. Otto and Shelef [32] also found an increase in the $NO+NH_3$ reaction rate upon reduction of CuO to metallic Cu. They suggested that progressive reduction occurs via Cu_2O intermediate formation, but probably the reduction mechanism over supported samples is more complex since phenomena of surface reconstruction during catalytic tests are also possible. The data reported in Fig. 3 on the oscillating catalytic activity of a copper-on-silica sample in the $NO+NH_3$ reaction clearly indicate this possibility.

When oxygen is present, however, Iizuka et al. [118] showed that the order of activity ($NO+NH_3/O_2$ reaction) is exactly the opposite of that found without oxygen ($NO+NH_3$ reaction). An analogous effect was reported by Centi et al. [42] in a study of the reactivity of a series of copper-on-silica samples with increasing copper content. Results are summarized in Fig. 10 which reports the change in the specific rate of NO depletion as a function of copper loading in $NO+NH_3$ and $NO+NH_3/O_2$ tests at the same temperature (300°C). As discussed in Section 3.1.2, the copper ions are stabilized by interaction with silica only to a small extent (up to 2–3 wt.-%), the remaining copper being present as microcrystallites of possibly defective CuO. The latter species reduces more easily to metallic Cu than the former [161] and taking into account the higher turnover frequency of metallic copper in the $NO+NH_3$ reaction it is thus reasonable that the specific activity increases with the copper loading. The question, however, is why the opposite effect is detected when oxygen is fed together with NO and NH_3.

Cu^{2+} ions, probably isolated, are active in the conversion of NO in the presence of ammonia [24,32,34–39,118,119]. Their reduction to Cu^+ leads to a decrease in activity, as shown for Cu partially exchanged Y zeolites [36]. The reduction of the copper ions is due to chemisorbed ammonia on Cu^{2+} which dissociates to give Cu^+-NH_2 and a Brønsted site which can react with ammonia to form an ammonium

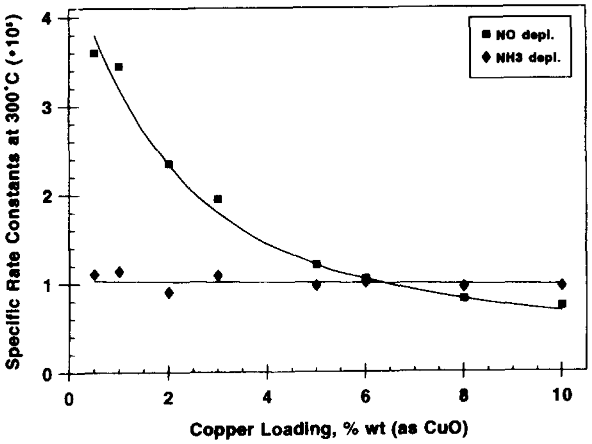


Fig. 11. Specific rate constant per mole of Cu ($l\ h^{-1}\ mol\ Cu^{-1}$) at 300°C for NO conversion in $NO+NH_3/O_2$ tests and for NH_3 conversion in NH_3+O_2 tests as a function of the copper loading [137].

The reduction of the copper ions thus leads to a change in the reaction mechanism of NO reduction to N_2 in the presence of NH_3 with a corresponding change in the surface reactivity driven by the reducibility of copper species. The latter aspect depends on the type of interaction with the oxide support or zeolite [118,160,161,386,387] (see also Section 3), explaining the observed increase in specific activity for the $NO+NH_3$ reaction with increasing copper loading (Fig. 10).

The opposite trend observed in the $NO+NH_3/O_2$ reaction (Fig. 10) may be interpreted in terms of higher activity of isolated Cu^{2+} ions interacting with silica in comparison with CuO microcrystallites. Similarly the presence of a maximum in activity as a function of copper content can be explained in Cu-exchanged natural zeolites [119], but not those obtained by Iizuka et al. [118] since the copper dispersion and species over zirconia and titania supports are comparable [279] (see also Section 3.1.3).

Recent data on the reactivity of copper-on-alumina samples for the $NO+NH_3/O_2$ reaction suggest a different model for the interpretation of results [137,305,388,389]. Reported in Fig. 11 is the dependence on copper loading of the specific rate of NO depletion per mole of copper in the $NO+NH_3/O_2$ reaction and of NH_3 depletion in the NH_3+O_2 reaction. The latter reaction is important, because the competitive reaction of direct ammonia oxidation to N_2 is always present, but becomes critical at higher temperatures where it is responsible for the decrease in NO conversion. The effect is not specific to copper catalysts, but more general and present also in V–TiO_2 catalysts [7]. In some catalysts such as Cu/ZSM-5, the effect is more limited, allowing the possibility of working in an extended temperature window (see Fig. 4). The data reported in Fig. 11 show that while the specific rate of NH_3 depletion in NH_3+O_2 tests is nearly independent of the copper loading, the specific rate of NO depletion decreased with increasing copper content of the catalyst. At the higher loadings, the reaction rate of ammonia oxidation is higher than that of NO depletion, even though ammonia is equimolecular fed with NO in the $NO+NH_3/O_2$ tests. Therefore, the rate of ammonia oxidation in the absence of NO is significantly higher than in its presence. The comparison of reactivity data with those of spectroscopic characterization of the samples with increasing copper loading on alumina and with IR data for NO, NH_3 and O_2 single and co-adsorption at various temperatures [137] indicates that the above reactivity phenomena can be attributed to the formation of nitrate species which block the reactivity of the copper sites and to the inhibition by NO of selective ammonia chemisorption on copper sites (see Section 7.3).

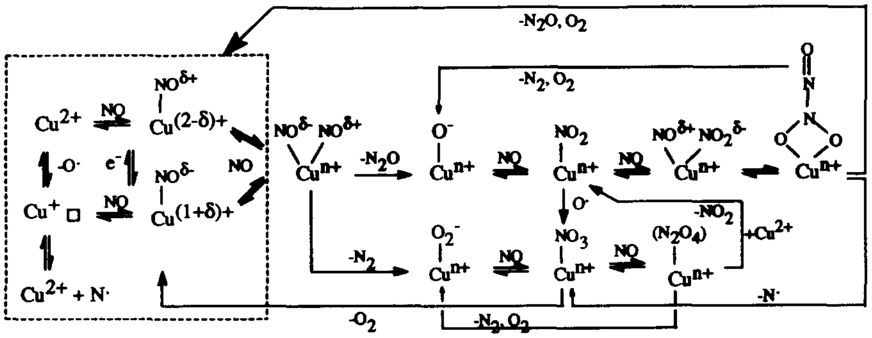
The interpretation is also supported by the results of non-stationary catalytic tests [305,389] which indicate that the main pathway for the reduction of NO to N_2 in the presence of NH_3/O_2 occurs via the intermediate formation of adsorbed NO_2. The role of NO_2 in the reaction mechanism of NO reduction with NH_3/O_2 over Cu–Ni/alumina catalysts was also shown by Blanco et al. [94], whereas Seiyama et al. [34–37] pointed out the formation of a copper–ammine–nitrite complex, but only when O_2 is absent. Recent kinetic data [302] also indicate the role of NO_2 adspecies in the mechanism of reaction. The results of transient catalytic tests [305] show, in addition, that the further oxidation of NO_2 to higher nitrogen oxides (presumably nitrate species) leads to deactivation of surface reactivity and to the formation of ammonium nitrate (intermediate to N_2O formation). Furthermore, transient experiments [305] have shown that a reduction mechanism via a nitrosoamide-like intermediate occurs under non-stationary conditions (depending on pretreatment), but is of secondary importance under stationary conditions where the mechanism via a copper–ammine–nitrite complex (or a NH_3NO_2 like species) predominates. This is related to the inhibition of dissociative chemisorption of ammonia and copper amide formation by nitrogen oxides adspecies. For this reason, the rate of direct ammonia oxidation to N_2 is inhibited especially in those catalysts, such as Cu/ZSM-5, which form stronger chemisorbed nitrosyl species. Dissociative chemisorption of ammonia, in fact, is the first step for its oxidation to N_2 in the presence of O_2 and stronger chemisorbed nitrosyl species inhibit this step.

Changing the copper loading and nature of the surface copper species (see also Section 3.1.1), thus changes the relative rates of these competitive pathways (dissociative chemisorption of ammonia to amide and further H-abstraction, reaction of ammonia with Brønsted sites to form ammonium ions, reaction of ammonia or its transformation products with O_2 to give N_2, NO reaction with amide-like copper species, NO oxidation to NO_2 and further to higher nitrogen oxides, reaction of these nitrogen oxide adspecies with ammonia adspecies, etc). The presence of oxygen also modifies the relative importance of all these surface reactions, as well as the valence state of copper. The effects are thus quite complex, but in general increasing the copper loading over the oxide support increases the rate of consecutive oxidation of intermediate NO_2 species with a double inhibition (reduction of the amount of this intermediate and formation of species such as nitrate which block the surface reactivity of the copper ions). This is the reason for the change in surface reactivity in the NO + NH_3/O_2 reaction, but not in the $NH_3 + O_2$ reaction (Fig. 11). Similar results regarding the partial inhibition of the reactivity of Cu/ZSM-5 catalysts in NO reduction with propane/O_2 due to the formation of copper nitrate species also were recently found [291,306].

7. Mechanism of reduction of NO to N_2

7.1. NO decomposition

The discussion of the relationship between copper species and activity of Cu/ZSM-5 in the decomposition of NO (Section 6.1) indicates that isolated copper ions inside the hexagonal or pentagonal oxygen rings facing ZSM-5 cavities and near to one Al framework atoms are probably responsible for the chemisorption of NO and for the N-pairing reaction, but the rate of reaction is controlled by a second near-lying site (probably multinuclear type copper oxide with low nuclearity or also a second co-cation) with an electron-transfer function. The latter function is necessary to efficiently modify the charge on the first copper site which then transfers charge to coordinating nitrogen oxide molecules via antibonding orbitals. This view of the nature of the active catalyst thus completely overcomes both the question of the role of isolated vs. multinuclear species (oxygen-bridged dicopper species or two near-lying copper ions) on the mechanism of NO decomposition and the question connected to the role of Cu^+ ions on the NO activation/transformation mechanism. Indeed, the valence state of copper (controlled, for example, by the spontaneous desorption of oxygen) is not important, but the cooperative synergic interaction between copper sites and the efficient electron transfer function between these sites are very important. Data on the chemisorption and transformation of NO adspecies (Section 4.1), furthermore, indicate that reduced copper may be active in transformation of NO to N_2, but the oxygen released remains bound as zeolite extralattice oxygen (ELO). This oxygen reacts faster with another NO molecule to form a copper–NO_2 like species than it is able to diffuse to another ELO site to desorb as O_2. Under transient conditions, thus, the direct N-pairing reaction between two chemisorbed NO molecules can significantly contribute to the overall rate of reaction together with another direct route involving dissociative NO chemisorption on reduced copper sites followed by surface migration and pairing of N. Under stationary conditions, in contrast, a third pathway prevails involving the N-pairing reaction between a nitrosyl (presumably partially positively charged) and a NO_2 molecule (presumably partially negatively charged). Both molecules coordinate at the same copper site (copper template reaction), otherwise the distance between copper sites is too far to allow an efficient orbital overlap. Furthermore, the two coordinated molecules must not have the same charge to avoid electrostatic repulsion. The $NO \cdot Cu \cdot NO_2$ intermediate rapidly rearranges to form a N_2O_3–copper species which is the main reaction intermediate to N_2 or N_2O



Scheme 4. Reaction pattern in the decomposition of NO over Cu/MFI.

formation under stationary conditions. The O-pairing reaction to O_2 occurs either simultaneously with the N-pairing reaction or in a second stage. In the latter case, a copper nitrate species forms, characterized by a slower rate of surface transformation which leads to a partial inhibition of the surface reactivity. Copper nitrate can decompose to a copper–mononitrosyl species and O_2 or further react with another NO molecule to form a (N_2O_4)–copper species. This species can either decompose forming N_2 and $2O_2$ or, in the presence of other copper sites, decompose to two Cu–NO_2 complexes. Summarized in Scheme 4 is this surface reaction network which may be proposed to take into account all experimental evidence reported in the literature.

7.2. *Influence of hydrocarbons and O_2 on the pathways of NO reduction*

Several studies have been published on the reaction mechanism of selective reduction of NO with hydrocarbons in the presence of excess oxygen. However, the data available do not allow an unequivocal reaction mechanism to be derived especially because of the absence of detailed data on the mechanism at a molecular level. Four main aspects of the reaction mechanism have been investigated and reported in the literature: (i) role of oxygen, (ii) role of hydrocarbon, (iii) role of acid sites and (iv) relationship between hydrocarbon oxidation and NO reduction.

7.2.1. *Role of oxygen and hydrocarbon*

Oxygen promotes both the conversion of NO and of hydrocarbon, but the conversion of NO passes through a maximum at a concentration of around 2%, whereas the conversion of hydrocarbon increases up to a limiting value which depends on the reaction temperature (Fig. 12). The data reported in Fig. 12 clearly show that the maximum in NO conversion is independent of reaction temperature and hydrocarbon conversion.

Several authors have indicated that the role of oxygen is the promotion of the oxidation of NO to NO_2 [293–300,325,390]. Burch and Scirè [300] pointed out that the problem should be correctly defined in terms of composition of oxidized nitrogen oxide adspecies, whereas most of the authors have instead analyzed the

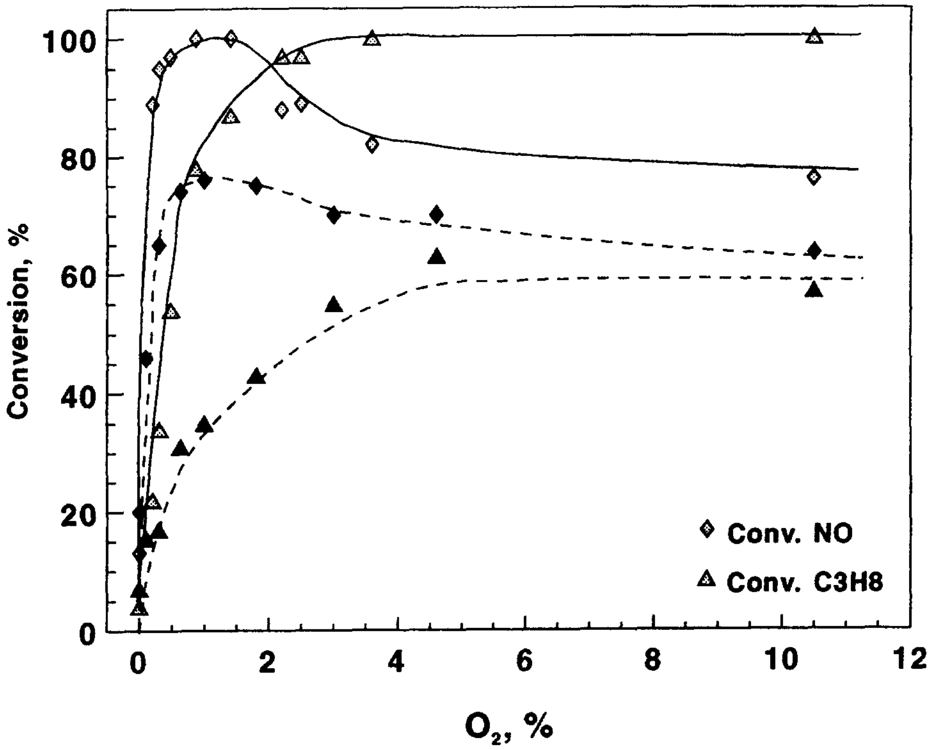


Fig. 12. Conversion of NO and propane at 300°C (dotted line) and 350°C (solid lines) as a function of the oxygen concentration over Cu/ZSM-5 [291].

relationship only with the gas phase equilibrium reaction between NO and NO_2. Nevertheless, in terms of both surface or gas phase equilibria between NO and NO_2, the data of Fig. 12 also found by several other authors [8,72,391–393] cannot be explained. In Section 4.2 it was shown that NO_2 is an intermediate in the oxidation of NO to higher nitrogen oxides and that the reduced reactivity of the final products (nitrate, in particular) leads to inhibition of the reactivity of the copper sites towards conversion of NO to its products of both oxidation and reduction. Reasonably also for NO reduction by hydrocarbons the maximum in NO conversion vs. oxygen concentration (Fig. 12) can be explained in terms of the role of oxygen in converting NO to higher nitrogen oxides such as N_2O_3 (intermediate in the mechanism of N_2 formation) and their further conversion to less reactive copper nitrate species. This hypothesis, however, requires further studies for confirmation.

Other authors have suggested different or additional roles for oxygen in the reaction mechanism, as well as other functions such as limiting zeolite dealumination [325] or increasing sticking probability of NO adsorption [296]: (i) oxygen eliminates the carbon deposits which poison the active sites [297–299,390,394,395] and (ii) O_2 avoids the reduction of Cu^{2+} to inactive metallic copper [297–299,391] or maintains together with hydrocarbons an optimal valence state (Cu^+) [312] and/or coordination of active copper sites [396–398].

When oxygen is in excess, no evidence has been reported of the formation of carbon deposits using alkanes, while coking occurs in the absence of oxygen [390]. With an alkene feed, on the contrary, carbon deposits form both in the presence and absence of oxygen, but the amounts formed are larger in the former case [394]. Oxygen thus certainly prevents coking of zeolite, but the question is whether this effect is relevant for the reaction mechanism of NO reduction and the rate of NO conversion or not. The first question is about the localization of carbon deposits. Ansell et al. [296] showed by TPD experiments that coke is not deposited on copper sites or in any case does not limit their reactivity. It is known, on the other hand, that alkene chemisorption occurs mainly, but not exclusively, over copper ions in Cu/ZSM-5 [399], due to the possibility of stronger bonding of the π-orbitals of alkene to d-orbitals of metal, whereas alkane only physisorbs on Cu/ZSM-5. It is also known that copper oxide readily activates alkenes such as propene, forming allyloxy intermediates [400]. The same intermediate may probably form when ELO species are present near to copper ions in Cu/ZSM-5. In agreement, the formation of traces of acrolein during propene conversion over Cu/ZSM-5 has been detected [296]. It is chemically not reasonable that alkene chemisorption over copper ion is responsible for the oligomerization process due to the absence of ionic or radical-like characteristics. It also is not reasonable that alkoxy or allyloxy species are intermediates in the oligomerization reaction. Reasonably alkene π-bonding at copper sites is an intermediate stage for oxygen insertion on the organic molecule (also see below), forming alkoxy, allyloxy or peroxo species, depending on the type of oxygen attack, that are intermediates to carbon oxides. Alkene oligomerization proceeds instead on other active zeolite sites (Brønsted or radical centres, the latter formed by oxygen interaction with acid or defect zeolite sites). Carbon deposits thus form at different sites than copper in ZSM-5, but when the amount of carbon deposit is too large, fouling of copper sites may also occur. The difference in the results of d'Itri and Sachtler [394,395] and Ansell et al. [296] is thus due to the different amounts of carbon deposits in the two cases.

A second question is whether oxygen prevents the formation of carbon residues or instead simply causes their removal by combustion. Due to its redox behaviour, copper ions in ZSM-5 can activate oxygen forming electrophilic O_2^--like species. Some IR spectroscopy evidence of their formation has also been reported [42]. It is known that electrophilic oxygen can be responsible for oxidative dehydrogenation of alkane to alkenes as well as for complete hydrocarbon combustion [401–404]. Oxygen may also promote alkane conversion over H-ZSM-5 [405], due to an enhanced rate of formation of alkenes connected with the formation of radical species by interaction of oxygen with Brønsted or defect zeolite sites [405,406]. Oxygen thus can promote alkane conversion to alkene over Cu/ZSM-5 with respect to an anaerobic carbocationic reaction mechanism only. Furthermore, the latter is inhibited in the presence of NO [390]. However, the rate of carbon deposit formation depends on the competition between combustion of activated hydrocarbon and its rate of oligomerization, the latter being considerably higher starting from the alkene than from the alkane. Furthermore, due to their strong chemisorption on copper ions, alkenes inhibit chemisorption and activation of oxygen [401,402]. With an alkane feed, notwithstanding the enhanced alkene formation by an oxide-hydrogenation mechanism, the rate of combustion of intermediates is far higher than that of oligomerization to heavier products, whereas carbon deposit formation is possible with an alkene feed due both to its higher rate of formation and inhibition of the rate of oxidation. The latter factor is clearly very dependent on the alkene concentration. In fact, with a feed of about 2000 ppm hydrocarbon and 5% oxygen, worse performances in NO conversion (lower conversion at the same temperature and lower maximum NO conversion to N_2) were found using propene instead of propane [291]. Comparable results have been reported by Petunchi et al. [390] in a comparative study of isobutane and propene. Using ten times lower hydrocarbon concentrations, on the contrary, a high activity is observed also with an alkene feed [8,9]. Gopalakrishnan et al. [76] also observed the difference in the order of activity between propene and propane for low and high hydrocarbon concentrations. The above discussion clarifies the reasons for these differences. The role of hydrocarbon concentration is thus of fundamental importance for a comparison of the results, but usually was not considered.

The role of oxygen primarily is in creating a faster surface pathway of oxidation to CO_x of surface hydrocarbon intermediates that is competitive to their oligomerization to higher hydrocarburic species. No evidence exists, on the other hand, that oxygen changes the nature of the carbon deposits due to the formation of products of partial oxidation (such as acrolein from propene) which then oligomerize. The reactivity towards consecutive oxidation of partially oxidized hydrocarbons is usually considerably greater than that of the hydrocarbon itself [407] and therefore it is not reasonable to expect that their contribution to the formation of carbon deposits will be significant. Oxygen, however, modifies the nature of the carbon deposits, because it enhances their oxidative dehydrogenation [408] and transformation to polycondensed aromatic species. No evidence, on the contrary, has been reported in the literature, even for the better documented case of removal of carbon deposits in zeolites by oxidative treatment [408], that O-containing species (ketonic groups in polycyclic carbon species, for example) form by oxygen interaction with carbon deposits. Reactivity data, however, show that the rate of combustion of carbon deposits is much lower than that of hydrocarbon combustion over Cu/ZSM-5 under conditions relevant for the NO reduction by hydrocarbons. O_2 thus reduces the formation of carbon deposits and induces their transformation from H-rich to H-poor deposits (graphitic-like coke, probably with a negligible or low oxygen content), but probably has a limited or negligible role in the oxidation of carbon deposits to CO_x.

7.2.2. Competitive surface phenomena and reaction pathways

The nature of surface adspecies has a considerable influence on the reactivity. This is shown in transient step-change experiments, where the concentration of NO or propane is rapidly increased (step-change) in the flow of other reagents (Fig. 13) results [291] are in agreement with this indication. Petunchi et al. [390] also indicated that their data "fairly conclusively eliminate the possibility that carbonaceous residues or coke deposited on the catalyst is the catalytically active surface", however in a subsequent paper [325] they indicated that the active sites are probably unpaired electrons on the carbon deposit. Obuchi et al. [412] originally proposed a correlation between carbonaceous radicals on γ-alumina and selective reduction of NO by organic compounds (propene and MTBE), but as pointed out above the reaction mechanism over Cu/ZSM-5 is probably different. Furthermore, no evidence for the formation of these radicals from propane has been found, nevertheless comparable or better results were obtained from propane than from propene over Cu/ZSM-5 (see above). Furthermore, Obuchi et al. [412] observed that NO conversion correlates well with the increase in the amount of carbon deposits and spin density of carbonaceous radicals over alumina, whereas d'Itri and Sachtler [394] demonstrated that over Cu/ZSM-5 the activity in NO conversion decreases with increasing carbon content in a range of carbon deposits comparable to that of Obuchi et al. [412].

