Selective catalytic reduction of NO_x with NH_3 over Cu-ZSM-5—The effect of changing the gas composition

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Abstract

The selective catalytic reduction of nitrogen oxides (NO_x) with ammonia over ZSM-5 catalysts was studied with and without water vapor. The activity of H-, Na- and Cu-ZSM-5 was compared and the result showed that the activity was greatly enhanced by the introduction of copper ions. A comparison between Cu-ZSM-5 of different silica to alumina ratios was also performed. The highest NO conversion was observed over the sample with the lowest silica to alumina ratio and the highest copper content. Further studies were performed with the Cu-ZSM-5-27 (silica/alumina = 27) sample to investigate the effect of changes in the feed gas. Oxygen improves the activity at temperatures below 250 °C, but at higher temperatures O_2 decreases the activity. The presence of water enhances the NO reduction, especially at high temperature. It is important to use about equal amounts of nitrogen oxides and ammonia at 175 °C to avoid ammonia slip and a blocking effect, but also to have high enough concentration to reduce the NO_x. At high temperature higher NH_3 concentrations result in additional NO_x reduction since more NH_3 becomes available for the NO reduction. At these higher temperatures ammonia oxidation increases so that there is no ammonia slip. Exposing the catalyst to equimolecular amounts of NO and NO_2 increases the conversion of NO_x, but causes an increased formation of N_2O.
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1. Introduction

One major source of nitrogen oxides (NO_x) is the combustion of fossil fuel. Nitrogen oxides may cause formation of ground-level ozone, production of acid rain and respiratory problems to mankind [1]. Oxides of nitrogen are difficult to reduce in the presence of excess oxygen that occurs in diesel exhaust. There is currently a need for a solution for NO_x abatement in light duty diesel engines. One possible approach for reduction of NO_x to N_2 is selective catalytic reduction (SCR) with urea or ammonia. The use of NH_3-SCR has been investigated for several years and is today a well established technique for DeNO$_x$ in stationary applications [2].

The catalysts studied in the literature for this reaction can be divided in three groups that are active at different temperatures [3]. Noble metals, like platinum, were first considered for the SCR

of NO_x. They are active in the selective reduction of NO_x at low temperatures, but the selectivity is poor at higher temperatures [1]. The second type of catalysts is metal oxides. Among the various investigated metal oxide mixtures, those based on vanadia supported on titania are commonly used. The catalyst is active at 350–450 °C, at higher temperatures the catalyst loses selectivity due to enhanced oxidation of ammonia [4]. For application in a wider temperature range, zeolite based catalysts have been developed, which are active at high temperatures, to a maximum of about 600 °C [5]. Among these, copper exchanged zeolites such as Cu-ZSM-5 have been widely studied for SCR with ammonia and also for applications such as NO decomposition and selective catalytic reduction by hydrocarbons [6–9].

NO_x in the exhaust gas from a diesel engine is usually composed of more than 90% NO. The overall SCR reaction with ammonia is usually assumed to involve stoichiometric amounts of NO and NH_3 in presence of oxygen to produce nitrogen and water [10]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$
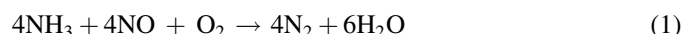
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The overall reaction of a mixture composed of equimolecular amounts of NO and NO_2 may also be important, since it is suggested to occur much faster than the main reaction [2]:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (2)$$
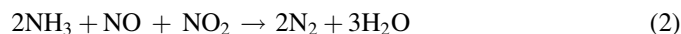
At high temperatures the oxidation of ammonia may lead to formation of additional NO over the catalyst [11]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (3)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (4)$$
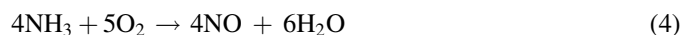
Other reactions may be taking place over the catalyst that could result in the reduction of NO_2 without concurrent NO reduction. In addition, formation of other products such as nitrous oxide and ammonium nitrate may be occurring.

