

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In <i>Inter Partes</i> 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 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 NO<sub>x</sub> 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<sub>2</sub>, 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 NO<sub>x</sub> 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 NO<sub>x</sub> at 350 °C and below and that maintained NO<sub>x</sub> conversion without excessive loss of NO<sub>x</sub> 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 NO<sub>x</sub> 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 NO<sub>x</sub> 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, silicalite, Beta, mordenite, and erionite.

15. Selective catalytic reduction of oxides of nitrogen in the presence of oxygen or providing good low temperature conversion of NO<sub>x</sub> below 350 °C is not discussed in Ritscher. Ritscher provides no information with respect to providing improved NO<sub>x</sub> 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<sub>2</sub>O) 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

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