Ansell et al. [296] have proposed the formation of 'long-lived' hydrocarbon species not better identified, and their role in the reduction of N_2. On the basis of key experiments obtained using the new temporal analysis of products (TAP) reactor for fast, time-resolved, catalytic studies, they observed that over Cu/ZSM-5 it is possible to form these species by interaction of C_3H_6/O_2 with the catalyst and then react these species with a pulse of NO to form N_2 and CO_2 (pump-probe experiments). The time-lag between formation of these species and their reaction with NO may be to up to 60 s without considerable change in N_2 formation, thus suggesting their carbon-like nature. These experiments, therefore, clearly show that the carbon-like residues can act as a reducing agent for NO. The main criticism, however, is that in these experiments it is not possible to really quantify the relevance of their proposed mechanism during the catalytic reaction.

Several other authors [8,9,72,392,393] have indicated the role of carbon deposits in the selective reduction of NO, but proposed the formation of generic $C_xH_y(O)$ species. A main observation in favour of this mechanism is that while oxygen promotes conversion of NO by propene over Cu/ZSM-5, oxygen inhibits conversion when propanol is fed instead of propene [393]. The very rapid dehydration of this alcohol to the corresponding alkene over zeolites at reaction temperatures much below those for catalytic tests in NO conversion is well known and therefore the demonstration is not very convincing. Furthermore, Montreuil and Shelef [393] have reported that more stable alcohols such as methanol, but that are known to give rise to heavier, polycondensed products over ZSM-5 in the same range of temperatures, are completely inactive for nitric oxide reduction.

A modification of the above hypothesis is that NO reacts with carbon deposits in the presence of oxygen forming $C_xH_y(O, N)$ surface species. Ukisu et al. [73,413,414], Iwamoto and co-workers [9–12,415] and Hayes et al. [416] have shown by infrared spectroscopy (bands at about 2260–2270 cm^{-1}) the formation

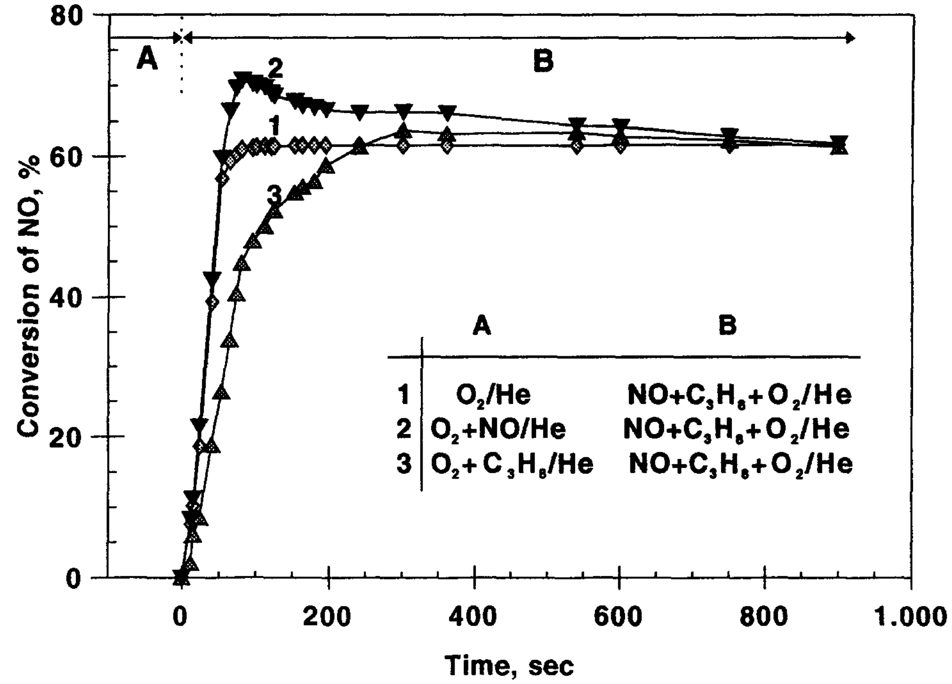


Fig. 13. Conversion of NO in transient catalytic step-change experiments at 300°C over Cu/ZSM-5: (1) change in NO + C_3H_8 concentration in a flow of O_2 in helium, (2) change in C_3H_8 concentration in a flow of NO + O_2 in helium and (3) change in NO concentration in a flow of C_3H_8 + O_2 in helium [291].

[291]. In these experiments the catalyst surface is equilibrated in terms of composition of adspecies of the reagents fed continuously. From the time response of catalyst reactivity when another reagent is added to the continuous feed (step-change in its concentration), the surface phenomena occurring up to the point that stationary state conditions are reached can be estimated. The data reported in Fig. 13 show that steady-state activity is quickly reached when NO and C_3H_8 are simultaneously fed over the catalyst equilibrated in a flow of O_2 in helium (curve 1 in Fig. 13). However, when the concentration of a single component is step-changed in a He flow of the other components, different transient responses for NO conversion are observed. NO conversion is initially higher upon addition of C_3H_8 to the NO + O_2/He flow (curve 2), while the conversion increases with a slower rate with respect to case 1 when NO only is added to the C_3H_8 + O_2/He flow (curve 3).

The addition of propane clearly promotes NO conversion, but the initial reactivity over the surface fully covered by nitrogen oxide (probably oxidized) adspecies is higher and later decreases due to competition of hydrocarbon chemisorption on the same sites. The activity curve towards NO conversion passes through a maximum. NO additions on the surface covered by hydrocarbon adspecies also leads to an obvious increase in NO conversion, but the attainment of steady-state activity is slower than when propane and NO are simultaneously added to the O_2/He feed. The effect is due to NO and propane competition on the same site. In agreement, kinetic data on the conversion of NO with propane/O_2 over Cu/ZSM-5 [291] show the presence of self-inhibition effects by NO and propane on their conversion. Petunchi et al. [390] also observed that hydrocarbon conversion and NO reduction occur on the same sites and that NO tends to exclude the hydrocarbon from these centres.

Since various types of catalysts, both zeolites and mixed oxides, are active in NO reduction with hydrocarbons, various reaction mechanisms are possible. Burch and Scirè [300] observed that two basic types of mechanisms are possible. One type of reaction mechanism involves decomposition of NO and removal of adsorbed oxygen by the hydrocarbon and occurs especially in the absence of oxygen. A second type of mechanism occurs in the presence of oxygen and involves instead the initial oxidation of adsorbed NO. The second mechanism is active with Cu/ZSM-5, while the first mechanism is active with Pt- and Rh-ZSM-5 [300].

Both redox and acid characteristics of the zeolite influence the pathways of reaction, as shown below. For this reason, care must be taken when doing extrapolations. Petunchi et al. [390], for example, argued that the redox chemistry of copper in Cu/ZSM-5 is not important mainly on the basis of the fact that acid oxides or zeolites are also active. Recent data [409], on the comparison of the activity of ZSM-5 and boralite zeolites in the Na-, H- and Cu-forms, have shown that while the number and acid strength of Brønsted sites play a role in the case of H-zeolites, no effect or a negative one was observed for completely copper ion-exchanged samples.

The data reported in Fig. 13 over Cu/ZSM-5 show that NO and hydrocarbons compete for chemisorption over the same copper site, but the relevance of this aspect with regard to the reaction mechanism is questionable. The various hypotheses on the reaction mechanism reported in the literature should be summarized briefly here before an answer to the above question is attempted. Two main classes of hypotheses have been suggested, based on the identification of copper sites as the reactive centre for NO reduction (due to a redox reaction or to the formation of a specific surface hydrocarbon–nitrogen oxides complex intermediate) or the identification of different active sites (carbon deposits and/or active sites or species formed on them) with the possible role of copper in catalyzing the NO to NO_2 reaction.

Burch et al. [300,312,410] have suggested a single redox reaction in which NO adsorption and decomposition on active (Cu^+) sites leads to the formation of gaseous nitrogen and adsorbed oxygen. This step is followed by the removal of the oxygen by the reducing agent, restoring the (reduced) active site. A slight modification of this hypothesis is that the hydrocarbon and oxygen maintain the active copper sites in an oxidation state or coordination suitable for direct NO decomposition [312,411]. Spectroscopic data on the characterization of the valence state of the copper during catalytic reaction (see Section 3.3.3), however, do not support this model.

Burch et al. [300,312,410] also indicated a negligible role of carbon deposits in the reaction mechanism. The data reported in Fig. 13 and other transient catalytic of isocyanate (–NCO) [413–415] or nitrile (–CN) [416] species during catalytic reaction. Hayes et al. [416] argued that both species absorb in this IR region and consequently cannot be distinguished. The isocyanate is expected to be rapidly hydrolysed to primary amine in the presence of water (a significant reaction product), whereas the stability of the species indicates that the assignment to an organic nitrile is more probable. However, these IR detectable species are observed only from propene and not from propane [414] notwithstanding the comparable activity or even better activity over Cu/ZSM-5 using propane. Therefore, two different reaction mechanisms operate in the NO reduction over Cu/ZSM-5 in the case of an alkane or alkene feed, or more likely, the reaction mechanism is the same and the detected organic isocyanate or nitrile species are spectator species or species indicative of a secondary reaction pathway. Witzel et al. [417] have suggested that the coupling of an isocyanate with NO forms a (NO·NCO) intermediate which thermally decomposes to $N_2 + CO_2$. On the other hand, isocyanate species may form by reaction of NO with CO. CO formation by hydrocarbon oxidation over Cu/ZSM-5 occurs especially at low temperatures and is higher from alkenes than from alkanes. Isocyanate species have been detected by IR spectroscopy by reaction of NO with CO over supported copper oxide [418] and the spectrum is nearly the same as that observed during NO reduction with propene/O_2 [413–416]. A new hypothesis on the reaction mechanism has been proposed recently based on IR in situ studies [419,420]: isonitrile species (Cu^+NC) form which in the presence of oxygen, propane and NO transform to ammonia or ammino species. The reaction mechanism of NO reduction with hydrocarbons, therefore, is closely related to that of reduction of NO by ammonia, at least in its final stage [420]. The authors, however, admitted that (i) various parallel and consecutive reactions exist, the relative importance of which depends on the reaction conditions, and (ii) it is not possible to indicate from their data if the reaction pathway proposed is the principal one [420].

Different pathways of reaction are thus possible, but quantitative data on their relative importance during the catalytic reaction are not available. Transient catalytic data, however, give useful indications about this problem. Reported in Fig. 14 are transient step-change experiments over a Cu/ZSM-5 catalyst pretreated with a propene + NO flow or propene + NO + O_2 flow before analyzing the time-response for NO conversion by adding NO in helium (cases a and b), NO + O_2 in helium (case c, pretreatment in the presence O_2) and NO + O_2 + C_3H_8 (case d, pretreatment in the presence of O_2). NO interaction with the pre-coked catalyst in a propene–NO flow (curve a) does not give rise to any conversion of NO, while an initial NO conversion is observed when pre-coking is made in the propene–NO–O_2 flow. Conversion is due mainly to NO chemisorption, since the N_2 yield is lower than the NO conversion (curve b', dotted line). Comparable results were obtained when the step change in NO concentration was made with or without O_2 (compare curve c and b), but considerably higher and constant activity is observed when the step change is made in the presence of propane together with NO + O_2 (curve d). These

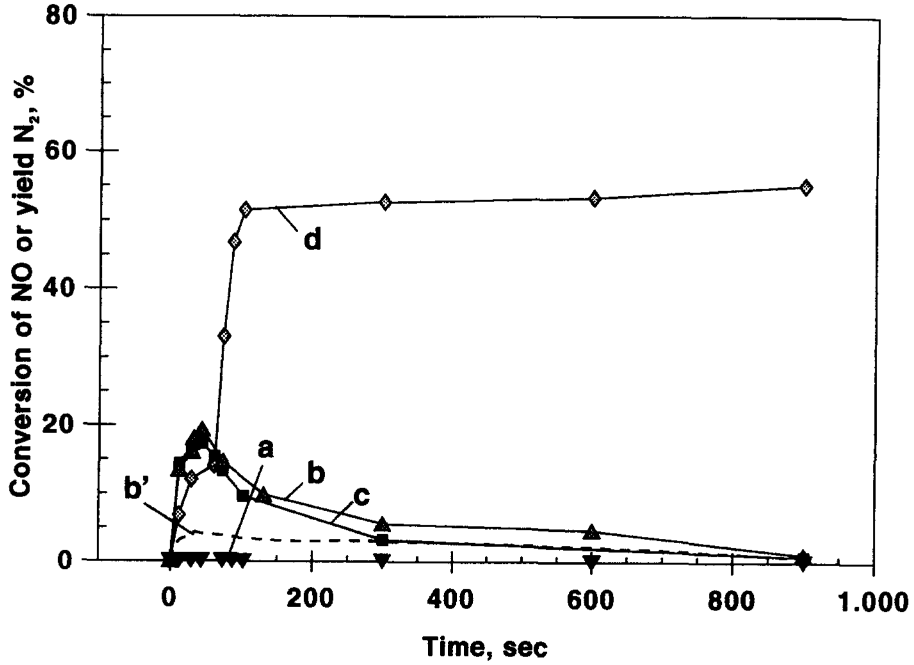
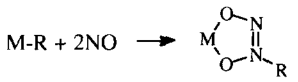


Fig. 14. Conversion of NO in transient catalytic step-change experiments at 300°C over Cu/ZSM-5 [430]. (a) and (b): NO step-change in a helium flow over a sample pretreated (15 min) in a flow of C_3H_6 + NO or C_3H_6 + NO + O_2, respectively. (c): NO + O_2 step-change in a flow of helium on a sample pretreated as for case b. (d): NO + C_3H_8 + O_2 step-change in a flow of helium for a sample pretreated as for case b. (b', *dotted line*): yield of N_2 during tests for curve b.

data thus indicate that NO may be reduced to N_2 by interaction with carbon deposits formed in the presence of both NO and O_2, in agreement with the hypothesis that C_xH_y(O, N) species may be responsible for the reduction of NO to N_2. However, when a hydrocarbon (propane) is present together with NO and O_2, a faster and more effective additional pathway is found (compare curve d with curves c and b in Fig. 14). Reasonably, this second pathway involves the formation of an intermediate species between the hydrocarbon, NO and possibly oxygen at the same copper sites.

Misono and co-workers [421–424] recently reported data obtained in a flow reactor IR cell on the catalytic reduction of NO by propene/O_2 over Ce/ZSM-5. They found the presence of a series of bands in the 1300–1750 cm^{-1} range assigned to organic nitro- (1558 cm^{-1}) and nitrito- (1658 cm^{-1}) compounds together with the bands at 2266 and 2241 cm^{-1} attributed to isocyanate species. They observed a poor correlation between activity in N_2 formation and intensity of the bands of nitrito and isocyanate species, while a good correlation with the intensity of the organic nitro compound was found. Adsorbed CH_3NO_2 was also shown to react readily with NO_2 to give N_2 and N_2O [423]. Tanaka et al. [424] proposed a similar intermediate in the reduction of NO by propene/O_2 over Pt–SiO_2. Shpiro et al. [198] proposed, mentioning unpublished results, that isolated copper ions activate propene forming a Cu allyl radical, while copper ions containing labile oxygen species (ELO) activate NO and hydrocarbon forming a nitrogen containing organo dimer species intermediate to the formation of N_2. Kharas [425] proposed instead the formation of a hyponitrite radical anion or dianion $[O\text{–}N{=}N\text{–}O]^{n-}$ ($n = 1, 2$) bound to a cupric site. This intermediate is that proposed as being responsible for NO decomposition. An analogous intermediate forms by reaction of 2 NO molecules with a metal alkyl species

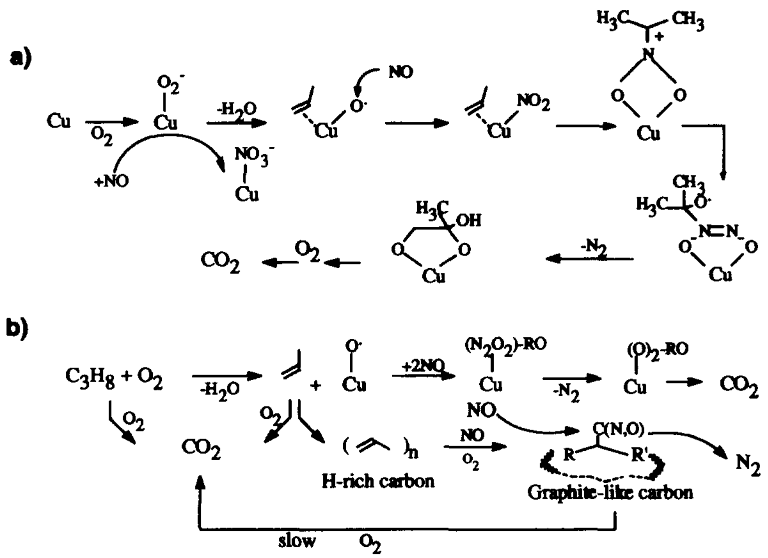


(7.1)

Kharas [425] has suggested, in particular, the formation of an oximate or *N*-nitroso-*N*-alkylhydroxylamate ligands on the basis of analogies with organometallic complexes able to promote nitric oxide reduction. In particular, d^{10} transition metals and copper have been shown to be able to give rise to complexes analogous to that shown above [426,427]. Crystallographic analysis of compounds containing the *N*-nitroso-*N*-alkylhydroxylaminato ligand indicate a short (1.27 Å) N–N distance consistent with double bond formation and a N–O distance (1.32 Å) larger than in NO (1.15 Å) [428], making these types of ligands conceptually attractive intermediates to N_2 formation from NO. Kharas [425] observed also that the above reaction is one member of a more general class of reactions where nucleophilic molecules reduce NO via an intermediate hyponitrite-type R–N(O)=N–O species. Recent IR evidences [429,430] about the mechanism of interaction of chemisorbed NO with propane and oxygen are in agreement with the suggestion of formation of a cyclic complex by reaction of nitrogen oxide adspecies and the hydrocarbon, even though no direct evidence was found about the presence of an hyponitrite species.

7.2.3. Model of the reaction mechanism

Data on the reaction mechanism for NO reduction with hydrocarbons in the presence of excess oxygen are very contradictory, limited and lack spectroscopic support. The data, however, do suggest, even though not conclusively, that two main pathways of reaction are possible, one at the copper sites involving an active complex between NO molecules and the hydrocarbon molecule, and a second at active centres located on the carbon-type deposits. The relative importance of the two pathways depends on the reaction conditions and nature of the catalyst. In the reduction of NO with propane/O_2 over Cu/ZSM-5 the former appears to be predominant, even though it is not exclusive (see Fig. 14). Scheme 5 (part b) summarizes these two competitive pathways and the main routes of carbon oxides formation. In part (a) of Scheme 5, the speculative reaction mechanism proposed for the formation of N_2 and CO_2 from NO and propane at the copper sites in Cu/ZSM-5 is reported. The proposed mechanism is in agreement with several of the observations reported above, such as (i) the inhibition of NO on the conversion of hydrocarbon, (ii) the analogies in the reaction mechanism with those of NO decomposition and NO conversion with O_2 in the absence of reductants, (iii) the paral-



Scheme 5. Working model for the reaction mechanism of NO reduction in the presence of propane/O_2 over Cu/MFI: (a) reaction pathway at isolated copper sites; (b) overall reaction network schematically showing the competitive reaction pathways at isolated copper sites and over polycondensed carbonaceous species and the main pathways of formation of carbon oxides.

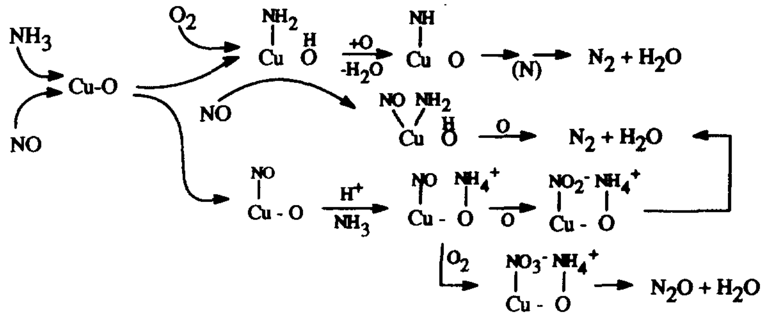
lelism between oxidation of hydrocarbon and NO conversion, (iv) some of the observed spectroscopic features, (v) the indication of the formation of an organonitrate or organo-hyponitrite intermediate, and (vi) the formation of carboxylate-type species as intermediates for carbon oxides. However, clearly the written mechanism must be considered only as a working model to be verified and improved on the basis of more detailed spectroscopic and reactivity studies. The basic difference in the proposed mechanism with respect to the 'Microscopic Sequential Reaction Mechanism' indicated by Inui and co-workers [411,431] should be noted, notwithstanding the several analogies shown by the two approaches to the microkinetics of reaction.

7.3. Surface transformations in the presence of NH_3 or CO

The mechanism of reduction of NO over copper-zeolites, but in the absence of oxygen, has been studied in detail by Seiyama and co-workers [34–37] and Lunsford and co-workers [38,39]. Several aspects of their hypotheses have already been discussed in Section 4.2 and Section 4.3. Only the mechanism proposed by Mizumoto et al. [36] is outlined here since it is the one for which the evidence is more conclusive:

$$\begin{aligned} &Cu^{2+}\text{-}(NH_3)_n + NO \rightarrow Cu^{2+}(NH_3)_nNO \\ &\quad \rightarrow Cu^{+}(NH_3)_{n-2} + N_2 + H_2O + (NH_4)^{+} \qquad (7.2) \end{aligned}$$

$$Cu^{+}(NH_3)_{n-2} + 3NO \rightarrow Cu^{2+}(NH_3)_{n-2}(NO_2)^{-} + N_2O \qquad (7.3)$$



Scheme 6. Reaction network in the reduction of NO with ammonia and oxygen over a copper-on-alumina catalyst.

$$Cu^{2+}(NH_3)_{n-2}(NO_2)^- + (NH_4)^+ \rightarrow Cu^{2+}(NH_3)_{n-2} + N_2 + 2H_2O \tag{7.4}$$

Two mechanisms of NO reduction thus co-exist in the overall reaction scheme. The first involves a reaction between NO and NH_2 on the same copper ion (possibly forming a nitrosoamide-like NH_2NO intermediate) and the second a reaction between a NO_2 and ammonium ions (thus via an ammonium nitrite NH_4NO_2 like intermediate). In the absence of oxygen, oxidation of NO occurs only by NO disproportionation, but when oxygen is present NO oxidation probably occurs directly by oxygen. Oxygen promotes NO conversion considerably, especially at temperatures above 120°C [37]. Mizumoto et al. [37] have suggested that oxygen only promotes conversion because it reoxidizes Cu^+, but clearly oxygen also has a direct role in the oxidation of NO to higher oxides (NO_2, in particular) promoting the second step of the reaction mechanism.

It has been shown that over copper–alumina catalysts (see Section 6.3) two possible reaction pathways of NO reduction to N_2 occur, one via a nitrosoamide-like intermediate and the second via an ammonium nitrite like intermediate or their equivalent Cu complexes [NO–Cu–NH_2 and NO_2–Cu–NH_4, respectively] [137,305,388,389]. The relative importance of the two pathways on the overall reaction rate was shown to depend on the reaction conditions. The latter pathway via an ammonium nitrite like copper complex prevails under stationary reaction conditions, whereas the former is faster but occurs only under transient conditions when chemisorption of NO does not inhibit ammonia dissociative chemisorption at copper sites [305]. Consecutive oxidation of nitrite to nitrate species also competes with N_2 formation via an ammonium nitrite like copper complex. Consecutive oxidation is negative for two main reasons: (i) it leads to an inhibition of surface reactivity since the copper nitrate complex is characterized by a slower rate of transformation and (ii) it leads to the formation of the side product N_2O via decomposition on an ammonium nitrate like intermediate species [137].