The importance of the different reactions above varies with both gas composition and temperature. Due to the transient conditions in vehicle application it is important to investigate the SCR activity at several settings to reach a high average NO_x conversion and to avoid ammonia slip. There are several studies that investigate zeolites such as Cu-ZSM-5 and their catalytic behavior in ammonia SCR [11–17]. However, neither of them investigates changes in the feed composition in order to evaluate the possible reactions that occur over coated monoliths. In this study, Cu-ZSM-5 coated catalysts of three different silica/alumina ratios have been evaluated. The catalyst that produced the highest conversion has been studied further. The aim is to investigate the catalytic activity at various concentrations of oxygen, ammonia, nitrogen oxides and water to provide knowledge about the different reactions that occur at the surface of a Cu-ZSM-5 catalyst.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared from zeolite powder of three different SiO_2/Al_2O_3 ratios obtained from Alsi-Penta. The starting material for the zeolites with SiO_2/Al_2O_3 ratios of 27 and 55 was H-ZSM-5 and the starting material for the zeolite with ratio 300 was Na-ZSM-5. Five different catalysts, H-ZSM-5-27, Na-ZSM-5-27, Cu-ZSM-5-27, Cu-ZSM-5-55 and Cu-ZSM-5-300, were prepared according to the method described below.

To ion exchange the H-ZSM-5 powder, a 108 mM $NaNO_3$ solution was stirred for 30 min and the pH was adjusted by adding NH_3. The zeolite was then added. This ion exchange was performed twice. The total amount of Na^+ in the slurries was two times the number of aluminum in the zeolite. The Na-ZSM-5 was placed in an oven and dried for 1 h at 80 °C, followed by a second drying at 125 °C for 30 min. The copper was introduced into the zeolite by exchange in an 11 mM $Cu(CH_3COO)_2$ solution at ambient temperature and the pH was adjusted with ammonia. The slurry was stirred for 14 h, followed by a second (8 h) exchange and then a third (14 h) exchange. The total amount of Cu^{2+} in the slurries was one and a half times the number of aluminum in the zeolite. After the last exchange, the powder was filtered and washed with 1 l distilled water. The Cu-ZSM-5 was placed in an oven and dried for 1 h at 80 °C, followed by a second drying at 125 °C for 5 h. For detailed information of the different catalysts, see Tables 1A and 1B.

The zeolite powder was washcoated on monoliths. The respective slurry was composed of a liquid phase of equal amounts of distilled water and ethanol and a solid phase of

Table 1A
Information about the ion exchange from H^+ to Na^+. The volume of $NaNO_3$ solution used in the ion exchange was determined from the number of Al present in the zeolite. The ion exchange was performed twice

SiO_2/Al_2O_3	Zeolite weight (g)	Volume, $NaNO_3$ solution (ml)	Concentration, $NaNO_3$ (mM)	Time (h)	pH
27	45.2	485	108	0.5	7.06
		485	108	0.5	6.90
55	31.6	170	108	0.5	7.10
		170	108	0.5	7.06

Table 1B
Information about the ion exchange from Na^+ to Cu^{2+}. The volume of $Cu(Ac)_2$ solution used in the ion exchange was determined from the number of Al present in the zeolite. The ion exchange was performed three times

SiO_2/Al_2O_3	Zeolite weight (g)	Volume, $Cu(Ac)_2$ solution (ml)	Concentration, $Cu(Ac)_2$ (mM)	Time (h)	pH
27	31.2	1643	11	14	5.64
		1643	11	8	5.75
		1643	11	14	5.73
55	23.2	618	11	14	5.80
		618	11	8	5.84
		618	11	14	5.85
300	31.1	151	11	14	5.80
		151	11	8	5.70
		151	11	14	5.80

Table 2
The amount of washcoat on the five catalysts prepared. The catalysts were first immersed in a 5% binder slurry, then in a 20% zeolite/binder slurry and finally in a slurry of 5% zeolite/binder to adjust the amount of washcoat on the catalyst. Drying and heating were performed between all steps in the washcoating procedure

Catalyst	Weight alumina layer (g)	Weight zeolite layer (80% zeolite, 20% alumina) (g)
H-ZSM-5-27	0.092	1.002
Na-ZSM-5-27	0.101	1.018
Cu-ZSM-5-27	0.073	1.038
Cu-ZSM-5-55	0.065	1.004
Cu-ZSM-5-300	0.078	1.018