Summarized in Scheme 6 is the reaction pattern in the reduction of NO with NH_3 in the presence of O_2 over a copper-on-alumina catalyst suggested by combined spectroscopic and reactivity data [137,305,388,389]. Ammonia can be activated

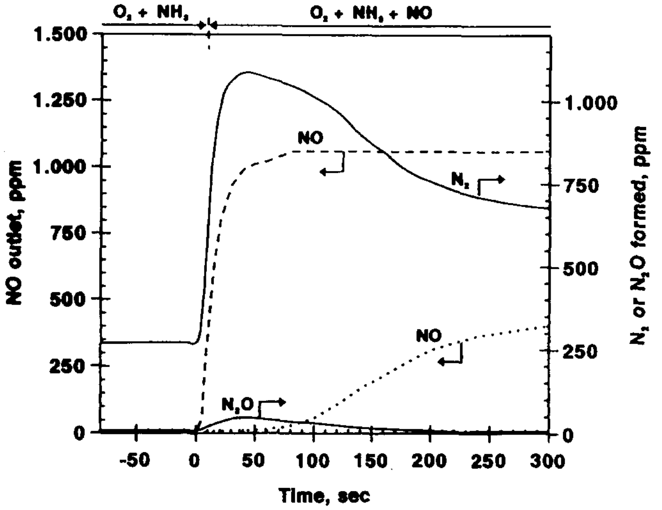


Fig. 15. Enhanced transient reactivity of a copper-on-alumina catalyst during NO step-change experiments in a flow of NH_3+O_2 in helium [305].

either dissociatively at copper sites with a Lewis acid character or at Brønsted sites, when the stronger adsorption of NO prevents its chemisorption. In the presence of NO the prevailing pathway thus follows the second route, but in non-stationary catalytic tests the first route dominates leading to an enhanced transient surface reactivity as clearly shown in NO step-change experiments over the copper-on-alumina catalyst maintained in a flow of ammonia + O_2 in helium (Fig. 15) [305].

The two routes of N_2 formation and the effect of reaction conditions on their relative importance can explain some of the literature data. For example, it can be understood why spectroscopic IR evidence on the reaction mechanism over oxide supported copper catalysts suggests a reaction mechanism via a NH_2NO-like species [384], whereas catalytic tests show the significant role of NO_2 on the rate of NO conversion to N_2 [94]. On the other hand, the model of two competitive reaction pathways can be used to understand other more general aspects of the surface chemistry of oxide catalysts in NO reduction with NH_3/O_2. For example, transient reactivity data show that on V–TiO_2 catalysts NO does not strongly chemisorb [389] and IR evidence [385] indicates that the reaction mechanism probably occurs via a nitrosoamide intermediate. Only the first route is thus possible on this catalyst, but it should be noted that the dissociative chemisorption of ammonia at the transition metal centre is probably also the first step in the side reaction of ammonia oxidation to N_2, presumably via consecutive H-abstraction by oxygen on coordinated amide-like (NH_2) species to form N species and water. At high reaction temperatures the consecutive H-abstraction on dissociatively coordinated ammonia is faster than its reaction with NO and therefore the rate of NO conversion passes through a sharp maximum as the reaction temperature is increased (see Fig. 4). On copper-based catalysts, instead, strong chemisorption of NO on copper sites limits the possibility of dissociative chemisorption of ammonia and its pathway to

N_2. On a catalyst such as Cu/ZSM-5, where the high dispersion of copper ions limits consecutive oxidation of nitrite to nitrate species and the higher copper–oxygen ionic character leads to the formation of a stronger copper–mononitrosyl bond (see Section 3.3), it is possible to couple high catalyst activity in NO conversion with NH_3/O_2 to a much wider temperature range for the maximum NO conversion (Fig. 4).

The same concepts regarding the influence of co-adsorbents on competitive surface pathways of transformation is also the key to understanding relatively old data on the oxidation of ammonia in wet and dry systems over CuO. Gandhi and Shelef [432], in fact, observed that over CuO, differently from molybdate catalysts, the addition of water inhibits ammonia conversion, but especially changes the selectivity to the N-pairing reaction ($N_2 + N_2O$) in favour of the formation of NO (unpairing reaction). Gandhi and Shelef [432] interpreted the effect in terms of pairing probability determined by the surface coverage of $N^{\cdot}$ adspecies. Competitive chemisorption of water decreases the amount of ammonia chemisorbed and thus also influences the probability of the N-pairing reaction. However, the selectivity in the N-pairing reaction observed for example at 550°C over CuO drops by half in the presence of 10% H_2O as compared to dry conditions [432]. Ammonia conversion, on the contrary, decreases from 100% to 95%. It is thus probable that water modifies the main form of ammonia adspecies (from dissociative chemisorbed species to ammonium ions) due both to inhibition on ammonia coordination at copper sites by competitive chemisorption and to its promotion on the formation of Brønsted sites. This clearly influences the possible pathway of further transformation and therefore surface selectivity.

A quantum-mechanical approach, such as those on the role of atomic and molecular oxygen as chemical precursors in the oxidation of ammonia over the Cu(111) surface [433] is probably the direction which could lead to a real breakthrough for the understanding of these catalytic transformations at surfaces, and the identification of the dependence of the selectivity on the nature and concentration of adspecies.

The mechanism of NO reduction by CO has been studied in detail in the past over copper oxide [418,434], Cu/SiO_2, $Cu/CuAl_2O_4$ and metallic copper [435], $CuCo_2O_4$ [436] and more recently over Cu/TiO_2 [113]. In all cases, the data refer only to the reaction in the absence of oxygen, because oxygen poisons the activity even when present in low amounts [372]. The high selectivity for oxidation of CO by O_2 rather than the oxidation of CO by NO is typical [437,438]. Furthermore, CO coordination over Cu^{2+} ions is rather weak, differently from coordination over Cu^{+}. A method based on this concept to determine Cu^{+} concentration only in Cu-zeolites was also proposed recently [439].

The role of NO reduction by CO was thus found negligible in the reaction mechanism of NO conversion over Cu/ZSM-5 in exhaust gas from lean-burn engines [425], where CO is present together with excess O_2 and where copper is predominantly present as Cu^{2+} (see Section 3.3.3). The study of the reaction mechanism of anaerobic NO conversion by CO is thus mainly interesting from the fundamental point of view, but is of limited relevance for practical applications.

While minor differences exist between the various authors [113,418,435,436] regarding the details of the reaction mechanism, agreement does exist in general that the reaction proceeds via a redox mechanism in which NO dissociatively coordinates at reduced copper ions forming N· and oxygen adatoms. The latter are picked up from CO (adsorbed or in the gas phase) to form CO_2 or consecutively even carbonate species [113]. Only Panayotov et al. [436] instead indicated the formation of a surface (NO···CO) complex with a carbonate, nitro or nitrate-type configuration. Data, however, about the existence and catalytic role of such types of surface complexes is not fully convincing. The overall mechanism may be written according to London and Bell [418] in the following nine elementary steps:

$$\mathrm{Cu + NO \rightleftharpoons Cu\text{–}NO} \tag{7.5}$$

$$\mathrm{Cu + NO + Cu^{+} \rightarrow Cu\text{–}N + Cu^{2+}O^{-}} \tag{7.6}$$

$$\mathrm{Cu\text{–}N + NO \rightarrow Cu + N_2O} \tag{7.7}$$

$$\mathrm{Cu^{+} + CO \rightleftharpoons Cu^{+}CO} \tag{7.8}$$

$$\mathrm{Cu + N_2O \rightleftharpoons Cu - ONN} \tag{7.9}$$

$$\mathrm{Cu\text{–}ONN \rightarrow Cu^{+}O^{-} + N_2} \tag{7.10}$$

$$\mathrm{Cu^{2+}O^{-} + CO \rightarrow Cu^{+} + CO_2} \tag{7.11}$$

$$\mathrm{Cu^{+}O + CO \rightarrow Cu + CO_2} \tag{7.12}$$

$$\mathrm{Cu - N + CO \rightleftharpoons Cu^{+}NCO^{-}} \tag{7.13}$$

The reaction rate based on a Langmuir–Hinshelwood approach and the above sequence of elementary steps correctly fit experimental data [418]. Rewick and Wise's [435] reaction mechanism is substantially in agreement with the above reaction steps, but they observed that the formation of isocyanate species (Eq. (7)) on the copper surface sites inhibits the reaction. The species, furthermore, acts as the precursor for formation of ammonia in the presence of water vapour. Their results further demonstrate that isocyanate species on copper sites cannot be intermediate in the NO conversion to N_2 as suggested in the case of NO reduction with propene/O_2 (see Section 7.2).

The mechanism proposed by Boccuzzi et al. [113] over Cu/TiO_2 is also in agreement with that reported above, even though they did not detect the formation of isocyanate species and suggest the possibility of N_2O formation by transformation of a copper–dinitrosyl species, as well as by reaction of NO with N adatoms. Furthermore, they suggested that the rate determining step of the NO + CO reaction is the dissociation of NO on defective titania in close contact with small metal particles, thus indicating an active catalytic role of the support.

7.4. Mechanism of N_2O decomposition

The mechanism of N_2O decomposition has never been studied in detail and is generally assumed to involve N_2O chemisorption at reduced copper sites which hold the oxygen released from N_2O to form N_2 (see Eq. (7)). Swamy and coworkers [440,441] have suggested, for example, that N_2O adsorption occurs preferentially by the interaction of N_2O π^* orbitals with the surface states of the oxide lattice (a non-stoichiometric cuprate catalyst in the specific case). At high N_2O pressure, multicentre adsorption leads to the population of the σ^* orbitals causing fission of the N–O bond. They suggested that a Cu^{2+}/Cu^{3+} couple acts as the active site for decomposition of N_2O, similarly to that proposed for decomposition of NO on analogous catalysts [243]. Catalytic data, however, were reported for 60 min only and thus it is not possible to understand if the reaction mechanism involving surface anion vacancies may be effective under stationary conditions. Belapurkar et al. [442] also found that an oxygen-deficient tetragonal form of YBCO high T_c superconducting cuprate showed much higher catalytic activity than an oxygen-rich orthorhombic form. They suggested therefore that the reaction mechanism involves adsorption of N_2O at oxygen vacancies adjacent to copper ions, followed by a change in the valence state of copper and release of nitrogen. The reaction rate is controlled by the thermal release of lattice oxygen. Recent data on the catalytic decomposition of nitrous oxides over metal-exchanged zeolites [103] also suggest a parallelism between NO and N_2O decomposition and a reaction rate controlled by spontaneous thermal reduction of the zeolite catalyst. Li and Armor [103], however, claimed a much higher reaction rate over these zeolites (especially over Cu/ZSM-5 and Co/ZSM-5) than over other types of catalysts. Data have also been reported for the reaction of N_2O with methane over Co/ZSM-5 [443]. It was found that (i) the addition of oxygen does not affect the rate of N_2O decomposition and (ii) the rate of N_2O conversion is not promoted by the addition of CH_4, but rather is considerably depressed when O_2 and CH_4 are present simultaneously. N_2O instead promotes NO conversion by methane in the absence of O_2. Even though data for Co/ZSM-5 only are reported, the effect of the addition of hydrocarbon and O_2 on the conversion of N_2O and the effect of N_2O on the conversion of NO suggest that possibly the catalyst activity is determined by surface factors other than the rate of spontaneous catalyst reduction. Schulz et al. [444] observed, in fact, that in an homologous series of Cu/Cr oxides the activity is not correlated with the partial pressure of the lattice oxygen, but rather with the integral overlap between surface states of the catalyst and the colliding N_2O molecule. Larsson [445] more recently suggested an analogous resonance mechanism based on re-examination of literature data. Recently the possibility of isothermal oscillations in the catalytic decomposition of N_2O on Cu/MFI was also shown [446]. The addition of oxygen did not change the oscillations, while the presence of NO immediately quenched the oscillations and increases the conversion of N_2O. This is probably due to a deactivation of NO over the rate of N_2O decomposition caused by the formation of nitrate species which block the reactivity of copper ions [306,447].

In conclusion, data on the mechanism of N_2O decomposition are limited, but recent evidences suggest that the reaction mechanism may be more complex than only the reoxidation of surface oxygen vacancies created during initial pretreatment or by spontaneous reduction.

8. Concluding remarks

Copper-based catalysts are a useful model for the investigation of the fundamental aspects of the chemistry of the interaction and surface transformation of nitrogen oxides over solid catalysts. The analysis of publications in this area show, however, that several points deserve more specific studies. More attention to a comparative analysis of the structure/activity relationship in other (active and inactive) copper-based catalysts is also needed. Furthermore, there are several specific topics which need more careful investigations:

- The nature/reactivity of copper species on the oxide surface, especially of multinuclear copper species with intermediate nuclearity between isolated copper ions directly interacting with the support through oxygen bridges and supported CuO crystalline particles.
- The relationship between global and local zeolite characteristics (Madelung potential, softness, etc.) and nature/reactivity of isolated copper ions interacting with the zeolite framework.
- The nature/reactivity of low nuclearity multinuclear oxide species inside structured microporous materials (zeolites).
- The adsorbate-driven relocalization or restructuring of active sites during the catalytic reaction, with particular reference to the case of Cu-zeolites.
- Cooperative and synergetic effects between active sites (also considering their modification in the presence of adspecies) in relation to the reaction mechanism.
- Presence of multiple surface pathways, dependence of the selectivity on the nature and concentration of adspecies, inhibition or promotion of adsorption driven by other adspecies, transient versus steady-state activity, active versus spectator (or with lower rate of transformation) species.
- Molecular and reaction modelling of the reaction mechanism using a quantum-mechanical approach and computer simulation.
- Analogies and differences between the mechanisms of transformation over surfaces and in enzyme systems.

All these topics are not only of specific interest for the conversion of nitrogen oxides at copper-based surfaces, but also indicate some of the guidelines for future research in catalysis. The reactions of nitrogen oxides in the presence or absence of reductants and/or oxygen on copper-based catalysts can be viewed as an optimal model system for fundamental catalysis investigation and for a more scientific approach to catalyst design by reaction modelling.

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EXHIBIT C

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Synthesis, Reactions and Applications

Volume 1

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The Editor

Prof. Dr. Jiří Čejka
Academy of Sciences of the Czech Republic
Heyrovský Institute of Physical Chemistry
Dokjškova
Dolejskova 3
182 23 Prague 8
Czech Republic

Prof. Dr. Avelino Corma
University Politecnica de Valencia
Institute de Tecnologia Quimica
Avenida de los Naranjos s/n
46022 Valencia
Spain

Prof. Dr. Stacey I. Zones
Chevron Texaco Energy Research
and Technology Company
100 Chevron Road
Richmond, CA 94802
USA

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Contents to Volume 2

Preface

One can safely say that the impact of zeolites in science and technology in the last 50 years has no precedents in the field of materials and catalysis. Although the first description of zeolites dates back up to 250 years ago, the last five decades experienced an incredible boom in zeolite research activities resulting in the successful synthesis of almost 200 different structural types of zeolites, numerous excellent scientific papers on the synthesis of zeolites, characterization of their properties, and applications of zeolites in adsorption and catalysis that have revolutionized the petrochemical industry. In addition, based on the knowledge of zeolites several other areas of porous materials have recently emerged including mesoporous materials, hierarchic systems, metal-organic frameworks (cationic-periodic polymers) and mesoporous organosilicas. All these materials have substantially increased the portfolio of novel porous materials possessing new interesting properties, but this topic is not covered in this book.

This book consists of two volumes. The first one is mostly concentrated on recent advances in the synthesis of zeolites and understanding of their properties while the second volume describes recent achievements in the application of zeolites mostly in catalysis.

More specifically, the first volume starts with a chapter by P. Cubillas and M.W. Anderson (Chapter 1) discussing mechanisms of the synthesis of zeolites and zeotypes, including nucleation and crystal growth, employing various microscopic techniques. This is followed by a chapter of K. Strohmaier (Chapter 2) providing a detailed survey on the synthesis of novel zeolites and different layered precursors incorporating different metal ions into the framework, and applying ever increasing number of structure-directing agents. A new approach to the synthesis of zeolites and other porous materials by ionothermal synthesis combining ionic liquids as the solvent together with the structure-directing agent is presented by R. Morris (Chapter 3). Zeolite synthesis can also be controlled by a simultaneous use of two different templates providing new tool for creative chemistry Nas discussed by the group of J. Pérez-Pariente (Chapter 4). Morphological control of zeolite crystals is one of the key issues to understand the mechanism of zeolite crystallization as well as to control the performance of zeolites in various applications as it is outlined by S.-E. Park and N. Jiang in Chapter 5. Introduction of other elements than silicon into the zeolite framework can be done not only via synthesis but also in the

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postsynthesis steps as highlighted for deboronation followed by realumination as described by C.Y. Chen and S.I. Zones (Chapter 6). P.A. Wright and G.M. Pearce show how the individual zeolite structures are built from basic secondary building units. The authors focus not only on general aspects of zeolite structures but also on the description of structures of zeolites determined very recently (Chapter 7).

Structural and textural characterization of zeolites starts in Chapter 8, written by E. Stavitski and B.M. Weckhuysen, providing good examples of application of vibrational spectroscopy under static conditions that can drive into *in situ* catalytic investigations. The group of K. de Jong (Chapter 9) makes an effort to evaluate different physicochemical methods used for textural characterization of zeolites. Gas physisorption, mercury porosimetry, electron microscopy (including 3D experiments), various NMR techniques up to *in situ* optical and fluorescence microscopy are discussed in detail. The location, coordination, and accessibility of framework aluminum are of key importance for acid-catalyzed reactions in zeolites and these issues are addressed by J.A. van Bokhoven and N. Danilina in Chapter 10. Theoretical background of zeolite reactivity employing different computational approaches and models is covered in Chapter 11 by E.A. Pidko and R.A. van Santen. S. Calero Diaz presents an overview of current developments in modeling of transport and accessibility in zeolites showing some recent models and simulation methods that are applied for systems of environmental and industrial interests (Chapter 12). The final chapter of the first volume is written by the group of F. Kapteijn (Chapter 13), in which diffusion in zeolites starting from basic models of diffusion up to the role of diffusion in adsorption and catalytic processes is discussed.

The second volume starts with a chapter of the group of J. Coronas concentrating on special applications of zeolites including green chemistry, hybrid materials, medicine, veterinary, optical- and electrical-based applications, multifunctional fabrics, and nanotechnology (Chapter 14). After that K.B. Yoon presents the opportunities to organize zeolite microcrystals into two- and three-dimensionally organized structures and the application of these organized entities in membranes, antibacterial functional fabrics, supramolecularly organized light-harvesting systems, and nonlinear optical films (Chapter 15).

The remaining chapters are exclusively devoted to the application of zeolites in catalysis. G. Bellussi opens this part with a broad overview of current industrial processes using zeolites as key components of the catalysts and further challenges in this area (Chapter 16). Generation, location, and characterization of catalytically active sites are discussed in depth by M. Hunger showing different aspects of shape selectivity and structural effect on the properties of active sites (Chapter 17). M. Rigutto (Chapter 18) stresses the importance of zeolites and the main reasons for their application in cracking and hydrocracking, the largest industrial processes employing zeolites as catalysts. Further, C. Perego and his coworkers focus on reforming and upgrading of diesel fractions, which with gasoline are by far the most important and valuable key fractions produced by petroleum refineries (Chapter 19). Transformation of aromatic compounds forms the heart of petrochemical processes with zeolites as key components of all catalysts. S. Al-Khattaf, M.A. Ali, and J. Čejka highlight the most important recent achievements in application of zeolites in various alkylation, isomerization, disproportionation, and transalkylation reactions of aromatic hydrocarbons (Chapter 20). With decreasing supply of oil, natural gas obtains more and more importance. A. Martinez and his coauthors discuss in some detail different ways of methane upgrading into valuable fuels and chemicals (Chapter 21). Methanol, which can be obtained from natural gas, could be one of the strategic raw materials in future. Novel processes transforming methanol into olefins or gasoline are covered in Chapter 22 by M. Stöcker. Incorporation of catalytically active species into zeolite frameworks or channel systems for oxidation reactions is covered in Chapter 23 by T. Tatsumi. The main attention is devoted to Ti-silicates. G. Centi and S. Perathoner focus on increasing applicability of zeolites in environmental catalysis with a particular attention to conversion of nitrogen oxides (Chapter 24). K.L. Yeung and W. Han describe the emerging field of application of zeolites in fuel cells for clean energy generation. The authors show that zeolites can play an important role in hydrogen production, purification, conditioning, and storage (Chapter 25). The final chapter by the authors from the group of A. Corma presents possibilities of application of zeolite as catalysts in the synthesis of fine chemicals. The examples discussed include, for example, acylation, hydroxyalkylation, acetalization, isomerization, Diels–Alder, and Fischer glucosidation reactions.

Bringing together these excellent chapters describing the cutting edge of zeolite research and practice provides an optimistic view for the bright future of zeolites. The number of new synthesized zeolites is ever increasing and particularly novel extra-large pore zeolites or even chiral zeolitic materials will surely be applied in green catalytic processes enabling to transform bulkier substrates into desired products. In a similar way, application of zeolites in adsorption or separation is one of the most important applications of this type of materials saving particularly energy needed for more complex separation processes if zeolites were not available to do the job. Fast development of experimental techniques enables deeper insight into the structural and textural properties of zeolites, while particularly spectroscopical methods provide new exciting information about the accessibility of inner zeolite volumes and location and coordination of active sites. Catalysis is still the most promising area for application of zeolites, in which novel zeolitic catalysts with interesting shape-selective properties can enhance activities and selectivities not only in traditional areas such as petrochemistry but also in environmental protection, pollution control, green chemistry, and biomass conversion. Last but not least, novel approaches in the manipulation and modification of zeolites directed to fuel cells, light harvesting, membranes, and sensors clearly evidence a large potential of zeolites in these new areas of application. The only limitation in zeolite research is the lack of our imagination, which slows down our effort and attainment of new exciting achievements.

It was our great pleasure working with many friends and excellent researchers in the preparation of this book. We would like to thank sincerely all of them for their timely reviews on selected topics and the great effort to put the book together. We believe that this book on zeolites will be very helpful not only for experienced researchers in this field but also students and newcomers will find it as a useful reference book.

Jiří Čejka	*Avelino Corma Canos*	*Stacey I. Zones*
Prague	Valencia	Richmond
October 2009		

List of Contributors

Michael W. Anderson
University of Manchester
School of Chemistry
Centre for Nanoporous Materials
Oxford Road
Manchester M13 9PL
UK

Sofía Calero Diaz
University Pablo de Olavide
Department of Physical,
Chemical, and Natural Systems
Ctra. Utrera km. 1
41013 Seville
Spain

Cong-Yan Chen
Chevron Energy Technology
Company
100 Chevron Way
Richmond, CA 94802
USA

Pablo Cubillas
University of Manchester
School of Chemistry
Centre for Nanoporous Materials
Oxford Road
Manchester M13 9PL
UK

Nadiya Danilina
ETH Zurich HCI
Department of Chemistry and
Applied Biosciences
Wolfgang-Pauli-Str. 10
8093 Zurich
Switzerland

Krijn P. de Jong
Utrecht University
Department of Chemistry
Inorganic Chemistry and
Catalysis Group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Petra E. de Jongh
Utrecht University
Department of Chemistry
Inorganic Chemistry and
Catalysis Group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

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Raquel García
Instituto de Catálisis y
Petroleoquímica
CSIC
Marie Curie 2
Cantoblanco
28049 Madrid
Spain

Jorge Gascon
TU Delft
DCT
Catalysis Engineering
Julianalaan 136
2628 BL Delft
The Netherlands

Luis Gómez-Hortigüela
Instituto de Catálisis y
Petroleoquímica
CSIC
Marie Curie 2
Cantoblanco
28049 Madrid
Spain

Nanzhe Jiang
Inha University
Department of Chemistry
Laboratory of Nano-Green
Catalysis and Nano Center for
Fine Chemicals Fusion
Technology
Incheon 402-751
Korea

Freek Kapteijn
TU Delft
DCT
Catalysis Engineering
Julianalaan 136
2628 BL Delft
The Netherlands

Russell E. Morris
University of St Andrews
EaStCHEM School of Chemistry
Purdie Building
St Andrews KY16 9ST
Scotland

Sang-Eon Park
Inha University
Department of Chemistry
Laboratory of Nano-Green
Catalysis and Nano Center for
Fine Chemicals Fusion
Technology
Incheon 402-751
Korea

Gordon M. Pearce
University of St Andrews
School of Chemistry
Purdie Building
St Andrews
Fife KY16 9ST
UK

Joaquin Pérez-Pariente
Instituto de Catálisis y
Petroleoquímica
CSIC
Marie Curie 2
Cantoblanco
28049 Madrid
Spain

Evgeny A. Pidko
Eindhoven University of
Technology
Department of Chemical
Engineering and Chemistry
Molecular Heterogeneous
Catalysis
P.O. Box 513
5600 MB Eindhoven
The Netherlands

Ana Belén Pinar
Instituto de Catálisis y
Petroleoquímica
CSIC
Marie Curie 2
Cantoblanco
28049 Madrid
Spain

Eli Stavitski
Utrecht University
Inorganic Chemistry and
Catalysis group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Karl G. Strohmaier
ExxonMobil Research and
Engineering Company
1545 Route 22 East
Annandale
NJ 08801-3096
USA

Jeroen A. van Bokhoven
ETH Zurich HCI
Department of Chemistry and
Applied Biosciences
Wolfgang-Pauli-Str. 10
8093 Zurich
Switzerland

Johan van den Bergh
TU Delft
DCT
Catalysis Engineering
Julianalaan 136
2628 BL Delft
The Netherlands

Adri N.C. van Laak
Utrecht University
Department of Chemistry
Inorganic Chemistry and
Catalysis Group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Rutger A. van Santen
Eindhoven University of
Technology
Department of Chemical
Engineering and Chemistry
Molecular Heterogeneous
Catalysis
P.O. Box 513
5600 MB Eindhoven
The Netherlands

Bert M. Weckhuysen
Utrecht University
Inorganic Chemistry and
Catalysis group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Paul A. Wright
University of St Andrews
School of Chemistry
Purdie Building
St Andrews
Fife KY16 9ST
UK

Lei Zhang
Utrecht University
Department of Chemistry
Inorganic Chemistry and
Catalysis Group
Debye Institute for
Nanomaterials Science
Sorbonnelaan 16
3584 CA Utrecht
The Netherlands

Stacey I. Zones
Chevron Texaco Energy Research
and Technology Company
100 Chevron Road
Richmond, CA 94802
USA

24

Environmental Catalysis over Zeolites

Gabriele Centi and Siglinda Perathoner

24.1

Introduction

The first widespread use of the term *environmental catalysis* to indicate catalysts and catalytic technologies for environment protection began around the beginning of 1990s, when the first large meetings on this specific topic were organized [1–6]. The original concept of environmental catalysis referred only to technologies for reducing polluting emissions. However, the applications addressed by environmental catalysis include a broad range of questions currently:

- catalytic clean-up technologies for gas (elimination of nitrogen oxides, conversion of volatile organic compounds – VOCs, etc.) and liquid phase (elimination of nitrate, toxic, and biorecalcitrant chemicals, etc.) emissions from stationary sources;
- catalysis for sustainable mobility (cleaner fuels, reduction of NO_x, CO, HC, and particulate in vehicle emissions, etc.);
- catalytic approaches for converting or recycling solid waste (conversion of polymer waste, recycling industrial solid waste, etc.);
- catalytic technologies for greenhouse gas reduction (reduction of N_2O, CH_4, CO_2, and fluorocarbon emissions);
- catalysis for in-house applications (improvement of air and water quality, self-cleaning surfaces and devices, etc.);
- catalytic approaches to clean energy production (H_2 production, use of renewables and biomass, fuel cells, energy storage, etc.); and
- new catalytic processes for sustainable production and eco-compatible technologies.

We restrict the discussion here, however, only to the original concept, because most of the other aspects are analyzed in other sections of this book. From the beginning, a significant part of the communications presented at the cited conferences on environmental catalysis regarded the use of zeolite catalysts or

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related materials. The largest part of these communications concerned the use of zeolites for NO_x and VOC removal.

24.2
A Glimpse into Opportunities and Issues

One of the first discoveries that has largely stimulated research in this field was the finding that Cu ions exchanged into the faujasite (FAU) and MFI microporous matrix exhibit higher activity among metal ions exchanged into zeolites in the decomposition of NO [7–9], in particular, the "overexchanged" Cu/MFI ($Cu^{2+}/Al > 0.5$). In the presence of O_2 and water vapor, the activity was significantly depressed, and thus these materials never reached practical applications. However, there is still active research in this field.

Kustova *et al.* [10, 11] reported recently that mesoporous Cu/ZSM-11 (MEL structure characterized by a two-dimensional 10-ring pore) and Cu/ZSM-12 (MTW structure, one-dimensional 12-ring pore), in addition to the original and most studied Cu/ZSM-5 (MFI structure; similar to MEL, but one set of pores is zig-zag, or sinusoidally shaped), are active catalysts for the direct decomposition of NO. They also reported that Cu/ZSM-5 has been recognized as a unique catalyst for direct NO decomposition for many years, but their "discover that both Cu–ZSM-11 and Cu–ZSM-12 are about twice as active as Cu–ZSM-5 indicate that the special pore structure of Cu–ZSM-5 is not a decisive factor for catalytic activity in NO decomposition."

A primary issue in Cu/zeolites, but of general relevance for all the field of transition-metal-ion-containing zeolites for environmental applications, concerns therefore the role of zeolite as a host material. The question is whether the zeolite provides only a good dispersion of the metal ions, the formation of specific species not being present on other oxides, or there is a specific effect of the zeolite pore structure ("shape-selectivity" or analogous aspects).

To discuss this issue in relation to the recent results of Christensen *et al.* [10, 11], it is useful to start with the observation that patents issued already 10 years earlier claimed the use of these zeolites for preparing catalysts active in the decomposition of NO. For example, Price and Kanazirev [12] claimed that "the zeolite should be preferably a ZSM-5, ZSM-11, or ZSM-12 zeolite." Kagawa and Teraoka [13] also claimed ZSM-11 and ZSM-12 among the active zeolites for the decomposition of NO. Many other patents indicated these and other zeolitic structures among those relevant for preparing active catalysts. However, these materials were tested but showed lower activity with respect to ZSM-5, which is in contrast with the recent finding of Christensen *et al.* [10, 11].

To clarify this point, it is necessary to recall that the basic idea of using transition-metal-containing zeolites was the possibility to realize extremely well-dispersed single active species within the zeolite cavities [14]. However, it was soon realized that multiple species usually form and that the nature of the species present depends greatly on the preparation. The distribution of these species depends on many parameters beyond the zeolite structure itself, such as the modality of preparation (including precursor compounds), zeolite Si/Al ratio, thermal treatment, and so on. Different reactivity orders in a zeolite structure series have been often observed when the preparation method was changed. Even though a unique behavior of Cu/MFI (ZSM-5) catalyst in this reaction has been indicated [15], it was known that this peculiar characteristics referred to a *nature of the active sites* (transition-metal ions) different to that present in oxide-supported catalysts, and not to the special properties associated with the zeolite pore structure (mono- or tridimensional, linear or sinusoidal channels, size of the channels, etc.) [16].

In fact, nitrogen oxide (NO) is a small molecule and the dimensions of possible reaction intermediates (dimeric species, for example) are small compared to the channel and cages sizes. Therefore, shape-selectivity effects cannot be present. The possible influence of the electrostatic field within the zeolite (in a zeolite structural series such as ZSM-5, ZSM-11, and ZSM-12) on the stabilization of the reaction intermediates, or the influence of zeolite pore structure on the diffusivity of molecules (NO, N_2), is also minimal. Therefore, the characteristics of zeolite pore structure (for equivalent nature of the active sites) are not expected to play a major role in the decomposition of NO, although they could be relevant in other reactions of nitrogen oxide conversion, such as for the selective reduction of NO with hydrocarbons.

On the other hand, it is known for a decade now that different sites for isolated species of transition-metal ions are possible in the zeolite structure [17–19]. The charge balance at the cationic sites in metal-ion-exchanged zeolites can occur (Figure 24.1a) as given below:

1) Bare cations coordinated exclusively to the framework oxygen atoms and thus exhibiting open coordination sphere.
2) Metal-oxo species coordinated to the framework, but simultaneously bearing extra-framework oxygen atom(s).
3) Metal-oxide-like species supported in the zeolite inner volume or mostly at the outer surface of the crystals.

The structure of the metallo-center depends on the type of the metal ion, the procedure of cation introduction into the zeolite, and the host zeolite matrix (Si/Al ratio and location of Al ions). Transition-metal ions such as Cu^{2+} or Co^{2+} are present as divalent cations predominantly coordinated only to framework oxygens. For higher charged ions such as Fe species, the lack of sufficient local negative framework charge, particularly in high-silica zeolites, to balance trivalent cations may instead induce the formation of Fe ions bearing an extra-framework oxygen ligand, that is, FeO^+ or dinuclear Fe–O–Fe type complexes.

Different metal ion sites in zeolites have been identified for the bare cations (Figure 24.1b) [17–19]. They were indicated as α, β, and γ positions. In the first two sites, the bivalent metal ions are coordinated to the framework by six-membered rings (α- and β-types), while in γ-type cations are in a boat-shaped site. The population of these different sites depends on Si/Al ratio, type of zeolite, method of preparation (both of zeolite itself and of loading of the metal ions), and so on.

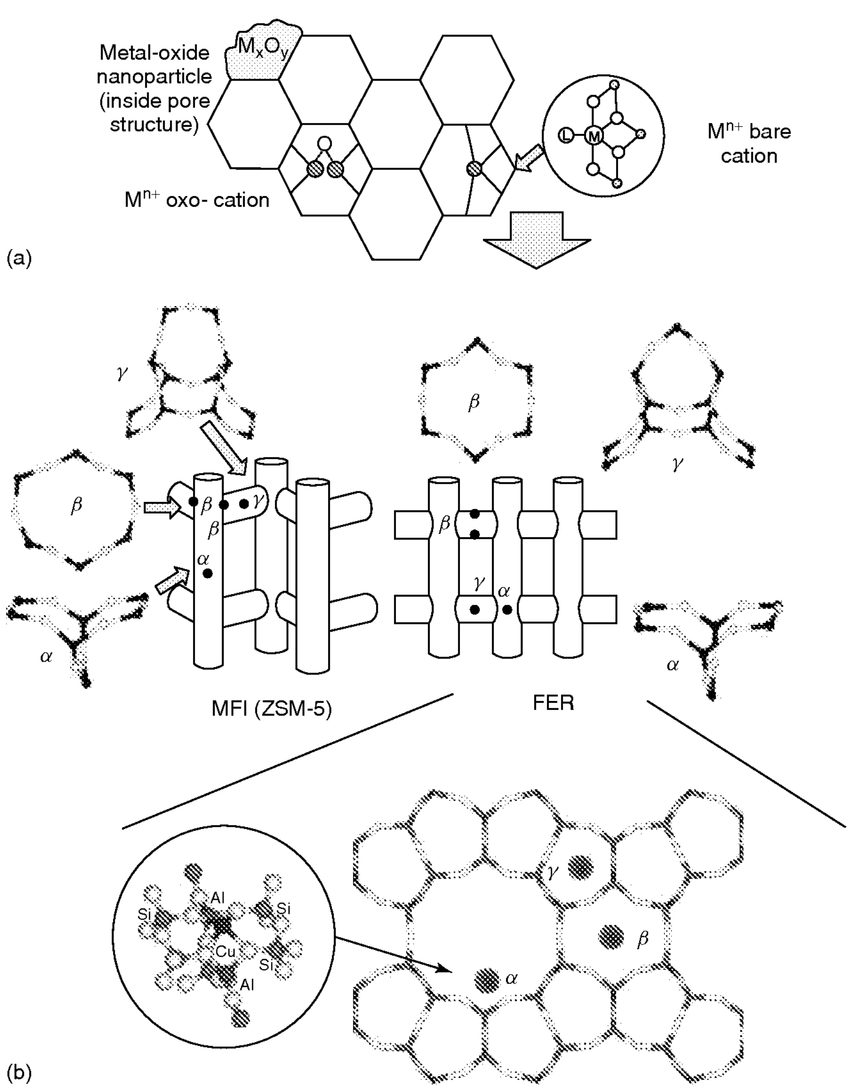


Figure 24.1 (a) Schematic model of cation location in zeolites. (b) Simplified sites and local framework structures of the α-, β-, and γ-type Me(II) ions in MFI and FER zeolites. Adapted from [19]. The model of localization of copper ions in ferrierite (FER) (bottom part of the figure) has been adapted from [33].

It is also known that, during ionic exchange, the electrostatic field within the zeolite causes precipitation of metal-hydroxo species in the larger zeolite cages. Depending on the thermal treatment, these precursor species may form isolated cationic copper species, oxocations, or metal-oxide nanoparticles [20]. On the other hand, by conventional impregnation, the low rate of diffusion within the zeolites causes a preferential precipitation of these metal-hydroxo species on the external surface of the zeolite crystals. It is, thus, known from the recent findings that the preparation of Cu/MFI by impregnation leads mainly to CuO particles on the external zeolite surface [21].

Therefore, the preparation method is a key parameter to maximize the concentration of the active copper species and their performance in the decomposition of NO [22–25]. However, the great sensitivity of the nature and distribution of the active species to the zeolite preparation and their characteristics, coupled with their difficult characterization associated with the low amount of transition-metal ions present in the zeolite (typically, few percentage by weight or less), has resulted in the often contradictory findings in the literature, which still are not completely resolved.

For this reason, the identification of the nature of active sites was for a long time, and still is, under discussion. Miyamoto *et al.* [26] using molecular dynamics (MDs) simulations and molecular orbital (MO) calculations suggested the presence of Cu(II)–O–Cu(II) species, when two Al atoms occupy T8 sites in the six-membered ring, and indicated this species as the active one. However, the Takaishi rule [27] indicates that two Al atoms cannot be placed in one pentasil ring. Catlow *et al.* [28, 29] also proposed by computational methods that the active site in Cu/MFI catalysts is associated with two copper ions bridged with extra-framework OH species. Figure 24.2 reports the model of active sites proposed by Catlow *et al.* [29].

Wichterlová *et al.* [30] using Cu^+ photoluminescence and infrared (IR) spectroscopy identified two main Cu sites (denoted as Cu_α and Cu_β). The Cu_β site is preferentially occupied at low Cu loadings and exhibits a more packed environment and higher positive charge. The Cu_α site is occupied in the whole concentration

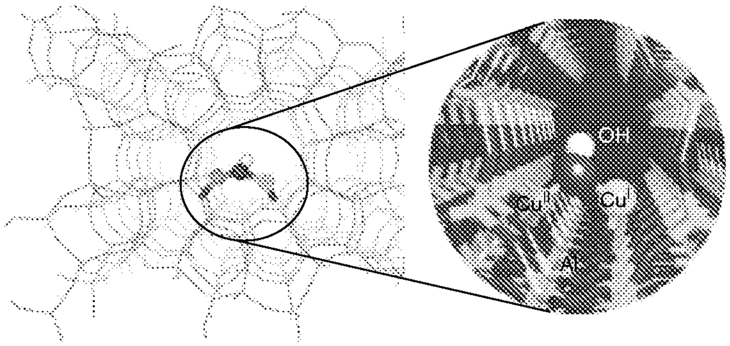


Figure 24.2 Model of active sites in Cu/MFI for NO decomposition proposed by Catlow *et al.* [29]. Adapted from [29].

range, but predominantly at high loadings, approaching and exceeding 100% degree of ion exchange. It is in a more open coordination, possesses lower positive charge, and was suggested to be balanced by a single framework Al atom, in contrast to two framework Al atoms for Cu_β. The reducibility of these Cu sites differs substantially and depends on the local negative framework charge. The latter depends on both the local Si–Al ordering adjacent to the Cu ion and the total framework charge given by the Si/Al ratio.

The analysis of the catalytic activity and reducibility versus the population of the Cu_α and Cu_β sites allowed the identification of the Cu_α site as the active center for NO decomposition. The results of Wichterlová *et al.* [30] thus indicate a single, bare cation as the active site in the decomposition of NO.

Various other authors have discussed the nature of active sites and the reaction mechanism in the decomposition of NO over copper-containing zeolites (see the review of Centi and Perathoner on the conversion of nitrogen oxides over copper-based catalysts [31]) using transient reactivity studies, spectroscopic investigations, and theoretical modeling. Specific overviews of the theoretical studies of the reaction of NO on metal-exchanged zeolites have been reported recently by Pietrzyk and Sojka [32], McMillan *et al.* [33], and Schneider [34]. General aspects of the reaction mechanism of conversion of nitrogen oxides have been discussed also by Busca *et al.* [35] and Centi and Perathoner [36].

The recent theoretical study of Pulido and Nachtigall [37] indicated a cyclic dinitrosyl complex (hyponitrite-like) as the key intermediate. The model is reported in Figure 24.3. Three types of dinitrosyl complexes with different coordination on the Cu^+ cation were identified by Pulido and Nachtigall [37]: (i) fourfold tetrahedral, (ii) fourfold square planar, and (iii) threefold trigonal planar. The most stable dinitrosyl complex, formed when the two NO molecules interact with Cu^+ via the N atom, has a tetrahedral coordination on Cu^+. The cyclic adsorption complex, having a square-planar arrangement of ligands on Cu^+ and interaction via O atoms, is only about few kilocalories per mole less stable than the N-down

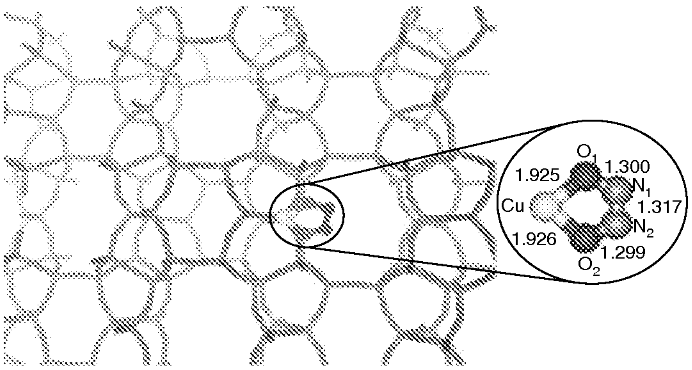


Figure 24.3 Active key intermediate (hyponitrite-like) in $DeNO_x$ reaction over Cu/FER proposed by Pulido and Nachtigall [37].

dinitrosyl complex. This cyclic dinitrosyl complex is suggested to be the key intermediate in the DeNO$_x$ process taking place in Cu/zeolites.

This model thus proposes that an isolated Cu^+ ion is the active site. The formation of *gem* dinitrosyl species on isolated copper ions has been identified from the earlier studies by IR spectroscopy and considered a key characteristic aspect. However, different ideas have been proposed about their role on the reactivity. Bell *et al.* [38] suggested the mechanism reported in Figure 24.4a, based on the evidences by IR spectroscopy of the gradual substitution of $Cu^+(NO)_2$ dinitrosyl species by $Cu^{2+}(NO)$ and $Cu^{2+}(O^-)(NO)$ species with formation also of $Cu^{2+}(NO_2)$ and $Cu^{2+}(NO_3{}^-)$ species. The key intermediate according to Bell *et al.* [38] is thus a $Cu^{2+}(NO_2{}^-)(NO)$ or $Cu^+(N_2O_3)$ species, supporting the original indications of Li and Hall [39] while studying the kinetics of decomposition of NO that the rate-limiting step is the adsorption of NO by an extra-lattice oxygen (ELO) containing site (e.g., $Cu^{2+}O^-$).

Zecchina *et al.* [40] proposed a slightly different reaction mechanism based on the role of single copper species and the key formation of a $Cu^{2+}(NO_2{}^-)(NO)$ intermediate (Figure 24.4b). They explicitly exclude the role of copper dimeric species. Schay *et al.* [41] also indicate $Cu^{2+}(O)(NO)(NO_2)$ as the key intermediate in NO decomposition. Ramprasad *et al.* [42] reported, in agreement with this hypothesis, density functional theory (DFT) results showing that the single-step, symmetric, concerted decomposition reaction of NO in the vicinity of Cu ion sites in zeolites is forbidden by orbital symmetry. On the contrary, metastable hyponitrite complexes display N–N coupling and may be precursors for multistep decomposition of NO.

Schneider [34] observed that in the "hyponitrite" structure (Figure 24.5, left) the bonding resulting from charge transfer from Cu to the adsorbate drives the formation of a short N–N bond resulting in the formation of N_2O and a ZCuO copper-oxo species, where Z indicates the zeolite.

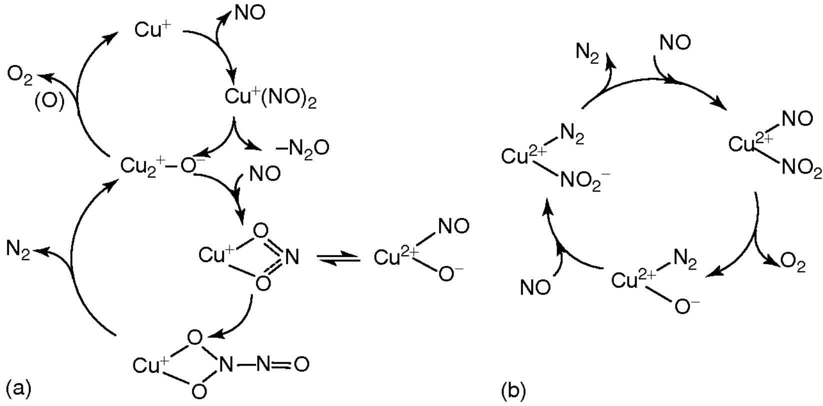


Figure 24.4 Reaction mechanisms in the decomposition of NO on Cu/zeolites proposed by Bell *et al.* [38] (a) and Zecchina *et al.* [40] (b).

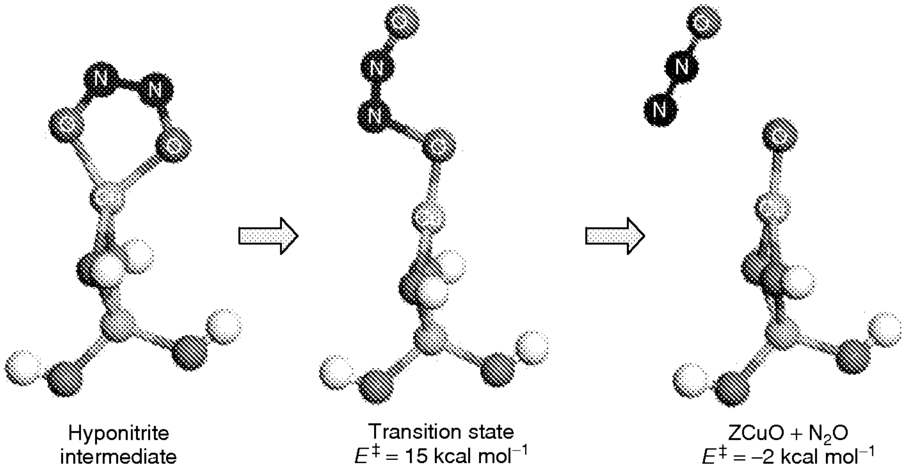


Figure 24.5 Conversion of metastable ZCu-bound hyponitrite intermediate to a copper-oxo (ZCuO) species and N_2O as proposed by Schneider [34]. Adapted from [34].

The copper-oxo species may further react with N_2O according to the following mechanism:

$$\text{ZCuO} + \text{N}_2\text{O} \rightarrow [\text{ZCuOO-NN}]^{\ddagger} \rightarrow \text{ZCuO}_2 + \text{N}_2 \qquad (24.1)$$

Subsequent desorption of O_2 from ZCu would complete the cycle. The second O-atom transfer reaction has an energy barrier of about 36 kcal mol^{-1} and is thus the more difficult step.