20 wt.% boehmite (Disperal D) and 80 wt.% Cu-ZSM-5. Two slurries with different liquid/solid ratios were prepared from each zeolite powder to prepare monoliths with similar washcoats for each of the zeolites. The liquid/solid weight ratios used in the slurries were 80/20 and 95/5. The monoliths consisted of 188 channels ($\approx$1 mm × 1 mm) and the length and the diameter of the monolith were 30 mm and 22 mm, respectively. All monoliths were heated to 550 °C for 1 h prior to washcoating. A thin layer of alumina was washcoated on the catalyst to generate an improved surface for the zeolite attachment. This sample was then calcined for 1 h at 550 °C before introducing the zeolite layer. The slurry used to prepare the thin layer of alumina was composed of distilled water and ethanol (50:50 mixture) and 5 wt.% binder (boehmite). The monolith was coated with the zeolite slurry by:

- immersing the monolith in the slurry;
- blowing away the excess slurry;
- drying in air at 85 °C for 30 s;
- heating in air at 500 °C for 1.5 min.

This procedure was repeated until the monolith was coated with the desired amount of washcoat. This catalyst was then calcined at 550 °C for 3 h. Properties of the washcoats of the different catalysts are shown in Table 2.

2.2. Catalyst characterization

The aluminum and copper amounts were determined using inductively coupled plasma and atomic emission spectrometry (ICP–AES), and the result is shown in Table 3. Impurities of Fe_2O_3 (<0.09%), K_2O (<0.08%), Na_2O (<0.07%) and TiO_2 (<0.04%) were also identified in the

Table 3
The alumina content, copper-ion-exchange level based on atomic ratio and the copper loading in the washcoat of the three Cu-ZSM-5 catalysts

Catalyst	Al_2O_3 content in zeolite (wt.%)	Ion-exchange level (Cu/Al)	Cu loading in washcoat (wt.%)
Cu-ZSM-5-27	5.9	0.35	2.03
Cu-ZSM-5-55	4.1	0.27	1.09
Cu-ZSM-5-300	1.1	0.10	0.11

Table 4
The BET surface of the zeolite starting material, the copper exchanged powder and the copper exchanged zeolites washcoated on monoliths

SiO_2/Al_2O_3	Powder		Monolith
	H- or Na-ZSM-5 (m^2/g)	Cu-ZSM-5 (m^2/g)	Cu-ZSM-5 (m^2/g washcoat)
27	313	319	304
55	344	308	299
300	413	412	349

three Cu-ZSM-5 powders. The specific surface areas of the zeolite powder and the catalysts were determined by nitrogen adsorption according to the BET method using a Digisorb 2600 (Micromertics) instrument. The specific surface areas are shown in Table 4.

2.3. Activity measurements

The activity of the catalysts was tested in a flow reactor consisting of a horizontal quartz tube, 800 mm long with an inner diameter of 22 mm. The heating unit consisted of a heating coil, a power supply and a Eurotherm controller. The catalyst was placed in the quartz tube with a thermocouple placed about 1 cm in front of the catalyst to control the temperature. A second thermocouple was placed inside the sample to measure the catalyst temperature. The catalyst was sealed in the tube with quartz wool. The inlet gas composition was controlled by an Environics 2000 gas mixer. An FTIR (Bio-Rad FTS 3000 Excalibur spectrometer with a Specac Sirocco series heatable gas cell, P/N 24102, with a 2 m pathlength and a volume of 0.19 l) was used to measure the concentration of NO, NO_2, N_2O and NH_3. The nitric oxide concentration was also measured by a chemiluminescence detector (CLD 700) connected to the system. The gas flow and the space velocity were 3500 ml/min and 18,400 h^{-1}, respectively, in all experiments. Prior to each experiment, the catalyst was pretreated with 8% O_2 in Ar for 20 min at 500 °C and cooled in Ar. All experiments were performed at atmospheric pressure and the inert balance was argon.

Steady-state activity tests were performed for all catalysts in the absence of water using a feed gas composition of 500 ppm NO, 500 ppm NH_3 and 8% O_2 in Ar. The catalyst was exposed to the gas mixture at 100 °C for 40 min, at 150 °C and 200 °C for 30 min and at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C for 20 min.

The Cu-ZSM-5-27 catalyst was used in further studies as described below, to investigate the catalytic activity at different concentrations of O_2, NO, NO_2, NH_3 and H_2O. Two tests were performed keeping the NO and NH_3 concentrations at 500 ppm but changing the O_2 concentration to either 1% or 4%. Additional steady-state experiments were performed in the same way using 500 ppm NO, 500 ppm NH_3 and 8% O_2 but in presence of 1% or 5% H_2O in order to investigate the effect of water.