Pietrzyk and Sojka [32], however, observed that the conversion of $\{\text{Cu}^{\text{I}}\text{N}_2\text{O}_2\}\text{Z}$ transient species is kinetically constrained by the intersystem crossing, because the spin singlet $\{{}^1\text{Cu}^{\text{I}}\text{N}_2\text{O}_2\}\text{Z}$ intermediate is converted to $\{{}^3\text{CuO}\}\text{Z}$ center which has a spin triplet ground state.

The alternative mechanism to this outer-sphere coupling leading to dimeric $\{\text{Cu}^{\text{I}}\text{N}_2\text{O}_2\}\text{Z}$ intermediate is an inner-sphere nitrosonium route [32]. The oxidative adsorption, giving rise to the bound $\text{NO}^{\delta-}$ species, defines a *nitroside pathway* of activation, while the reductive adsorption leading to $\text{NO}^{\delta+}$ species defines a *nitrosonium pathway* of activation. In the latter case, the M–N–O moiety is highly bent (130–140°), the N–O bond length shortened, and its polarization increased by about three times in comparison to the free NO molecule. The second NO molecule can coordinate to the metal center and, when the spin density is largely on the metal, the dinitrosyl complex may thermally decompose giving rise to the N_2O formation via an inner-sphere route.

These two pathways thus largely depend on the characteristics of dinitrosyl conformation, which in turn depends on the characteristics of the metal and its charge as well. As discussed in detail by Pietrzyk and Sojka [32] in analyzing the characteristics of mononitrosyl complexes in various transition-metal-ion-exchanged zeolites, the coordination of NO leads to a pronounced redistribution of the electron and spin densities, accompanied by modification of the N–O bond order and its polarization. The zeolite framework participates in the electron density and spin-density repartitions. Therefore, not only the nature and valence state of the transition-metal ion determine the characteristics of the NO coordination complexes (and possible pathways of transformation) but also the site of the transition metal in the zeolite (Figure 24.1) and the zeolite framework, which determines the effectiveness of the zeolite in charge and spin-density redistribution.

The situation is therefore more complex than that usually considered from theoretical modeling. In addition, the question is whether the model of a single (isolated) metal complex is valid for this type of catalysts. The presence of multiple copper sites, as well as their possible electronic interaction that modifies the charge and spin-density redistribution, is a clearly issue. In addition, an unsolved question is also the coupling effect, that is, the influence of chemisorption coverage. As pointed out earlier, there is a relevant role of the zeolite framework itself in determining the configuration of the mononitrosyl complexes. This is also demonstrated by IR studies, which have provided evidence that NO chemisorption on Cu/MFI modifies the skeletal vibrations of the zeolite. There is thus a relaxation effect due to chemisorption, that is, the configuration of the sites at low chemisorption coverage is not exactly the same of that at high chemisorption coverage. It is still an unsolved question whether this effect could be also relevant in terms of reaction mechanism.

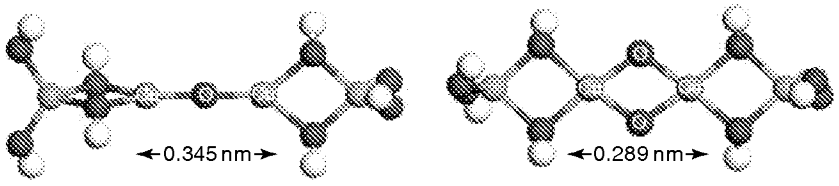
In addition to single copper sites, multinuclear copper sites could be present and be the active sites. In particular, much attention has been focused on the possibility of having two copper ions in a close enough proximity to act in concert for catalysis [43]. A number of possible single-O-bridged and di-O-bridged Cu pairs can be identified by theoretical modeling [34] (Figure 24.6) and are quite strongly bound:

$$\text{ZCuO} + \text{ZCu} \rightarrow \text{ZCu-O-CuZ}, \quad \Delta E = -60\ \text{kcal mol}^{-1} \tag{24.2}$$

$$\text{ZCuO}_2 + \text{ZCu} \rightarrow \text{ZCu-O}_2\text{-CuZ}, \quad \Delta E \sim -40\ \text{kcal mol}^{-1} \tag{24.3}$$

Oxygen desorption being the rate-limiting step in the decomposition of NO, a copper pair would facilitate this reaction. Kuroda *et al.* [44, 45], while studying the X-ray absorption spectroscopy of the oxidation–reduction processes during NO adsorption on Cu/MFI, concluded that zeolite having an appropriate Si/Al ratio, in which it is possible for the copper ion to exist as dimer species, may provide the key to the redox cycle of copper ion as well as catalysis in NO decomposition. The role of the multi-ionic structure of the active copper centers in Cu/MFI has also been indicated recently [46].

It is out of the scope of this review to go into the details of the different observations and conclusions on the reaction mechanism of the decomposition of NO. The comments above evidence the complexity of the problem and the still on-going discussion after many years even for such a simple reaction as the decomposition of NO on apparently well-defined copper ions in an ordered environment (the zeolite host).



Single O-bridged Cu pair

μ di-oxo bridged Cu pair

μ-η^2–η^2 di-oxo-bridged Cu pair

Peroxo bridge Cu pair

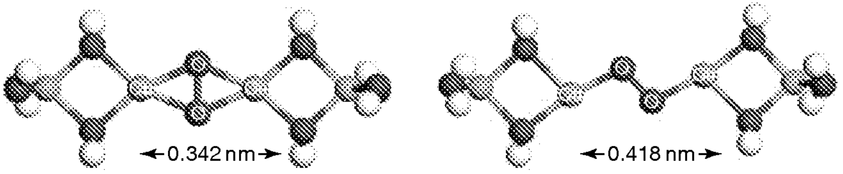


Figure 24.6 Spin-polarized local density approximation structures of O-bridged Cu pairs, calculated for a single T-site (AlO_4 tetrahedra). Adapted from [34].

The idea behind most of the hypotheses of the reaction mechanism, and the stimulus of several theoretical investigations, is that in Cu/zeolite a single well-defined site is present. As commented above, different copper sites are present, and they can change reversibly during the catalytic reaction or during the various procedures necessary for their characterization. The relocation of copper ions depending on temperature and gas composition, as well as the easy and spontaneous reduction of copper ions, is known. Furthermore, the site of the copper ions depends on the coordination of chemisorbed molecule.

For example, IR results show that the coordination of NO to Cu^+ ions moves them to more open positions in the cage. Broclawik *et al.* [47] reported recently that Cu^+ in site II binds NO molecule more weakly than it does in site III. It is due to the very stable planar threefold coordination to the framework O atoms that is achieved in site II. However, the heats of adsorption of the second NO molecule are only slightly higher at site III than at site II, because upon the first NO molecule adsorption on site II, Cu(I) ions are displaced to the position more resembling site III. Similarly, CO coordination on Cu^+ ions in ZSM-5 induces a displacement of copper ions, and the coordination of NO oxidizes Cu^+ ions as was observed [48].

As mentioned, by IR it is observed that the overtone bands of the skeletal vibration of the zeolite structure depend on the chemisorption coverage, indicating that the adsorption of a molecule on the copper site does not have only a local (short-range) influence. The local coordination of copper ions would depend on the chemisorption coverage.

All these indications point to the highly mobile situation of the copper ion species in the zeolite and thus limit considering the presence of a well-defined type of copper species, as made in theoretical approaches. We should also consider that a synergetic effect between the various copper species could be also present. It is known, for example, that extra-framework Al ions influence the acidity of the nearby Brönsted sites. Extra-framework copper ions may thus influence the behavior of isolated copper species either directly (e.g., participating in the reaction mechanism) or indirectly (e.g., acting as a sink for charge and spin density, thus influencing the stability of the different nitrogen oxide complexes or, instead, mediating the oxygen desorption and thus increasing the rate-limiting step).

All these aspects should be considered in discussing the reaction mechanism. As mentioned, the starting observation from reactivity tests is that the specific activity is higher in overexchanged Cu/MFI, for example, when the amount of copper ions is higher than the amount to balance all Al ions (one Cu^{2+} each for two Al ions). The typical maximum specific activity was observed for the level of exchange in the 100–140% range. This observation was the starting point to postulate that dimeric copper ions (with one or two bridging oxygen atoms) are the active sites. In overexchanged zeolites, the deposition of $[CuOH]^+$ species occurs during ion exchange and these species could form by dehydration of oxygen-bridged copper species or chains. The question, however, is whether they are the active sites. In fact, other factors could explain the need of overexchange: (i) multinuclear copper species (such as the Cu pairs shown in Figure 24.6) are the active sites and they form predominantly in overexchanged Cu/zeolites; (ii) isolated copper ions in more open positions (Cu_α sites), which show higher activity than the other isolated copper species, form only when the other positions are occupied and at high exchange level; and (iii) there is a synergism between isolated and multinuclear copper sites, but only when they are in close proximity (as occurs in overexchanged samples). More interpretations are also possible, but already these three show the difficulty in reaching unique conclusions.

We may conclude, as is often remarked, that these zeolites containing metal ions in extra-framework positions can be considered as enzyme-like materials because of the presence of an isolated metal ion surrounded by a 3D environment that orients the adsorption and reactivity of the incoming molecules. The brief discussion reported above shows that the situation is far more complex, with multiple sites that could be in a dynamic equilibrium. Also from the characterization perspective, the system is more complex and far more difficult that initially supposed. This is one of the reasons for the still on-going debate on the mechanism of one of the (apparently) simplest reactions that can be considered, namely the decomposition of NO.

From the application point of view, the main characteristic is the possibility to have isolated and well-accessible metal ions, but typically for very low loadings, which can determine a low productivity per total catalyst weight. The redox and reactivity characteristics of these metal ions, however, are different from those of the same ions supported over conventional oxides (silica, alumina, etc.). The relatively high mobility, however, determines a general low stability especially under hydrothermal conditions.

In the case of decomposition of NO on Cu/MFI, the presence of gaseous O_2 decreases the reaction rate because it competes with NO for the chemisorptions on reduced copper ions. The self-reduction of copper ions is thus the rate-limiting step.

Recently, however, alternative zeolitic materials have been proposed that apparently overcome this problem. Shi *et al.* [49] investigated the direct decomposition of NO in the presence of oxygen over a series of Fe–Mn/H-beta catalysts with Mn/Fe = 1. When Mn is incorporated to Fe/H-beta, NO_x conversion is improved, and the active temperature window is lowered. The Fe(5%)–Mn(5%)/H-beta exhibits the highest activity. Neither O_2 nor CO_2 inhibits the reaction. These results thus prove that there is still ample research space to develop improved Me-zeolite catalysts for the decomposition of NO.

24.3
Fields of Applications

Transition-metal-containing zeolites have been very successfully applied in refinery and petrochemistry, but a significant interest has also raised their application in the field of environmental protection although their practical use is still much more limited as shown by the number of studies on these catalysts.

There are two main areas of applications of zeolites in the field of environmental catalysis, within the limits discussed in the introduction:

- conversion of nitrogen oxides (NO_x and N_2O) and
- conversion of VOCs.

Other areas of applications include wastewater treatment, photocatalytic conversion of pollutants, air purification, and soil remediation, although often it is not well demonstrated that zeolite-based catalysts offer clear advantages over alternative catalysts such as oxide-supported materials. An overview of the applications of zeolites in environmental catalysis has been reported by Larsen [50] and earlier by Delahay and Coq [51]. More specific reviews to be cited are the followings:

- the use of zeolite catalysts for dehalogenation processes [52];
- the use of metallo-zeolites (particularly, Co/MFI, Fe/MFI, ferrierite (FER), and mordenite (MOR)) for NO_x selective catalytic reduction (SCR) with hydrocarbons [19];
- the use of metal-ion-exchanged zeolites as $DeNO_x$ catalysts for lean-burning engines [53];
- the reaction mechanisms of lean-burn hydrocarbon SCR over zeolite catalysts [54], and the use of zeolites in the field of nitrogen monoxide removal [55, 56];
- the quantum mechanical modeling of the properties of transition-metal ions in zeolites, with particular reference to the SCR of nitrogen oxides in the presence of NH_3 [57];
- the use of zeolites in pollution control, in particular the abatement of NO_x and N_2O emissions from stationary sources [58];
- the characterization, modeling, and performances (particularly for NO_x removal from the tail gas of nitric acid plants) of Cu^I/Cu^{II}-Y zeolites [59];
- the SCR of NO_x by ammonia (NH_3-SCR) over metal-exchanged zeolites (especially Fe/MFI) for diesel engine exhaust applications [60];

- the use of transition-metal oxides (Ti, V, Mo, Cr) incorporated within the framework of zeolites as well as transition-metal ions (Cu^+, Ag^+) exchanged within the zeolite cavities for the photocatalytic conversion of NO_x (NO, N_2O) or the reduction of CO_2 with H_2O [61], or as photoanode [62];
- the use of microporous and mesoporous materials to prepare single-site photocatalysts [63, 64] or to enhance the photocatalytic activity of TiO_2 through spatial structuring and particle size control [65];
- the use of zeolite and other novel materials for wastewater treatment [66];
- the use of natural zeolites for environmental applications in water purification [67] and greywater treatment [68];
- the use of zeolites in the wet hydrogen peroxide catalytic oxidation of organic waste in agro-food and industrial streams [69]; and
- the use of zeolite films for trace pollutant removal from air, and other applications [70].

Selected examples of the uses of zeolites as environmental catalysts are reported in Table 24.1 to show the very broad range of materials and applications that have been investigated. However, it should be remarked that their commercial application is still dominated by their adsorption properties rather than by their use as catalysts [71], at least for for niche applications, although we are probably close to seeing their use in large-scale applications. As an example, Zeolyst International (one of the world's leading producers of zeolite catalysts) reports in its web site (*www.zeolyst.com*) the use of zeolite for environmental waste reduction and secondary treatment of effluents (reduction of NO_x and VOCs, including automotive cold-start emissions), as well as the removal of automotive combustion products (particularly for lean NO_x), even though only their "potential" use is indicated.

BASF Catalysts (*www.catalysts.basf.com*, the world leader in catalyst manufacture) has recently announced (November 2008) at the SAE (Society of Automotive Engineers) International Commercial Vehicles Congress in Chicago a new copper-zeolite SCR catalyst that provides more than 90% NO_x (nitrogen oxides) removal for on-road and off-road heavy-duty diesel vehicles. The catalytically active component is coated on a ceramic honeycomb and will be used with urea as a reductant. On January 2009, the opening of a new R&D facility focused on commercializing the new zeolite catalysts that would boost diesel and gasoline yields compared to conventional zeolites was also announced.

A number of papers at the SAE (the most important society in this field) meetings from leading car manufacturers indicate that Cu/MFI or Fe/MFI zeolites are close to being introduced commercially for the control of diesel emission. For example, researchers of Ford Motor Co. (USA) [101] reported that the SCR is a viable option for the control of oxides of nitrogen (NO_x) from diesel engines using urea as a reductant, in particular to meet certification under Tier 2 Bin 5 (USA) emission requirements (passenger and light-duty diesel vehicles will require up to 90% NO_x conversion over the Federal Test Procedure – FTP).

Currently, copper-zeolite (Cu/zeolite) SCR catalysts are favored for configurations where the exhaust gas temperature is below 450 °C for the majority of operating

Table 24.1 Selected examples of the use of zeolites as environmental catalysts (Y, FAU structure; ZSM-5, MFI structure; Beta, BEA structure; ferrierite, FER structure).

Catalyst	Application	References
Cu/FAU	NO_x removal from tail gas of nitric acid plants	[51]
Fe/MFI	N_2O abatment in nitric acid plants	[72]
Cu/MFI	NO-assisted N_2O decomposition	[73]
Cu/BEA	NO_x conversion with propane	[74, 75]
Cu/MFI	NO_x conversion with decane	[76]
Fe/MFI, Cu/MFI	Urea-SCR (diesel vehicles)	[77]
Ag/MFI, Ag/BEA	NO reduction with propane in the presence of H_2	[78]
Ag/FAU	NO_x reduction with oxygenates	[79]
Ir/MFI	Simultaneous removal of soot and NO_x	[80]
Zeolites (as additives)	NH_3 transient storage to enhance NO_x conversion in storage-reduction catalysts	[81]
Co, Mn/FER	NO_x SCR with methane	[82]
Pd/MCM-41	Low-temperature catalytic combustion (CO, HC)	[83]
Cu/ and Pt/MFI on cordierite	VOC removal	[84]
CeO_2/FAU	Deep oxidation of 1,2-dichloroethane	[85]
Pt/P-MCM-41	Catalytic combustion of trichloroethylene	[86]
Zeolites and MCM-41	Catalytic ozonation of toluene	[87]
Pd/BEA, Pd/FAU	VOC catalytic ozonation	[88]
Fe/MFI, Cu/MFI	Wet oxidation of pollutants with H_2O_2	[69, 89–92]
Pd/hydrophobic FAU	Hydrodehalogenation of chlorocarbons in water	[52]
Natural zeolites	Soil amendment, wastewater purification	[93]
Fe/MFI	(Cr/VI) photoreduction for water and soil remediation	[94]
Ti- and TiO_2-micro and mesoporous materials	Photocatalytic elimination of pollutants (air)	[62–64, 95, 96]
FAU, MFI	Elimination of nitrosamines in cigarette smoke	[97, 98]
Fe/MFI	Oxidation of lignin with H_2O_2 (pulp and paper mill wastewater)	[99]
Ag/clinoptilolite	Water disinfection	[100]

SCR, selective catalytic reduction.

conditions, while iron zeolite (Fe/zeolite) SCR catalysts are preferred where NO_x conversion is needed at temperatures above 450 °C.

The key issue in the control of NO_x emissions of light-duty diesel engines is to have activity at very low temperatures (the catalytic converter has a temperature below 350 °C for most of the emission cycle), while higher temperature performances and stability is more critical in heavy-duty diesel engines.

The selection of Cu/zeolite or Fe/zeolite SCR catalysts is based on the different performance characteristics of these two catalyst types. Cu/zeolite catalysts are generally known for having efficient NO_x reduction at low temperatures with little or no NO_2, and they tend to selectively oxidize ammonia (NH_3) to N_2 at temperatures above 400 °C, leading to poor NO_x conversion at elevated temperatures. Fe/zeolite catalysts are very efficient at NO_x conversion at temperatures as high as 600 °C or even higher, but they are not as efficient as Cu/zeolite catalysts at lower temperatures in the absence of NO_2. A combined SCR system consisting of an Fe/zeolite catalyst in front of a Cu/zeolite catalyst could thus widen the operating temperature range of the SCR catalyst. At low temperatures, the Cu/zeolite improves NO_x conversion efficiency versus an Fe-only system. At elevated temperatures, the Fe/zeolite is more active. In addition, one can overdose NH_3 at elevated temperatures with the combined Fe–Cu system without NH_3 slip, while the Fe-only system leads to substantial NH_3 slip when overdosing.

One of the key aspects of the performance is the ability of the zeolitic materials to store both hydrocarbons and ammonia [102]. Ammonia storage on zeolite has a beneficial effect on NO_x conversion; hydrocarbons, however, compete with ammonia for storage sites and may also block access to the interior of the zeolites, where the bulk of the catalytic processes take place.

Another issue is the hydrothermal stability. The high-temperature SCR deactivation is unavoidable due to the requirements necessary to actively regenerate diesel particulate filters and purge SCRs from sulfur and hydrocarbon contamination. Careful temperature control of these events is necessary to prevent unintentional thermal damage, which is not always possible. As a result, there is a need to develop thermally robust SCR catalysts. Fe/zeolite formulations are known to exhibit superior hydrothermal stability over Cu/zeolite formulations [103]. However, current Fe/zeolite formulations are not very active for NO_x conversion in the desired 200–350 °C temperature regime under conditions of low NO_2/NO_x ratios. Cu/zeolite, however, may be stabilized, and the latest state-of-the-art Cu/zeolite formulations show remarkable high-temperature hydrothermal stability up to 950 °C while maintaining stable low-temperature NO_x activity [103].

The deactivation by sulfur is another issue [104]. Even with the use of ultralow-sulfur fuel, sulfur poisoning is still a durability issue for base metal/zeolite SCR catalysts. The impact of sulfur is more severe on Cu/zeolite than on Fe/zeolite SCR catalysts for the NO_x activity, but the sensitivity of thermal aging status to the sulfur poisoning impact is different [104]. The most thermally durable SCR catalysts are not necessarily the most resistant to sulfur poisoning. Control of sulfur poisoning and strategy for $DeSO_x$ might be different depending on the formulation and thermal aging status.

The alternative catalytic system for urea-SCR is based on vanadium oxide supported on titania. These SCR catalysts are now available in mass production for heavy-duty vehicles in Europe. The SCR-active material can either be applied as a coating on an inert carrier honeycomb or be worked up to a homogeneous honeycomb by extrusion. The homogeneously extruded catalysts have the advantage that they contain 100% of the active material. Especially in the lower temperature range, higher NO_x conversions can be achieved compared to coated systems. In addition, they feature superior resistance against poisoning (e.g., by sulfur).

However, to establish this technology for the new US 2010 and EURO 6 systems containing a particulate filter and to meet the demands of the US market for a catalyst that does not contain vanadium, there is the need to use alternative zeolite-based catalysts. The reason for not using vanadium in these future systems is that filter regeneration demands high-temperature stability of the SCR catalyst and that there are concerns about vanadium loss during operation.

Researchers of $SINO_x$ Emission Control (former Argillon GmbH, and now Johnson Matthey Catalysts Germany) [105] have developed a homogeneous catalyst honeycomb catalyst consisting of 100% active material based on zeolite and containing no vanadium. The catalyst features superior low-temperature activity and provides high-temperature stability to withstand particulate filter regenerations upstream in the exhaust. Additionally, the low bulk density helps to reduce efforts in canning and system design.

Another relevant example of zeolites as environmental catalysts, which will probably become a major application in the near future, concerns the abatement of N_2O emissions in the production of nitric acid. The industrial production of nitric acid (HNO_3) involves oxidizing ammonia (NH_3) with air over a platinum/rhodium gauze catalyst to produce nitrogen oxides. This process yields nitrogen monoxide (NO), which then reacts with oxygen and water to form nitric acid. However, it also produces nitrous oxide (N_2O) – a powerful greenhouse gas and ozone killer (N_2O has a greenhouse effect about 300 times higher than that of CO_2 [106]) – as an undesired by-product. Unlike NO, the nitrous oxide is not involved in the HNO_3 production process and is emitted into the atmosphere with the tail gas.

The N_2O emissions in nitric acid plants vary from about 3 to 4 kg of N_2O per metric ton of HNO_3 to as much as 20 kg of N_2O per metric ton of HNO_3 depending on the type of nitric acid plant. An estimated 400 000 metric tons of nitrous oxide is emitted each year by nitric acid plants worldwide. Nitric acid plants are now the largest single source of greenhouse gas emissions among industrial manufacturing facilities. Although still very few countries have introduced limits on emissions of N_2O from nitric acid plants, the recent agreement on greenhouse gas emissions will soon extend these limits to more countries or there will be the need to include N_2O emissions in the implementation of mechanisms of Kyoto Protocol carbon trading protocols (Emissions Trading, Joint Implementation, and Clean Development Mechanism).

Uhde (a world leader in nitric acid technology) in collaboration with Süd-Chemie AG (a world leader in special zeolite manufacture) has developed a technology for removing N_2O from the nitric acid production process (in particular from the tail gas), which is based on the use of Fe/MFI catalysts [107, 108] (see also Uhde publications no. 5000008.00 – EnviNOx® Setting Emission Standard for Nitric Acid Plants – which can be downloaded from the site *www.uhde.eu*). The Fe/MFI-based catalyst is active either in decomposing N_2O into N_2 and O_2 – an effect increased significantly by the presence of NO_x in the tail gas (cocatalytic NO_x effect; the NO_x acts as scavenger for the oxygen left on the iron site as a result of the N_2O decomposition and thus accelerates the reaction rate, because oxygen desorption is the rate-limiting step in the reaction), or by reducing N_2O using various reducing agents, such as hydrocarbons [109, 110]. In addition, the iron zeolites have also proved to be excellent $DeNO_x$ catalysts in a wide temperature window. The special iron-exchanged zeolite catalysts for use in its EnviNOx® process are indicated EnviCat®-N_2O and EnviCat®-NOx, and are commercialized in the pellet form.

The advantages of these zeolite catalysts compared to conventional $DeNO_x$ catalysts are their resistance to typical catalyst poisons, such as sulfur or chlorine, and their operating range over a wide temperature window of approximately 200–600 °C.

There are different possible EnviNOx® process variants: (i) catalytic decomposition of N_2O and the catalytic reduction of NO_x, (ii) catalytic reduction of N_2O and NO_x, and (iii) catalytic decomposition of N_2O. Figure 24.7 shows the simplified flow sheet of the first two process variants [111]. In the first option, the reactor is usually located between the final tail gas heater and the tail gas turbine and contains two catalyst beds filled with iron zeolite catalysts operating at the same pressure and temperature, and a device for the addition of NH_3 between the beds. In the first O stage, the N_2O abatement is effected simply by the catalytic decomposition of N_2O into N_2 and O_2. Owing to NO_x promotion of the decomposition of N_2O, the $DeNO_x$ stage is downstream. This process variant is especially applicable for tail gas temperatures between about 425 and 520 °C. The first commercial-scale plant using this option was realized in 2003 by Uhde in Linz (Austria) for Agrolinz Melamine International (AMI), which produces about 1000 t per day of HNO_3 and in which the tailgas has a flow rate of 120 000 $Nm^3\ h^{-1}$ at a temperature of 430 °C. A conversion rate of 98–99% is achieved.

In the second variant, N_2O is removed by catalytic reduction with a hydrocarbon such as natural gas or propane. Unlike with N_2O decomposition, the NO_x content of the tail gas inhibits the N_2O reduction reaction. It is, therefore, necessary to completely eliminate the NO_x in the tail gas. Depending on the tail gas composition and the particular operating conditions, this can be accomplished in a $DeNO_x$ unit located upstream of the DeN_2O stage or, preferably, simultaneously with the N_2O reduction in a single common stage. Either the common stage process or the two-stage process with its hydrocarbon reducing agent feed mixer can be accommodated in a single reactor vessel. This option is suitable for temperatures between about 300 and 520 °C depending on the specific conditions in the nitric acid plant. The first commercial plant using this option was realized in 2006 in Egypt for the company Abu Qir Fertilizers. It uses ammonia for NO_x SCR and methane for N_2O SCR. The plant has a nitric acid production of 1870 t per day and the tail gas flow rate is 225 000 $Nm^3\ h^{-1}$ (temperature = 410 °C). The N_2O conversion is 99%, while NO_x outlet concentration is below 1 ppm.

Several other plants were realized by Uhde/SCAG for a total removal of about 8 million tons per year of equivalent CO_2. Other companies have also developed similar processes using Fe/zeolite catalysts.

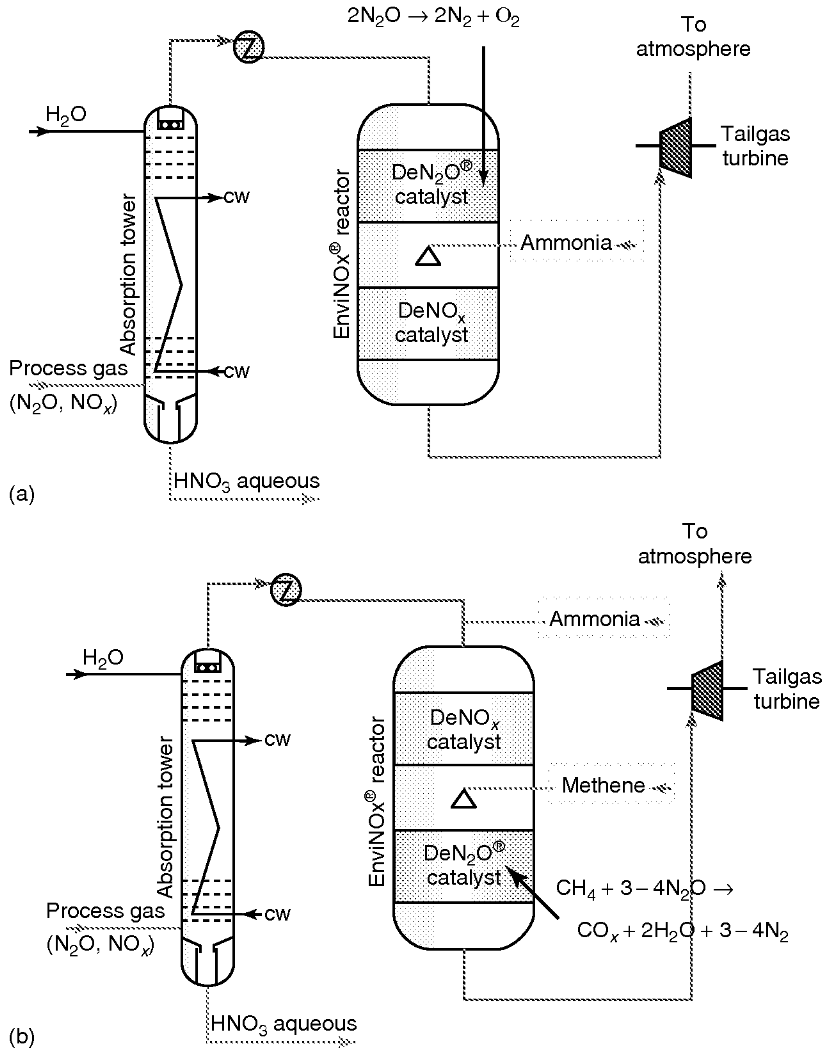


Figure 24.7 EnviNOx® (Udhe) process of catalytic decomposition of N_2O and catalytic reduction of NO_x (a), and catalytic reduction of N_2O and NO_x (b). DeN_2O catalyst = Fe/MFI, $DeNO_x$ catalyst = Fe/MFI or $V_2O_5/TiO_2/WO_3$. Adapted from [111].

The choice of the hydrocarbons for nitrous oxide abatement depends on various criteria [112]: (i) DeN_2O activity and operation temperature, (ii) hydrocarbon utilization, that is, the selectivity to react with N_2O in O_2 excess, (iii) emission of CO and CO_2, (iv) sensitivity to NO and NH_3, and (v) cost. Alkanes are generally more effective reducing agents than unsaturated hydrocarbons. In particular, alkynes require a higher temperature to activate N_2O and are unselective because of their proneness to react with O_2. Ethane is an optimal reductant, featuring a high DeN_2O activity, high selectivity, and compared to methane, a lower degree of inhibition by NO.

Usually, steam activation is necessary to promote the performances of Fe/MFI catalysts, but the preparation method has also a relevant effect. Other zeolite structures have also been shown to be active in the reaction. Recently, Sobalik *et al.* [113] showed the superiority of Fe/FER over Fe/BEA and Fe/MFI with Fe/Al ratios below 0.15 in the decomposition of nitrous oxide in the absence of NO. The higher performances were tentatively attributed to the presence of a unique FER structure containing two close collaborating Fe(II) cations accommodated in the cationic sites of FER. This local structure with unique spatial properties could, due to their distance and orientation, provide for N_2O splitting by mutual action of two adjacent iron cations in Fe/FER. These isolated cationic sites are located in two adjacent β sites facing each other across the channel (Figure 24.8). The distance between two iron cations is about 7.5 Å. A strong attraction between the oxygen atom of Fe$\cdots$ NNO complex and the adjacent iron cation (distance O$\cdots$ Fe <3 Å) could be expected.

Regarding the probability of the existence of the active sites with such an arrangement of close Fe(II) cations, the occupation of various cationic positions by divalent cations indicates that the two close Al atoms forming mainly β sites prevail in the FER framework [114]. If the iron exchange leads to a random occupation of the cationic sites, then at least 5% contains two Al atoms in the β site balancing Fe(II) in the arrangement that a neighboring unit cell also accommodates Fe(II) in the β site, thus forming the active site containing two closely collaborating Fe(II) cations accommodated in the cationic sites.

Such an arrangement of two Fe(II) cations located in the β sites of two neighboring unit cells allowing the formation of collaborating Fe(II) cations in Fe$\cdots$ Fe

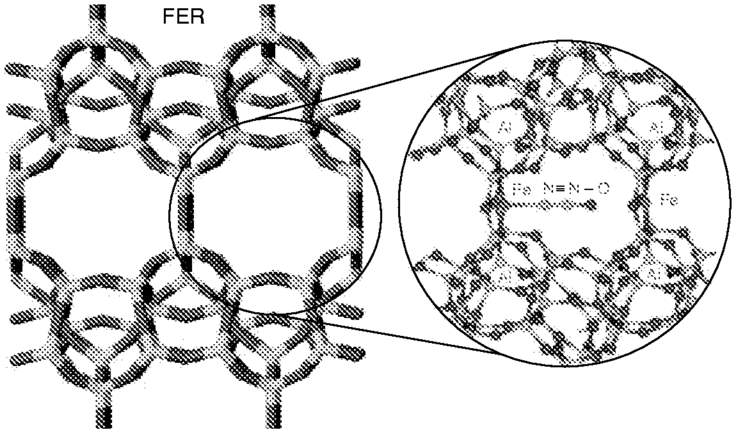


Figure 24.8 Periodic DFT-optimized structure of Fe/FER including N_2O interacting with two Fe cations occupying adjacent beta cationic positions. Adapted from [113].

pairs is quite unique and exists only for the FER sample used because of two reasons: the distribution of Al atoms in this FER framework as well as the optimal structural arrangement of the β sites in the FER framework.

Sobalik *et al.* [113] noted that for highly loaded Fe/zeolites and for the NO_x-assisted N_2O decomposition, the catalytic activity could be connected to other types of iron sites. Comparing Fe/MFI and Fe/BEA, Pérez-Ramírez *et al.* [115] claimed that the microporous matrix does not play a decisive role in the decomposition of N_2O, provided similar forms of iron are present in the final catalyst. However, the results appear less convincing, but it is not the aim here to discuss in detail the nature of the active sites. It is to be mentioned, however, that many groups have investigated iron in MFI and other zeolitic structures [116–121]. A review on the properties of iron in various zeolite structures has been recently published by Nováková and Sobalík [122].

A recent review of Pirngruber [123] has compared in detail the properties of iron- and copper-containing zeolites in the decomposition of N_2O and NO, and other reactions. In fact, a common aspect of the various mechanisms also discussed here is the formation of a Me–O active species, which can be usefully applied in selective oxidation reactions, such as the benzene hydroxylation to phenol and methane to methanol reactions.

Pirngruber [123] observed that iron zeolites work best as selective oxidation catalysts at low iron concentrations. Moreover, the active sites for selective oxidation react specifically with N_2O, but not with O_2. This indicates that site isolation is an important premise for obtaining selective iron zeolite catalysts, although this aspect is in contrast with the conclusions reported above by Sobalik *et al.* [113]. The activity of iron zeolites increases when they are pretreated under steaming conditions, which causes the partial reduction of Fe^{3+} to Fe^{2+} and probably creates lattice defects. The Fe^{2+} sites in the vicinity of lattice defects are most probably the sites where the surface oxygen atoms, which were generated by dissociation of N_2O, are stabilized in a highly reactive form. In agreement with this conclusion, we earlier reported [124] the model of active sites in benzene hydroxylation reported in Figure 24.9 based on $(-Si-O)_2Fe^{2+}$ species located at zeolite defect sites which react with N_2O forming a $(-Si-O)_2Fe^{4+}{=}O$ in equilibrium with the $(-Si-O)_2Fe^{3+}-O^-$ species which was proposed to be the effective hydroxylating species.

Pirngruber [123] also observed that copper zeolites catalyze similar reactions as their iron analogs, but there are some distinct differences. Cu zeolites work best at high copper loadings and their catalytic activity is strongly related to the formation of Cu dimers. He concluded that the active site is a bis(μ-oxo)dicopper species that is generated by the reaction of a Cu^+ dimer with N_2O, NO, and O_2. However, as commented before, there is less than conclusive evidence on this statement. It is true, however, that the ability to react with O_2 strongly distinguishes the active sites in copper zeolites from the selective oxidation sites in iron zeolites. There are thus not only analogies but also relevant differences between the two systems that have to be taken into account in studying their use as catalysts.

As shown in Table 24.1, there are many types of zeolites investigated other than Cu/ and Fe/zeolites for the conversion of nitrogen oxides. To look at the general

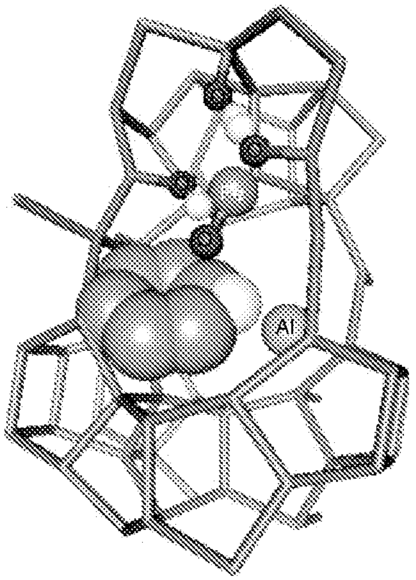


Figure 24.9 Model of the iron active sites ($(-Si-O)_2Fe^{2+}$ species located at zeolite defect sites) for benzene hydroxylation in Fe/MFI. Adapted from [124].

interest on these systems, Table 24.2 reports a short survey made using SCI-Finder on the number of publications (limiting to journals/review and English as the language) in the last 10 years using keywords as "Zeolites and ... ". In general, it may be observed that there is still a large interest on the use of zeolites as environmental catalysts and they represent a significant fraction of the publications on the use of zeolites as catalysts (see last items in the Table 24.2). It may be also observed that the new and more correct name of "microporous materials" is much less used.

In terms of topics, the area of nitrogen oxide conversion is the dominant, even though already a large part of the activity was made before the year 2000, as shown also in this contribution. VOC and catalytic combustion is a second large area of interest, but the potential for practical applications is much more limited, as discussed later.

The general area of water treatment (which includes wet oxidation, peroxidation, etc.) is also quite significant in terms of the number of publications. It should be noted, however, that a large part of the publications deals with the use of zeolites (synthetic and natural) as adsorbent rather than as catalysts.

Two major fields of application in this area are given below:

1) Use of Cu/ or Fe/zeolites as heterogeneous Fenton catalysts to activate H_2O_2 and convert organic pollutants (dyes, recalcitrant, or toxic organics, etc.) to CO_2. The technique can be used, in particular, as pretreatment to remove toxic chemicals and facilitate consecutive biological treatment (aerobic, anaerobic)

Table 24.2 Number of publications (SCI-Finder) in the period 1999–2009 (limited to journals/review and English) find using as keywords "Zeolites and … " or "Microporous materials and … ", where the second keyword(s) are those reported in the following list. The results refer to the number of publications where the keywords are present as entered, or when both are found as concepts. Analysis updated on Jan. 15th, 2010.

Topic	Both of the Concepts	As entered
Zeolite and		
NO_x	867	6
N_2O	633	5
Nitrogen oxides	1270	1
$DeNO_x$	112	9
SCR	552	48
VOC	272	1
Catalytic combustion	565	1
Dehalogenation OR hydrodehalogenation	62	5
Wastewater	1124	69
Water treatment	1424	1
Wet oxidation	84	–
Wet peroxidation	47	–
Photocatalytic OR photocatalyst	989	112
Photodegradation	88	1
Photo	1848	2
Ozone	108	9
Nitrate	1367	11
Membrane	1662	747
Organic pollutants	95	–
Non thermal plasma	41	–
Environmental catalysis OR environmental catalyst	688	3
Catalysis	14944	123
Catalytic	14640	211
Catalyst	14640	3856
Microporous materials and		
Catalysis	813	11
Catalytic	756	6
Catalyst	751	1
Environmental catalysis OR environmental catalyst	38	–

or as post-treatment to the biological step to decolorize the water [69, 91, 125]. In terms of application, however, the major limitation is the leaching of the transition metal. Zeolites offer the advantage of a better protection of the active center from the fouling by humic and other macromolecular substances, but in general the advantages over oxide-based catalysts are limited.

2) Use of Pd (or other noble metal) zeolite for hydrodehalogenation of organohalogen compounds of environmental concern [52]. Pd/zeolite, in comparison with other Pd-based catalysts, may have the advantage of better hydrophobicity (in high Si/Al materials), and this could be an advantage for a higher stability

against ionic poisons. An example is the use of Pd-ZSM-23 (1 wt% Pd) for catalytic hydrodehalogenation of bromobenzene [126]. The activity is good as well as the recyclability, but there is no cost effectiveness in using these catalysts. The presence of alkali ions is important for the activity. Kanyi *et al.* [127] have discussed the dehalogenation versus dehydrohalogenation reactions of alkyl halides in zeolite NaX (Faujasite). Balance between substitution and elimination can be understood in terms of various factors: (i) Relative rates of C–X (X = Cl, Br, I) and C–H cleavage, which, upon substitution, is predominant when the C–X cleavage rate is greater than the C–H cleavage rate. C–X cleavage rates decrease in the order I > Br > Cl. (ii) Relative stability of the framework alkoxy species as a result of steric hindrance in the zeolite. This stability decreases in the order primary > secondary > tertiary.

The area of use of micro- and mesoporous materials (containing isolated ions such as Ti or nanosized oxide particles such as TiO_2) is a very fast growing area of interest. Many reviews have appeared on this topic [61–65, 95, 96 128–130] and the number of publications is exponentially rising, as also seen in Table 24.2. However, from the application point of view, this large interest does not correspond to significant advantages that may be provided by these systems.

It is true that the compartmentalized intracrystalline void space of zeolites allows incorporating and organizing photoactive guests that can be used as photocatalysts. The rigid micropores allow assembly of multicomponent systems comprising antennas and relays reminiscent of natural photosynthetic centers. Besides inorganic metal-oxide clusters, zeolites as host are particularly attractive to construct organic photocatalysts since the guest becomes significantly stabilized by incorporation [96]. However, this potential has still to be demonstrated to lead to practical applications as catalysts, besides in perhaps niche cases.

Large relevance has also been given to photocatalytic solids, in which the absorption occurs at isolated, spatially well-separated centers, such as isolated Ti ions in micro- or mesoporous materials (single-site photocatalysts) [63]. Their use for the decomposition of NO to N_2 and O_2 and for the selective oxidation of CO in the presence of H_2 has been widely discussed [95]. However, the reaction rates are too low and they do not offer advantages over alternative photocatalytic materials. It should be noted that isolated Ti ions absorb in the UV region, and thus these systems go in the opposite direction of the recent large effort in developing photocatalysts active in the visible region. The same is true when the dimension of the TiO_2 particles is reduced by incorporation in micro- or mesoporous materials [65]. There is an advantage of an increase in the surface area, but a blue shift of the absorption band overshadows often the first advantage.

However, the inclusion of photoactive centers in an ordered porous matrix may have the potential to allow shape-selective catalysis. The classic example is the use of the microporous titanosilicate ETS-10 [131, 132]. The photoactivated ETS-10 shows catalytic activity driven by the size and polarity of the substrates. ETS-10 efficiently catalyzes the conversion of substrates of a size larger than the pore diameter of ETS-10. In contrast, the reactivity of small substrates depends strongly on the substrate polarity; less polar substrates show higher reactivity on ETS-10. Large substrates or less polar substrates hardly diffuse inside the highly polarized micropores of ETS-10 and, hence, react efficiently with the hydroxyl radicals formed on titanol (Ti-OH) groups exposed on the external surface of ETS-10. In contrast, small polar substrates diffuse easily inside the micropores of ETS-10 and hardly react with hydroxyl radicals, resulting in low reactivity. The photocatalytic activity of ETS-10 may be applicable to selective transformations of large reactants or less polar reactants to small polar products, enabling highly selective dehalogenation and hydroxylation of aromatics.

Zecchina *et al.* [133] have investigated in detail how to tailor the selectivity of Ti-based photocatalysts (TiO_2 and microporous ETS-10 and ETS-4) by modifying the surface morphology and electronic structure. While microporous ETS-4 and ETS-10 exhibit significant selectivity in the photodegradation of various molecules using both UV and visible lights, TiO_2 (P25) selectivity is observed with visible light only. This means that besides the inverse shape-selectivity effect already observed for the microporous materials [132], selectivity may be achieved also by selecting the excitation light in accordance with the electronic transition of the adsorbed molecule. In such a case, the photodegradation may occur if the conduction band of the Ti-based material is opportunely matched with the lowest unoccupied molecular orbital (LUMO) level of the adsorbed molecule so that it can receive the electron of the excited adsorbate (concept of band alignment).

These materials, thus, offer interesting opportunities for selective degradation of some specific organic compounds in solution, but the practical cases where these properties could be used in a cost-effective way with respect to alternative solutions (for example, removal using selective adsorption, membranes, etc.) are quite limited.

Therefore, notwithstanding the large research interest on the use of micro- and mesoporous-material-based photocatalysts for environmental protection, there is no apparent match, at least at the current state of the art, between research effort and potential of application.

The elimination of VOCs from gas emissions is another area in which there is a mismatch between research effort and potential of application. However, in this case, there are some examples of commercial application. We limit the discussion here to the use of zeolite (or related materials) as catalysts, not as adsorbents.

Zeolites are extremely good adsorbents for many applications involving the adsorption of VOCs from polluted water or air. The main characteristic, besides the high surface area and controlled porosity, is the possibility to tailor the hydrophobic/hydrophilic properties for applications in particular chemical environments. For example, MFI could be functionalized with octamethylsilane to drastically increase the hydrophobicity and greatly enhance the adsorption of aromatics in aqueous solution. Zeolite rotor concentrators are commercially available (for example, by Munters – *www.munters.us*) for the removal of diluted VOCs from the air stream by adsorption onto the hydrophobic zeolite. After passing through the rotor, the cleaned air is discharged into the atmosphere. The rotor continuously rotates at several revolutions per hour, transporting VOC-laden zeolite into the regeneration zone and the regenerated zeolite back into the process zone.

In the isolated regeneration section, a small, heated stream of air is drawn through the rotor to desorb the VOCs from the zeolite, forming a highly concentrated VOC-laden air stream. This concentrated stream is normally only 5–10% of the process volume and is typically sent to a small oxidizer.

The zeolite operates only as an adsorbent. Although, in principle, it is possible to introduce a catalytic active component (i.e., to use Pd-MFI, for example), the rate of desorption is typically faster than the rate of heating and, thus, it is not possible to avoid the downstream oxidizer (usually a catalytic converter).

In terms of commercial use of zeolite or related materials as catalysts in VOC abatement, the cost effectiveness is typically not in favor of these materials. However, their hydrophobic properties (in high-silica materials) could be useful in some cases. Zeochem (*www.zeochem.ch*), for example, commercializes various strongly hydrophobic high-silica zeolites for the removal of VOCs from air, although their main use is in regenerative adsorber systems.

The most common metals introduced in zeolites (typically by ion exchange) to increase VOC oxidation activity are noble metals (Pt and Pd) and some transition metals (Sr, Co, Cu, Fe, Mn, and V), but the activity varies greatly with the type of VOC used. Zeolites offer a better dispersion with respect to metal oxides, and thus, for example, the noble metal loading in zeolites is typically lower than in equivalent metal-oxide-supported materials. This could appear an advantage, but the higher substrate cost and greater difficulty in preparing in a technically suitable form (for example, to deposit on a ceramic monolith) make zeolitic catalyst less cost effective in the end. However, in some cases, they show a higher resistance to deactivation than oxide catalysts [134].