In another set of experiments the gas contained fixed NO and

concentration was varied. The experiment was performed at 175 °C fixing the NH_3 concentration at 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm, 700 ppm and 800 ppm for 60 min. The experiment was performed both with and without 5% H_2O in the gas mixture. An additional experiment was performed at 175 °C changing the inlet NO concentration and keeping the concentration of ammonia and oxygen constant at 500 ppm NH_3 and 8% O_2. Initially the catalyst was exposed to the mixture using 50 ppm NO for 30 min and then it was exposed to the mixture using 100 ppm, 150 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm, 700 ppm and 800 ppm NO for 20 min at each concentration. Similar experiments were performed changing either the NH_3 or the NO concentration at 350 °C.

Experiments were also performed to investigate the NO_x reduction at various NO_2/NO_x ratios at both 175 °C and 350 °C. The gas composition was 500 ppm NO_x, 500 ppm NH_3 and 8% O_2 but the NO_2/NO_x ratio was changed. At 175 °C the activity was measured as the catalyst was exposed to the gas mixture with a NO_2/NO_x ratio equal to zero for 40 min. Then the NO_x reduction activity was measured at NO_2/NO_x ratios of 0.2, 0.4, 0.5, 0.6, 0.8 and 1 for 20 min at each ratio. The activity was also measured at 350 °C as the catalyst was exposed to the gas mixture with a NO_2/NO_x ratio equal to zero for 30 min. Then the NO_x reduction activity was measured at NO_2/NO_x ratios of 0.2, 0.4, 0.5, 0.6, 0.8 and 1 for 15 min at each ratio.

The ammonia oxidation was investigated in a steady-state experiment at temperatures from 100 °C to 400 °C with a feed gas mixture containing 500 ppm NH_3 and 8% oxygen. The temperature was held constant at 100 °C for 50 min, at 150 °C for 20 min and at 200–400 °C for 10 min. The experiment was repeated using 500 ppm NH_3, 8% O_2 and 5% H_2O to investigate the effect of water.

An experiment was performed to oxidize NO to NO_2 at steady-state conditions. The catalyst was exposed to 500 ppm NO, 8% O_2 and 5% H_2O at 100 °C for 60 min. Thereafter, the activity for NO oxidation was measured at 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C and 500 °C for 20 min at each temperature. The experiment was also performed without water present in the feed.

3. Results and discussion

3.1. NO_x conversion over ZSM-5 catalysts

The result of activity measurements over the Cu-ZSM-5-27 catalyst is shown in Fig. 1. The catalytic activity was measured using a feed gas composition of 500 ppm NO, 500 ppm NH_3 and 8% O_2 at temperatures from 100 °C to 500 °C. The catalyst was kept at each temperature for 20–40 min as shown in the figure. The concentration of measured NO_x increases to 500 ppm after a few minutes, but the concentration of NH_3 does not increase until after approximately 20 min. This indicates that there is more ammonia than nitrogen oxides stored on the surface. There is ammonia slip as the temperature increases
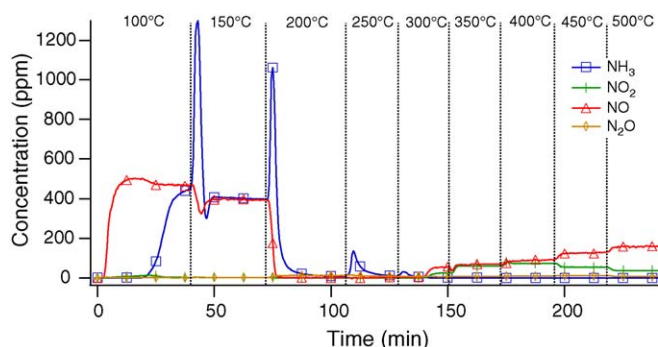

Fig. 1. Catalyst out concentrations over Cu-ZSM-5-27 from 100 °C to 500 °C are shown from a feed gas composition of 500 ppm NO, 500 ppm NH_3 and 8% O_2.

oxidized and there is no ammonia leaving the catalyst. There is almost no conversion of NO_x at 100 °C, but the conversion increases and reaches 100% at 200 °C. The NO_x conversion decreases at temperatures from 300 °C to 500 °C, which may be due to the oxidation of ammonia. Less than 20 ppm of N_2O is formed during the experiment. The NO/NO_2 ratio of NO_x exiting the catalyst decreases above 300 °C because the NO oxidation increases with the temperature and reaches equilibrium at 400 °C.