An interesting area is chlorinated VOC abatement. The problem is related to the deactivation of protonic zeolites in the catalytic oxidation of these compounds [135]. In general terms, coke formation is the main reason for zeolite catalyst deactivation, but the coke derives from the reaction intermediates (for example, vinyl chloride, which results from a first dehydrochlorination step of 1,2-dichloroethane [135]). Strong acid Brönsted sites are necessary for the reaction. In Y zeolites, the development of strong acidity due to dealumination leads to a large increase in the activity [136]. Likewise, 50% dealuminated sample showed an improved catalytic behavior for the destruction of other typical chlorinated pollutants, namely, dichloromethane (DCM) and trichloroethylene (TCE). The ease of destruction was found to follow the trend 1,2-dichloroethane > dichloromethane > trichloroethylene [136].

24.4
Summary and Outlook

A large variety of zeolite materials have been studied for use in environmental applications from the conversion of nitrogen oxides over transition-metal-exchange zeolites to the conversion of VOCs on noble metal or non-noble-metal containing micro- or mesoporous materials (typically hydrophobic). The presence of a well-defined pore structure and topology provides a unique environment for catalysis, although most of the expectations to have well-defined (enzyme-like) materials have to be reconsidered. Some of the problems and issues in terms of the nature of the active sites and reaction mechanism have been discussed, not with the aim to provide a complete review or to arrive to definitive conclusions but to present the complexity of the problem and the limitations of some conclusions.

In terms of applications, Cu/ and Fe/zeolites (MFI, FER) are the most interesting and relevant, and very soon their large use in the control of emissions of NO_x from light-duty diesel engines will appear. A second relevant area concerns their use in the removal of N_2O or combined removal of N_2O and NO_x from the tail gas of nitric acid plants. Although already in use, a marked expansion of this application is expected as a consequence of the increasing concerns and regulations on greenhouse gas emissions.

More limited is the use of these materials in VOC combustion, although some opportunities in particular related to high-silica zeolite materials with strong hydrophobic properties exist. Lower perspectives are instead suggested for their use as photocatalysts, notwithstanding the large research effort.

A general observation is the mismatch between areas of investigation and the more promising areas of applications. Also in the area of nitrogen oxides removal, the largest effort has been done on the identification of the active sites and the reaction mechanism, but it should be remarked that there appears to be limited transferability of these fundamental studies to the development of improved catalysts.

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EXHIBIT D

2008-01-1025

Enhanced Durability of a Cu/Zeolite Based SCR Catalyst

Giovanni Cavataio, Hung-Wen Jen, James R. Warner, James W. Girard,
Jeong Y. Kim and Christine K. Lambert
Ford Motor Company

ABSTRACT

Passenger and light duty diesel vehicles will require up to 90% NOx conversion over the Federal Test Procedure (FTP) to meet future Tier 2 Bin 5 standards. This accomplishment is especially challenging for low exhaust temperature applications that mostly operate in the 200 - 350°C temperature regime. Selective catalytic reduction (SCR) catalysts formulated with Cu/zeolites have shown the potential to deliver this level of performance fresh, but their performance can easily deteriorate over time as a result of high temperature thermal deactivation. These high temperature SCR deactivation modes are unavoidable due to the requirements necessary to actively regenerate diesel particulate filters and purge SCRs from sulfur and hydrocarbon contamination. Careful vehicle temperature control of these events is necessary to prevent unintentional thermal damage but not always possible. As a result, there is a need to develop thermally robust SCR catalysts. Fe/zeolite formulations are known to exhibit superior hydrothermal stability over Cu/zeolite formulations. However, current Fe/zeolite formulations are not very active for NOx conversion in the desired 200 – 350°C temperature regime under conditions having low NO_2/NOx ratios. From previous studies, Cu/zeolite formulations have demonstrated never-to-exceed temperatures up to 775°C. In this work, a laboratory flow reactor was utilized to hydrothermally age and evaluate the latest state-of-the-art Cu/zeolite formulations. Results confirm remarkable high temperature hydrothermal stability up to 950°C while maintaining stable low temperature NOx activity. A broad range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range. The aging time was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. The catalyst performance was evaluated under a synthetic exhaust gas mixture commonly known as the "Standard" SCR reaction.

INTRODUCTION

The operating conditions over the Federal Test Procedure (FTP) results in high NOx emissions in the 200 – 350°C temperature range. From current light-duty diesel applications, the future Tier 2 Bin 5 emission standards will require up to 90% reduction in the tailpipe NOx emissions.

Implementation of zeolite based components has been extensively studied for application in gasoline and diesel aftertreatment devices. However, the harsh high exhaust temperatures observed in typical gasoline vehicles have limited their widespread use. On the other hand, the relatively milder diesel exhaust temperatures have encouraged continued development of zeolites as a major component in aftertreatment devices.

One promising diesel aftertreatment technology containing zeolite is the Selective Catalytic Reduction (SCR) of NOx with an ammonia-based reductant such as aqueous urea. As stated in equation (1), NOx reduction is possible due to the high selectivity of the ammonia (NH_3) and nitrogen oxide (NO) reaction to form elemental N_2. In the absence of nitrogen dioxide (NO_2), this reaction is referred to as the "Standard" SCR reaction [1]. Additionally, the SCR reaction containing 50% NO and 50% NO_2 is referred to as the "Fast" SCR reaction (equation 2).

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{"Standard"} \qquad (1)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad \text{"Fast"} \qquad (2)$$

Vanadium, Fe/zeolite, and Cu/zeolite based SCR formulations are very active for the "Standard" SCR reactions. However, vanadium based formulations have been shown to easily deactivate when exposed to temperatures necessary to actively regenerate Diesel particulate filters (DPFs) with oxygen [2]. This cannot be avoided since a DPF is currently required to meet Tier 2 Bin 5 particulate matter (PM) emission standards. Fe/zeolites have been shown to be much more durable to high temperature exposure. However, in the absence of NO_2, Fe/zeolites lack the low temperature (200 - 350°C) NOx activity necessary for high FTP efficiency. In this critical temperature range, Cu/zeolite formulations have been reported to have much lower sensitivity to the NO_2/NOx ratio. As a result, Cu/zeolite formulations have been shown to achieve high NOx conversion at the desired low operating temperatures. Their lack of hydrothermal stability above 775°C has drawn questions about their long-term in-use durability and robustness to occasional over-temperature events.

Improvements in the thermal durability of Cu/zeolite based SCR formulations has been highly desirable and pursued by many research institutes and catalyst suppliers.

This paper discusses the performance and hydrothermal durability of an enhanced Cu/zeolite based SCR formulation exhibiting durable low temperature NOx activity under a wide matrix of time-at-temperature aging conditions. On key aged samples, surface area measurements and Cu reduction measurements are performed to investigate changes in the zeolite and Cu state, respectively.

EXPERIMENTAL

SAMPLE PREPARATION

A full size monolith washcoated with a state-of-the-art Cu/zeolite based SCR formulation was obtained from a catalyst supplier in 2007. The cordierite-based monolith measured 20.3cm diameter x 15.2cm length with 400 cells per square inch (CPSI) and 4.5 mil wall thickness. The SCR monolith was completely cored and cut into 160 round samples measuring 2.54cm diameter x 2.54cm length. From this, a normal distribution was observed where the 95% confidence interval around the mean mass was determined to be ± 0.4%. Older formulations mentioned in this paper did not necessarily exhibit the same distribution in mass.

HYDROTHERMAL AGING

As configured in Diagram 1, sample cores were hydrothermally aged in flowing gas from an automated flow reactor system. The total flow rate utilized was 6.44 liters/min. The synthetic gas composition consisted of 14% O_2, 5% H_2O, 5% CO_2, and balance N_2. For each aging, three samples measuring 2.54cm diameter x 2.54cm length were placed in a quartz reactor tube and labeled A, B, and C. The three SCR samples were separated by 30mm to ensure well distributed gas flow in all channels. An uncoated cordierite monolith was placed upstream to serve as a gas heat exchanger. The uncoated monolith ensured an isothermal gas temperature across each sample. Samples positioned in location "A" were used for surface area measurements. Samples positioned in location "B" were used for temperature-programmed reduction measurements (TPR). Samples positioned in location "C" were used for the NOx conversion evaluation tests.

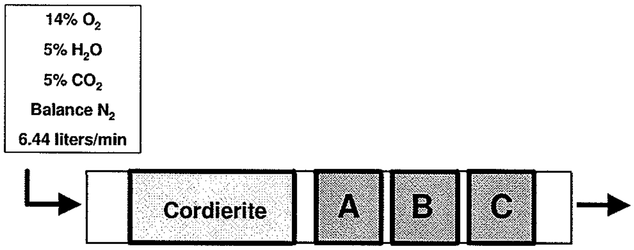

DIAGRAM 1. Sample configuration during hydrothermal aging.

A wide range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range of a promising Cu/zeolite SCR formulation. The hydrothermal aging duration was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. Totaling 1116 aging hours, Table 1 defines the 24 different aging conditions utilized in this study. Special attention was considered to determine the short-term never-to-exceed (NTE) temperature and the long-term SCR durability necessary to withstand the temperature resulting from DPF regeneration events. For a given aging duration, the NTE is defined as the temperature at which the NOx conversion decay accelerates significantly.

Temp. (°C)	Hydrothermal Aging Duration (hours)								
	1	2	4	8	16	32	64	140	256
670							X		
700	X				X	X	X		X
750									
800	X				X	X	X	X	X
850							X		
900	X		X	X	X		X		
950	X	X	X	X					
1000	X								
1100	X								

TABLE 1. Time-at-temperature hydrothermal aging matrix.

LABORATORY CATALYST EVALUATION

Fundamental catalyst activity data were obtained using an automated laboratory-scale flow reactor system. Custom-written LabVIEW based software with National Instruments data acquisition hardware controlled MKS mass flow controllers and Lindberg Mini-Mite tubular furnaces. A computer controlled evaluation protocol was developed and run for each sample to decrease the test-to-test variations commonly observed by manual operation. Table 2 shows the simulated diesel exhaust gas composition flowed through each sample core to study the "Standard" SCR reaction.

Gas Compositon	Concentration
NO (ppm)	350
NO_2 (ppm)	0
NH_3 (ppm)	350
O_2 (%)	14
CO_2 (%)	5
H_2O (%)	5
Balance	N_2

TABLE 2. Simulated gas composition used to study performance for the "Standard" SCR reaction.

For all evaluations, the total gas flow rate was held constant at 6.44 liters/min while the sample size was held constant at 2.54cm diameter x 2.54cm length. As a result, a space velocity equal to 30,000/hr was used in this study. For the typical light-duty diesel vehicle operating over the FTP drive cycle, this space velocity corresponds to a SCR monolith size between 100% - 150% of the engine swept volume.

The SCR inlet gas temperature was maintained with one preheat tubular furnace followed by a second tubular furnace. SCR samples were loaded in quartz tubing and placed in the second tubular furnace. A Thermo Electron Antaris IGS FTIR Gas Analyzer with a heated sample cell was used at the outlet of the reactor to measure NO, NO_2, N_2O, NH_3, CO_2, and H_2O levels. To cover the full exhaust temperatures expected on diesel vehicles, data were taken at SCR inlet gas temperatures from approximately 150°C to 700°C in 25-50°C steps. The computer-controlled evaluation protocol stepped the reaction temperature setting from a high temperature to low temperature for a prescribed duration. At each temperature setting, the duration was chosen so that post SCR gas composition was allowed enough time to completely equilibrate.

The flow reactor used in this study was examined to determine the test-to-test variability of the entire measurement system. Among numerous variables, the FTIR measurement, the thermocouple measurement, and precision of the mass flow controllers may collectively contribute large discrepancies in the data. This may make it difficult to conclude with confidence that one result is statistically different than another result. Repeated evaluation runs were made on a single pre-aged (64hr/670°C) SCR sample to determine the 95% confidence interval. Five evaluation runs were performed over the entire temperature range.

SURFACE AREA MEASUREMENTS

A Micromeritics ASAP 2400 instrument in conjunction with the well-known Brunauer, Emmet, and Teller (BET) equation was employed to determine the surface area of each SCR sample. The BET equation determines the surface area by establishing the relationship between the volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage [3].

TEMPERATURE PROGRAMMED REDUCTION (TPR)

The Cu state within zeolite formulations changes during the SCR reaction and after hydrothermal aging. These physical-chemical changes yield different reduction temperatures. The TPR results reveal direct evidence of changing Cu-species in the catalyst and may be correlated to the deactivation of SCR activity after aging.

Temperature-Programmed-Reduction (TPR) was conducted on a Micromeritics AutoChem II 2920 instrument. Part of a catalyst sample (location "B") was sliced off and cut into small pieces, about 3 mm long. These small pieces were then loaded into a quartz reactor for TPR. Typically, 0.5 gram of sample was used in the experiment. The temperature was measured with a thermocouple in the catalyst bed. Prior to TPR, the catalyst sample was pretreated in 10%O_2/He at 600°C for 30 minutes and then cooled down to room temperature in 10%O_2/He. After the pretreatment, the gas flow was changed to 9%H_2/Ar at 20 ml/min. During TPR, the catalyst bed was heated to 600°C at a linearly increasing rate of 10°C/min. The change in H_2 concentration was monitored using Thermal-Conductivity-Detector (TCD). The consumption of H_2 indicated the reduction of oxidized Cu.

RESULTS AND DISCUSSION

FLOW REACTOR VARIABILITY

The variability of the evaluation flow reactor was determined by running a pre-aged SCR sample five times. The steady state "Standard" SCR reaction results for each of the five runs are overlaid in Figure 1. In addition, the 95% confidence interval around the mean

NOx conversion is shown in Figure 2. From Figure 1, the NOx conversion traces are virtually line on line for operating temperatures below 600 °C. Above 600 °C, the NOx conversion drops slightly after each subsequent evaluation run. For this particular SCR formulation, the explanation for this slight deactivation has to do with the additional aging the sample experiences during high temperature performance evaluations. This trend becomes more apparent with data presented later in this paper. Figure 2 more clearly defines the variability in the overall flow reactor system. The data from Figure 1 was manipulated in Minitab to yield the 95% confidence interval at each evaluation temperature. For evaluation temperatures below 600 °C, the 95% confidence interval around the mean NOx conversion was better than ±2%. Due to catalyst deactivation with testing, the higher temperature points showed variability up to ±6%.

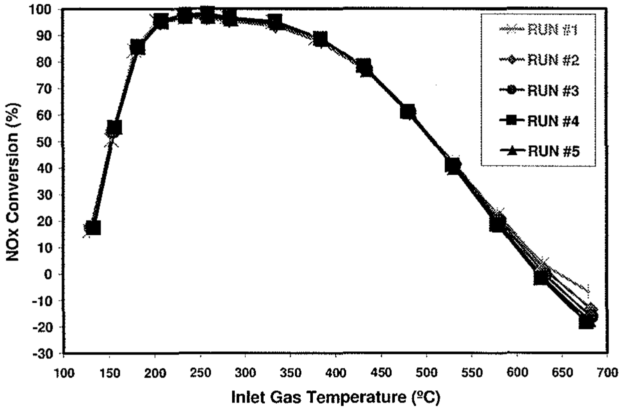

FIGURE 1. NOx conversion results for the STANDARD SCR REACTION. Five consecutive evaluation runs on a single sample aged 64 hours at 670 °C.

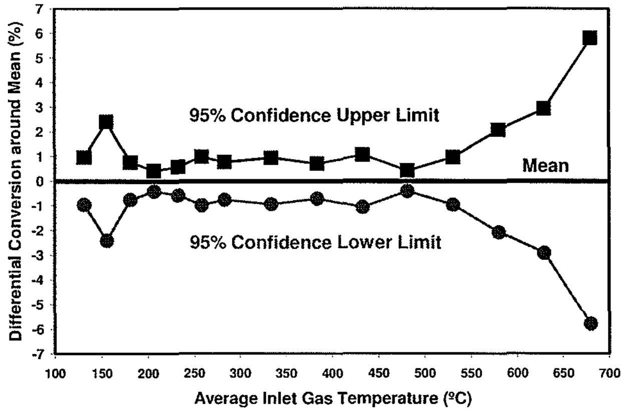

FIGURE 2. Calculated from Figure 1, the differential NOx conversion variability around the mean as determined by the 95% confidence interval.

RECENT SCR DURABILITY IMPROVEMENTS

Since current and future diesel aftertreatment systems contain DPFs, SCR formulations are required to withstand the high temperature process of regenerating soot-loaded particulate filters. A robust engine control strategy that lessens the variability of the actual regeneration temperature is critical to the durability of the SCR. For this study, the target active DPF temperature has been determined to be 670 °C. Also, the total cumulative duration for the full vehicle useful life has been determined to be 64 hours. Therefore, the long-term hydrothermal stability of base metal-zeolite SCR catalysts for typical light-duty diesel applications must be able to endure, at minimum, 670 °C for 64 hours.

Figure 3 shows the recent progress that has been made in Cu/zeolite SCR development. Many Cu/zeolite formulations have been aged and evaluated between 2005 and 2007. Steady improvements of NOx conversion have been made in the low temperature range (200 – 350 °C). For example, at 200 °C, the NOx conversion has been enhanced from 70% to 90%. In addition, the 2007 state-of-the-art SCR maintained 90%+ NOx conversion over a much larger temperature range. However, note that the enhanced low temperature activity came with a trade-off in the performance above 400 °C.

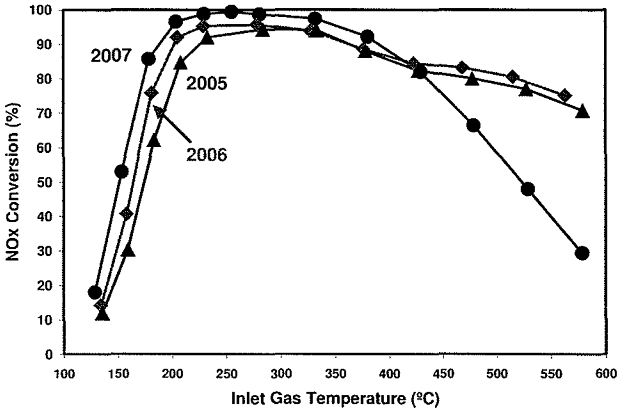

FIGURE 3. NOx conversion results for the STANDARD SCR REACTION. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670 °C.

As shown in Figure 4, the three SCR formulations generate measurable levels of N_2O as a by-product. The N_2O formation has a bi-modal profile as a function of temperature. The low temperature N_2O formation around 200 °C is a result of NH_3 oxidation by NO whereas the high temperature N_2O formation around 525 °C is mainly from the oxidation of NH_3 by O_2. The latest SCR formulation generates much less N_2O. At 200 °C, the 2007 SCR formulation yielded up to 3 times less N_2O compared to the two older formulations.

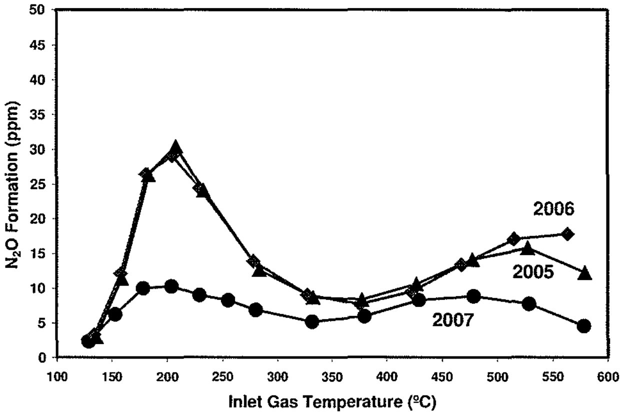

FIGURE 4. N_2O formation results for the STANDARD SCR REACTION in Figure 1. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

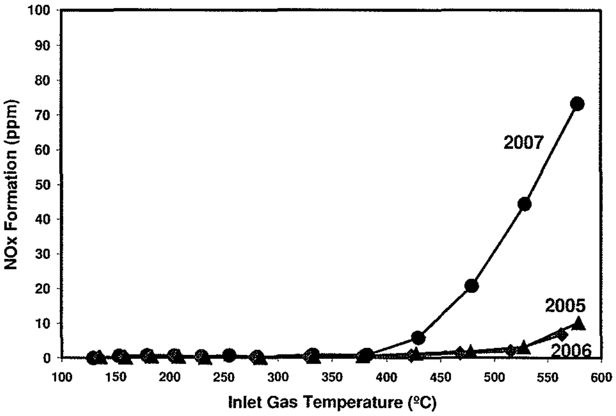

FIGURE 6. NOx formation (ppm) results for the ammonia oxidation reaction in the absence of NOx (FIGURE 5). Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

Durable low temperature NOx performance is desirable for light-duty diesel applications. However, a considerable amount of NOx is emitted at high temperature during the time when the vehicle undergoes an active DPF regeneration. This added NOx emission must be compensated by additional NOx conversion during low temperature operation. As mentioned previously, the high temperature NOx performance of the 2007 SCR catalyst drops sharply as the temperature increases beyond 400°C (Figure 3). Figure 5 plots the NH_3 oxidation of the three catalysts in the absence of NOx. Ammonia is more strongly oxidized by the 2007 SCR catalyst. In addition, a clear inflection point at 400°C is observed which corresponds to the formation of NOx (Figure 6). As a result, the NOx performance in Figure 3 declines rapidly due to, in part, the remake of NOx from NH_3 oxidation (Figure 6).

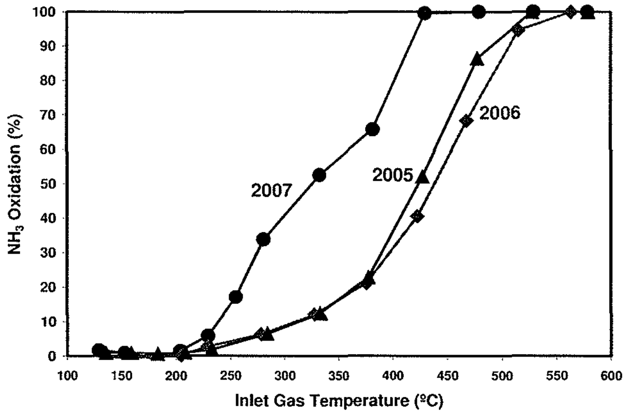

FIGURE 5. NH_3 conversion results for the ammonia oxidation reaction in the absence of NOx. Best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 64 hours at 670°C.

Unrefined engine exhaust temperature control during DPF regeneration events coupled with inexact temperature measurement may expose SCR catalysts to an occasional unexpected over-temperature. As a result, the SCR formulations are screened with a robustness test protocol consisting of hydrothermal exposure at 900°C for 1 hour. These types of data are used to define the short-term never-to-exceed (NTE) temperature. The NTE testing provides a higher degree of discrimination among similar performing formulations compared to the less severe 64hr/670°C standard aging.

Figure 7 illustrates the remarkable progress that has been made in the past year with the durability of the 2007 Cu/zeolite based SCR formulation. Among the dozens of Cu/zeolite formulations tested in past years, no formulation has been able to withstanding exposure up to 900°C while maintaining stable NOx performance at 200°C. Under the 1 hour/900°C aging condition, the 2007 SCR catalyst retained 90% NOx conversion at 200°C. All older SCR formulations have achieved no better than 20% NOx conversion. The enhanced durability of the 2007 SCR formulations has been mainly attributed to advances in the zeolite type and composition.

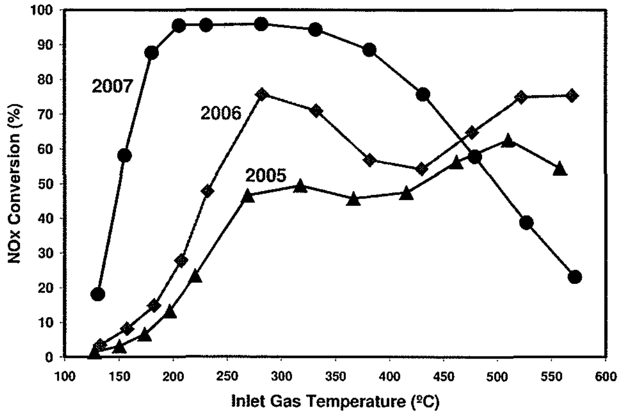

FIGURE 7. NOx conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900°C.

Based on these encouraging results, a more severe time-at-temperature aging study was undertaken with the 2007 SCR formulation defined in Figure 7. The aging and evaluation helped determine the full robustness map of this promising Cu/zeolite based SCR formulation.

TIME-AT-TEMPERATURE PERFORMANCE

Current diesel engines require a DPF to meet the Tier 2 particulate matter standards. As a result, the SCR must be able to tolerate extreme temperature swings due to typical and non-typical active DPF regenerations. Also, the durability requirement of the SCR formulation will hinge largely on the location of the SCR relative to the DPF. SCR formulations placed directly upstream must withstand high exhaust temperatures generated from the engine or over a DOC. SCR formulations placed directly downstream of the DPF will need to withstand extended temperatures coming from soot regeneration. However, the most severe conditions will likely arise from future combination systems where the DPF filter is coated with a SCR formulation. Clearly, for promising SCR formulations in close relationship to the DPF, there is a need to determine the full temperature based durability map to better assess the thermal robustness.

A broad range of time-at-temperature hydrothermal aging was carried out to clearly define the full durability range. The aging time was varied from 1 hour to 256 hours while the aging temperature was varied from 670°C to 1100°C. The catalyst NOx performance was based on the "Standard" SCR reaction, the "Fast" SCR reaction, and ammonia oxidation reaction (in the absence of NOx).

For the typical light-duty driving conditions, the "Standard" SCR reaction is considered to be the most challenging since little or no NO_2 is expected below 250°C.

The effect of long-term hydrothermal aging at 700°C versus duration was carried out in the laboratory. The duration was varied from 1 hour to 256 hours while the aging temperature was held constant at 700°C. NOx conversion as a function of temperature was measured on each individual sample. Results show that the 2007 Cu/zeolite SCR catalyst demonstrated outstanding stability (Figure 8). Recall that the 64 hour aging duration has been calculated to be an equivalent of 120,000 miles for a typical light-duty diesel. As long as the SCR catalyst temperature does not exceed 700°C, these results heighten the industry's confidence for successfully implementing a Cu/zeolite SCR formulation into production.

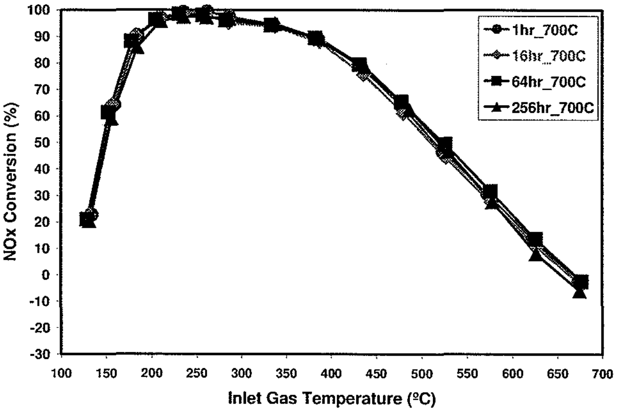

FIGURE 8. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 700°C for 1 hour – 256 hours.

For configurations where the SCR catalyst is placed upstream of the DPF, temperatures greater than 700°C are not expected normally. However, higher temperatures may be apparent for SCR catalysts placed immediately downstream of a DPF and for SCR formulations coated on the DPF itself. Therefore, the effect of long-term hydrothermal aging for up to 256 hours at 800°C was also conducted. The results showing the NOx conversion as a function of temperature are plotted in Figure 9. The Cu/zeolite SCR catalyst proved to demonstrate durable NOx conversion up to 64 hours. Further aging out to 140 hours and then out to 256 hours resulted in a continual decline in the low temperature NOx conversion. The high temperature NOx conversion declines steadily from 1 hour to 64 hours but then mildly improves from 64 hours to 256 hours. Recall, the high NOx conversion becomes negative due to aggressive oxidation of NH_3 with O_2 to yield NOx.

Given the observed hydrothermal aging limitation of 64 hours at 800℃, these data provide encouragement for the potential development of a single combined SCR/DPF substrate where the SCR formulation is coated within the DPF substrate. This consolidation would provide smaller vehicle packaging and lower cost possibilities.

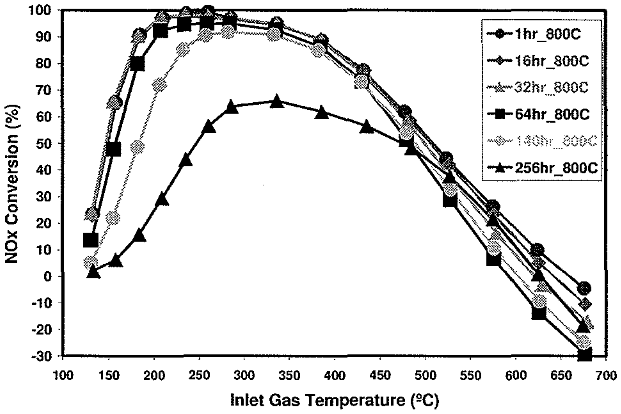

FIGURE 9. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 800℃ for 1 hour – 256 hours.

Figure 10 shows the NOx conversion results for samples hydrothermally aged at 900℃ for durations from 1 hour to 64 hours. Durable NOx conversion is observed up to 4 hours. The Cu/zeolite cannot tolerate 8 hours and the performance is completely destroyed with the individual samples aged out to 16 hours and beyond.

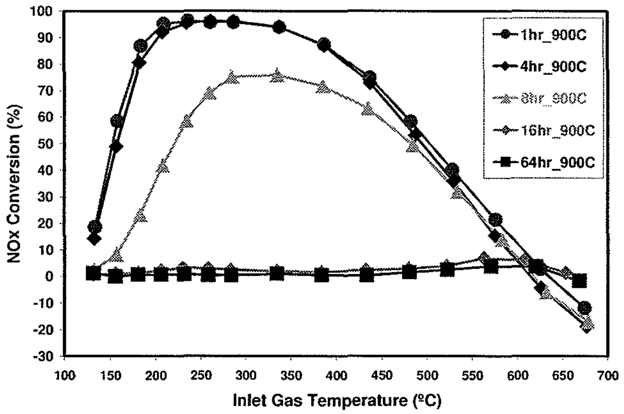

FIGURE 10. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 900℃ for 1 hour – 64 hours.

Figure 11 shows the NOx conversion results for samples hydrothermally aged at 950℃ for 1, 2, 4, and 8 hours. The Cu/zeolite formulation can only tolerate 1 hour exposure to 950℃. There is a significant drop in performance after 2 hours and complete deactivation after only 4 hours of exposure.

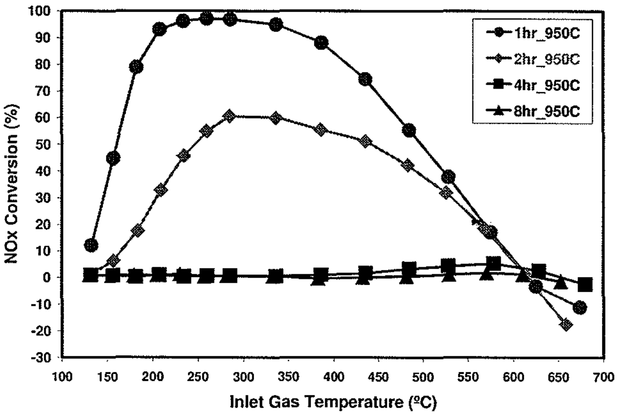

FIGURE 11. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 950℃ for 1 hour – 8 hours.

For a 1 hour exposure, the short-term never-to-exceed (NTE) temperature is defined as the maximum temperature the SCR formulation can tolerate without showing signs of significant deactivation. This is particularly helpful for use by engine control calibration engineers. Figure 12 shows the NOx conversion results for samples hydrothermally aged for 1 hour with temperatures ranging from 700℃ to 1100℃. The results indicated that the NTE temperature was 950℃ but without much margin for error. For example, at 250℃, increasing the aging temperature from 950℃ to 1000℃ decreased the NOx conversion from 95% to 18%. At 1100℃, the NOx conversion was further reduced to 0%. It was clear that structural damage occurred and further work to understand the deactivation will be carried out in the near future.

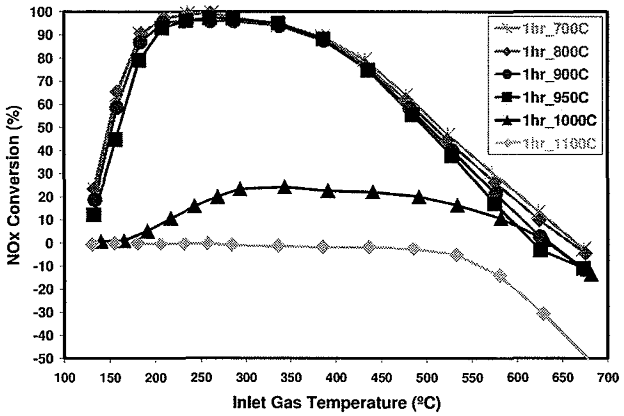

FIGURE 12. Short-term Never-To-Exceed (NTE) Temperature: NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 1 hour from 700°C – 1100°C.

Figure 13 shows the NOx conversion results for samples hydrothermally aged for 64 hours and temperature exposure from 670°C to 900°C. For the baseline, 64 hours at 670°C aging (120k mi equivalent), the Cu/zeolite activity data clearly shows > 90% NOx conversion in the 200°C – 350°C temperature window. However, the maximum temperature for this extended duration is 800°C. An additional 50°C, corresponding to 850°C, had a severe impact on the catalyst durability.

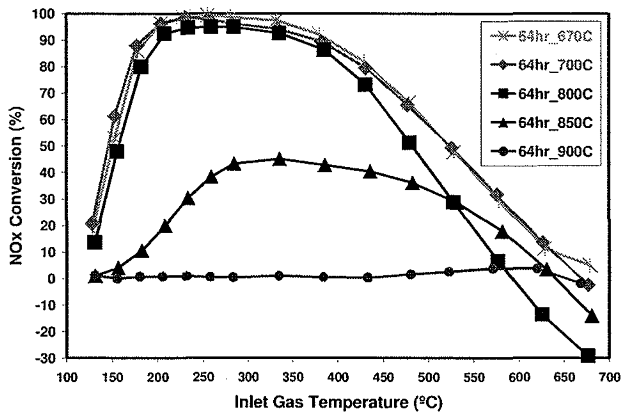

FIGURE 13. NOx conversion results for the STANDARD SCR REACTION. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

The same identical samples presented in Figures 8 - 13 were further evaluated under two other SCR reactions. These reactions were the "Fast" SCR Reaction and "Ammonia Oxidation" Reaction in the absence of NOx. Comparison of Figure 13 and Figure 14, the data resulting from the "Fast" SCR Reaction experiments yielded the same trends in NOx performance as the "Standard" SCR Reaction but with slightly better activity at the low to moderate temperatures.

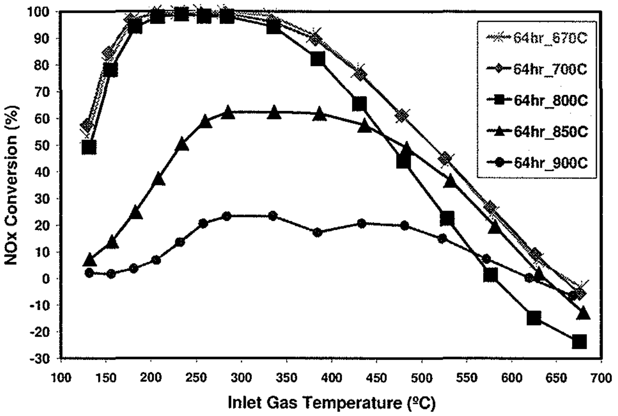

FIGURE 14. NOx conversion results for the FAST SCR REACTION. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

As illustrated in Figure 15, the ammonia oxidation evaluation in the absence of NOx yielded curves showing the deactivation of the catalyst with respect to time-at-temperature. The results show a similar deactivation trend as the NOx performance.

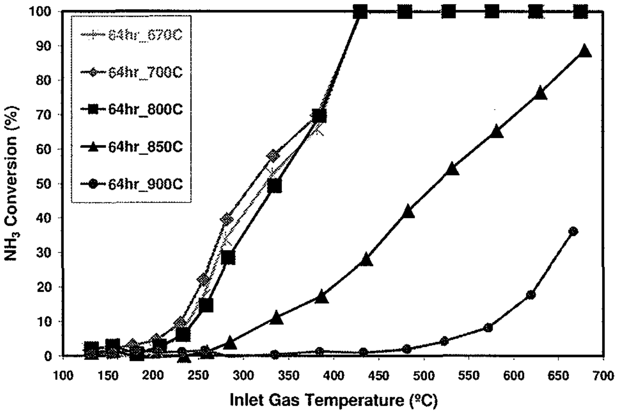

FIGURE 15. NH_3 conversion results for the AMMONIA OXIDATION REACTION in the absence of NOx. SCR samples hydrothermally aged at 64 hours from 670°C – 900°C.

The results just described were for samples aged for 64 hours but at varying temperatures. Furthermore, the corresponding samples aged at the various other aging conditions showed a similar deactivation trend as the corresponding NOx performance. As a result, these data sets of NOx conversion and NH_3 oxidation have been excluded from this paper for brevity.

BET SURFACE AREA MEASUREMENTS

The BET surface area of samples located in aging position "A" were measured to determine if a trend can be developed with the NOx activity measurements. For post mortem analysis, this type of relationship is particularly useful for determining the likely temperature exposure experienced on field returned SCR parts. The zeolite framework is known to de-aluminate steadily with mild temperatures and suddenly at high temperatures. These changes are accompanied with changes in the total surface area.

The normalized BET surface area results for samples aged up to 950°C are presented in Figure 16. The results have been normalized to the sample aged for 1 hour at 700°C. For all samples aged at 700°C, the surface remained relatively stable. A 10% reduction in surface area was observed with the 256hours/700°C aged sample. This observation is in good agreement with the NOx performance data. Recall from Figure 8 that there was no significant change in the NOx performance for all samples aged at 700°C. At 800°C, the surface area dropped suddenly from the 64 hour aging to the 140 hour aging. This drop-off in surface area corresponds to the drop-off in NOx performance observed in Figure 9. At 900°C, the surface area declined after 4 hours of aging. This also corresponds quite well with Figure 10 where the first sign of NOx conversion deterioration occurred beyond 4 hours of aging. At 950°C, the results on Figure 16 show that the surface area immediately drops after the 1st hour of aging. This coincides nicely with the NOx performance data presented in Figure 11.

Comparing the NOx performance data in the previous section to the surface area data in this section, a general trend exists that links the sudden drop in NOx conversion with the sudden drop in surface area. The first 20% drop in surface area is associated with a marginal impact on the NOx conversion. However, the rapid decline in NOx conversion is associated with the aged samples measuring greater than 20% decrease in the surface area.

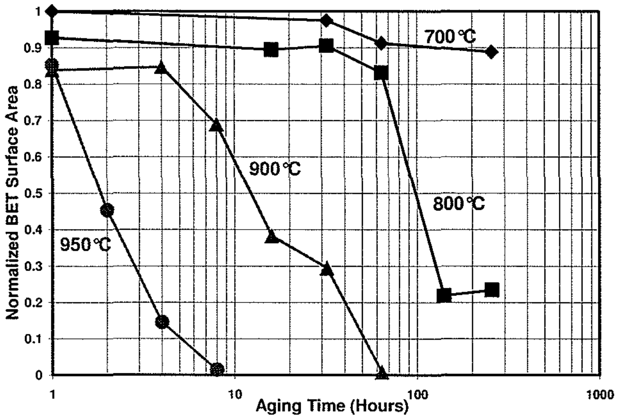

FIGURE 16. Normalized BET surface area results from laboratory aged samples at as function of time 1 - 256 hours and temperatures between 700°C – 950°C.

Figure 17 shows the normalized BET surface area for two sets of samples aged as a function of temperature. The first set of samples was aged for 1 hour in duration to represent the short-term never-to-exceed (NTE) temperature. The second set of samples was aged for 64 hours in duration to represent the long-term SCR durability needed for DPF regeneration conditions. For the 1 hour case, results indicated that the surface area steadily dropped as the temperature was increased to 950°C. However, the SCR surface area completely collapsed by increasing the temperature by an additional 50°C. The surface area for the 64 hour aged samples also collapsed sharply once the temperature exceeded 800°C. Vehicle events resulting in conditions beyond 1hr/950°C or 64hr/800°C will cause catastrophic deactivation from both the NOx conversion and surface area points of view.

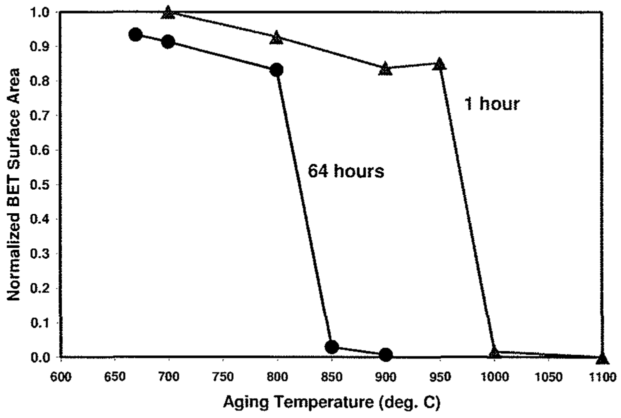

FIGURE 17. Normalized BET surface area results from laboratory 1 hour and 64 hour aged samples as a function of temperature.

TEMPERATURE PROGRAMMED REDUCTION (TPR)

Different Cu-species can yield different reduction temperatures. Therefore, the TPR result may reveal direct evidence of changing Cu-species in the catalyst and may be correlated to the deactivation of SCR activity after aging.

The effect of aging temperature on TPR for the 2007 SCR catalyst is shown in Figure 18. As the aging temperature increased from 800°C to 950°C, the reduction peak at 330°C increased proportionally. The upward shift in TPR peak temperatures, due to the increase in aging temperature, was reported for zeolite-based SCR catalysts [4]. For Cu/ZSM-5 catalysts, a prolonged hydrothermal aging process was also reported to cause an upward shift of TPR peak temperature due to some Cu-species on de-aluminated zeolite [5]. Therefore, the increase in the 330°C peak from aging at 800°C to 950°C in Figure 18 indicated that the extent of de-alumination increased. This observation agreed with the result in BET surface areas (Figure 17) that had a 15% decrease from 800°C to 950°C because of an increase in de-alumination or subsequent collapse of zeolite structure. However, it was noted that the three catalysts aged from 800°C to 950 °C for 1 hour still yielded good NH_3-SCR catalytic activities (Figure 12).

After aging at 1hr/1100°C, the catalyst had almost zero surface area (Figure 17). Since the zeolite was destroyed, no TPR peak around 330°C was observed (Figure 18). However, there was an elevated TPR curve above 400°C extending up to 600°C. This high-temperature TPR curve corresponds to the Cu species that strongly interacted with destroyed zeolite materials after 1hr/1100°C lean hydrothermal aging. Yan et al. experimentally showed that Cu-aluminate ($CuAl_2O_4$) yielded similar TPR features above 400°C [5]. It was likely that our observed Cu-species was reminiscent of $CuAl_2O_4$. The small TPR peaks between 200°C and 250°C are probably from discrete CuO particles or CuO/SiO_2 after the 1hr/1100°C aging. These Cu-species associated with materials from destroyed zeolite were not catalytically active for the NH_3-SCR reaction (Figure 12). In fact, the 1hr/1100°C aged sample had no NOx conversion below 500°C and negative NOx conversion above 500°C. This was the result of non-selective NH_3 oxidation with O_2 to yield additional net NOx.

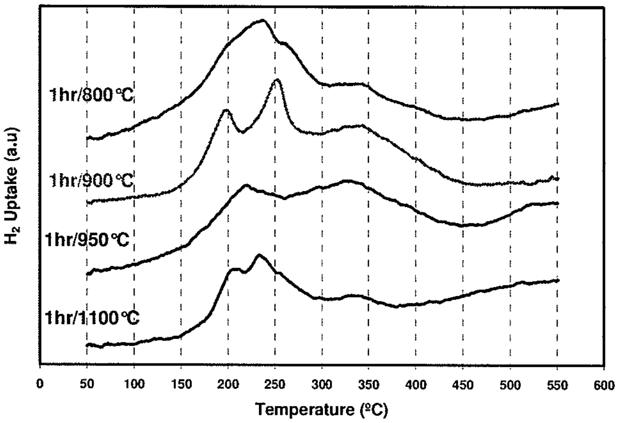

FIGURE 18. TPR results of 2007 SCR formulation aged for 1 hour and temperatures between 800°C – 1100°C.

At 900°C, an increase in aging time from 1 to 8 hours yielded an additional TPR peak at 400°C (Figure 19). This peak became more prominent after aging for 64 hours. As discussed above, the Cu-species responsible for the TPR peaks above 400°C were likely interacting strongly with materials from destroyed zeolite and not active for the desired NH_3-SCR reaction. As a result, for increasing aging time at 900°C, the growth of this 400°C TPR peak in Figure 19 corresponded to the decline in observed SCR activity in Figure 10. For the samples that were aged at 950°C, an increase in aging time also produced an extra TPR peak at 450°C. Apparently, the Cu-species interacting strongly with materials from destroyed zeolite became harder to reduce as the aging temperature became higher. After aging at 1hr/1100°C, the Cu-species likely would yield a TPR peak above 600°C as indicated in Figure 18.

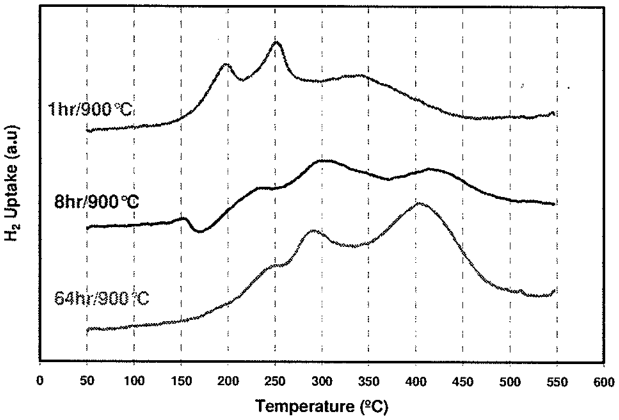

FIGURE 19. TPR results of 2007 SCR formulation aged at 900°C and durations from 1 hour – 64 hours.

CONCLUSIONS

The following conclusions emerge from this study:

- In past years, no reported Cu/zeolite SCR formulation was able to yield stable low temperature NOx performance after exposure to hydrothermal conditions consisting of 1 hour at 950°C. Within the last year, a remarkable Cu/zeolite SCR formulation was identified with high NOx conversion in the 200°C – 350°C temperature range. At the 950°C aging condition, the 2007 SCR formulation became more sensitivity as the duration was increased beyond 1 hour.

- Upon the completion of a full time-at-temperature durability study, the newly developed Cu/zeolite SCR formulation was confirmed to tolerate the following hydrothermal conditions:
    - > 256 hours at 700°C.
    - 64 hours at 800°C.
    - 4 hours at 900°C.
    - 1 hour at 950°C.

- The BET surface area results trended with the NOx conversion. The first 20% drop in surface area was associated with a marginal impact on the NOx conversion. Beyond the initial 20%, a further decline in the surface area was rapid and closely related to the negative impact on NOx performance.

- TPR of aged Cu/zeolite catalysts was used to correlate the change in Cu-species to the status of zeolite or to NH_3-SCR activity after aging. The observation of a TPR peak above 400°C indicated a strong interaction of Cu with destroyed zeolite and a decline in catalytic activity. Since the temperature of this TPR peak increased with increasing aging temperature, this feature may be used to diagnose the exposure temperature of a deactivated Cu/zeolite SCR catalyst.

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CONTACT

Giovanni Cavataio, Ph.D.
Ford Motor Company
Research and Innovation Center
2101 Village Road
P.O. Box 2053, MD3179, RIC
Dearborn, Michigan 48124
(313) 322-3357
jcavatai@ford.com