Similar experiments were performed for the Cu-ZSM-5-55 and the Cu-ZSM-5-300 catalysts. The steady-state conversions of NH_3 and NO_x as a function of temperature for the three Cu-ZSM-5 catalysts are compared in Fig. 2.

The analysis of NO reduction by NH_3 in the presence of O_2 shows a continuous NO reduction. The Si/Al ratio determines the number of Brønsted acid sites in ZSM-5 and therefore also the capacity to introduce copper ions at exchangeable sites [18]. The Cu-ZSM-5-27 catalyst holds the largest number of acid sites and the result shows that this catalyst, with the lowest ratio, reveals the highest NO_x conversion, and, as the ratio increases, the conversion decreases. Similar Si/Al effects were shown by Long and Yang [19], who reported decreasing NO conversions with increasing Si/Al ratio over Fe-ZSM5 catalysts with similar ion-exchange levels. Komatsu et al. [11] reported that a decreased Si/Al ratio improves the specific activity (per Cu^{2+} ion) over Cu-ZSM-5, because the aluminum concentration increases resulting in an increase in the copper concentration. They also reported an increased specific activity to an ion-
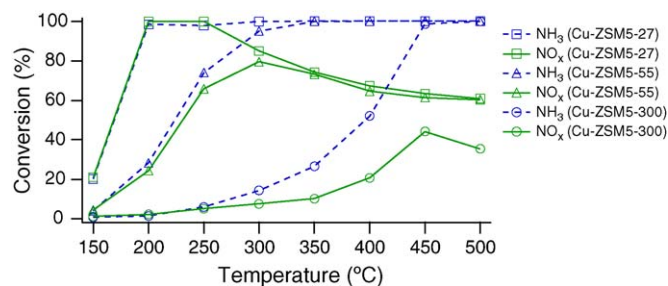

Fig. 2. Steady-state conversions at temperatures from 150 °C to 500 °C over Cu-ZSM-5 with different silica to alumina ratios. The catalysts were exposed to

exchange level of a Cu/Al ratio equal to 1, and concluded that the specific activity is governed by the concentration of the copper ions in Cu-ZSM-5. At higher Cu/Al ratios they suggest that aggregates of CuO may be formed which are much less active than Cu^{2+} and may block the pores of ZSM-5, resulting in decreased activity. The ion-exchange level differs between the Cu-ZSM-5 samples in this study, increasing in an order of Cu-ZSM-5-300 < Cu-ZSM-5-55 < Cu-ZSM-5-27. All three catalysts have a Cu/Al ratio < 0.5, which implies that the samples are under-exchanged, i.e. no formation of CuO is expected, and an enhancement in NO conversion with increased ion-exchange level can thus be expected. Since the Cu-ZSM-5-27 sample contains both the largest number of Brønsted acid sites and copper ions, the highest activity was observed over this catalyst.

It can also be seen in Fig. 2 that the conversions of NO and NH_3 are similar for the respective catalysts at low temperatures. This indicates that the reduction of NO occurs selectively at low temperatures according to reaction (1), consuming equimolecular amount of NH_3 and NO. At higher temperatures the conversion of ammonia and nitric oxide deviate, indicating that some ammonia is consumed without simultaneous NO reduction. It is noted that all three catalysts show decreased conversion of nitric oxide after reaching a maximum, but the conversion of ammonia shows a continuous increase to 100% with increasing temperature. One explanation for the decrease in NO reduction activity suggests that the selectivity for NO reduction decreases at high temperatures and a competition between NO reduction and NH_3 oxidation occurs. If NH_3 is oxidized, a lower amount of NH_3 is available for SCR and more NO may be produced resulting in a lower conversion of NO. Several authors have observed similar behavior over various catalysts and attributed the decreased NO_x conversion at high temperatures to an effect caused by ammonia oxidation [11,13,20,21].

The copper exchanged catalyst was prepared from H-ZSM-5 via Na-ZSM-5 and activity tests were performed to study the NO_x conversion over both the H-ZSM-5 and the Na-ZSM-5 as described above. The steady-state results from the H-ZSM-5-27, Na-ZSM-5-27 and the Cu-ZSM-5-27 catalysts are compared in Fig. 3. The activity for reduction of nitrogen oxides over the H- and the Na-ZSM-5-27 catalysts is similar but introducing copper ions into the zeolite greatly enhances the catalytic activity. The result is in accordance with Komatsu et al. [11], who found that the conversion of nitric oxide was
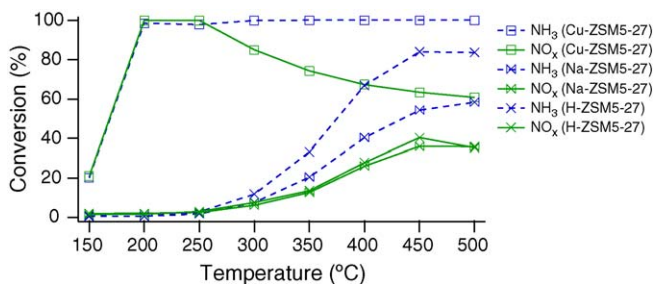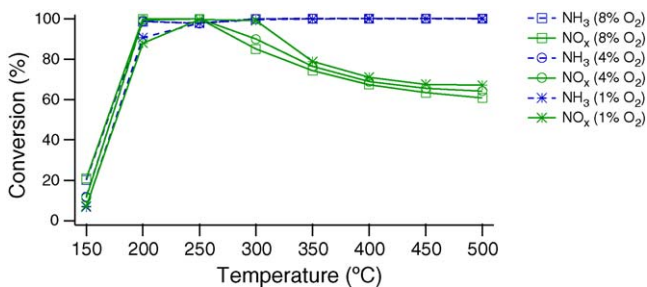

Fig. 4. Steady-state NO_x reduction over the Cu-ZSM-5-27 catalyst performed at different O_2 concentrations and temperatures from 150 °C to 500 °C. The catalyst was exposed to 500 ppm NO, 500 ppm NH_3 and 1–8% O_2.

much lower for the H-ZSM-5 than for the Cu-ZSM-5 catalyst, and, that the reduction is catalyzed by the copper ions exchanged into the zeolite. Ammonia oxidation occurs in all catalysts but the ammonia conversion does not reach 100% over the H and Na catalysts.

3.2. Influence of gas composition

The presence of oxygen has been reported to influence both the reaction mechanism and the nature of the active copper species [6], which in turn may influence the catalytic activity. In this study, changing the concentration of O_2 from 8% to 1% and 4% and performing similar tests as described above examined the influence of O_2. A comparison between the steady-state activity at 1%, 4% and 8% oxygen is shown in Fig. 4. The result reveals that the O_2 concentration affects the NO conversion and even though the separation between the curves is rather small, the difference between the experiments is consistent with the change in oxygen concentration. Increased O_2 concentration results in decreased conversion at high temperatures, but at low temperatures the opposite behavior is observed. Several explanations have been given to the observation that an increased oxygen concentration enhances the NO reduction rate at low temperatures. Two possible explanations may be that O_2 can be needed to activate NO by oxidation to nitrites and/or nitrates, and secondly, oxygen may be needed to maintain the proper oxidation state of the copper ions. Ham et al. [22] reported that oxygen plays an important role in the reoxidation of cuprous ions to cupric ions in copper exchanged mordenite. However, Eng and Bartholomew [23] studied NO reduction over H-ZSM-5 and concluded that the main role of oxygen is to react with NO to form an active intermediate species that can adsorb on the surface. Komatsu et al. [24] concluded that NO_3^- can be one of the key intermediates for the reduction of nitric oxide with ammonia over Cu-ZSM-5. The decrease in conversion with increasing oxygen concentration at high temperatures seen in this study may be due to NH_3 oxidation. The NH_3 oxidation rate increases with higher O_2 concentrations resulting in decreased conversion of NO_x.

Additional experiments were performed as described above with water present in the feed gas (Fig. 5). The NO conversion is enhanced by the presence of water both at low and high temperatures. The improved conversion is particularly pro-

Fig. 3. Steady-state conversions at temperatures from 150 °C to 500 °C over ZSM-5-27 with different ions. The catalysts were exposed to 500 ppm NO,

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