Project : **Chemical Interactions in Multimetal/Zeolite Catalysts**
Project Code: DE FG02-87ERA 13654
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This two-year project has led to a significant improvement in the fundamental understanding of the catalytic action of zeolite-supported redox catalysts. It turned out to be essential that we could combine four strategies for the preparation of catalysts containing transition metal (TM) ions in zeolite cavities:

(1) Ion exchange from aqueous solution
(2) chemical vapor deposition (CVD) of a volatile halide onto a zeolite in its acidic form
(3) solid state ion exchange
(4) Hydrothermal synthesis of a zeolite having TM ions in its lattice, followed by a treatment transporting these ions to "guest positions".

Technique (2) enables us to position more TM ions into cavities than permitted by the conventional technique (1).*viz* one positive charge per Al centered tetrahedron in the zeolite lattice. The additional charge is compensated by ligands to the TM ions, for instance in oxo-ions such as $(GaO)^+$ or dinuclear $[Cu\text{-}O\text{-}Cu]^{2+}$. While technique (3) is preferred over CVD where volatile halides are not available, technique (4) leads to rather isolated "*ex lattice*" oxo-ions. Such oxo-ions tend to be mono-nuclear, in contrast to technique (2) which preferentially creates dinuclear oxo-ions of the same TM element.

A favorable element for the present research was that the PI is also actively engaged in a project on the reduction of nitrogen oxides, sponsored by EMSI program of the National Science Foundation and the US Department of Energy, Office of Science. This combination created a unique opportunity to test and analyze catalysts for the one step oxidation of benzene to phenol and compare them with catalysts for the reduction of nitrogen oxides, using hydrocarbons as the reductant. In both projects catalysts have been used which contain Fe ions or oxo-ions in the cavities the zeolite MFI, often called ZSM-5.

With Fe as the TM element and MFI as the host zeolite we found that catalysts with high Fe content, prepared by technique (2) were optimal for the De-NO_x reaction, but extremely unselective for benzene oxidation to phenol. Conversely, the catalysts prepared with (4) had the highest turnover frequency for benzene oxidation, but performed very poorly for NO_x reduction with *so*-butane.

In fact the Fe concentration in the former catalysts were so low that it was necessary to design a special experimental program for the sole purpose of showing that it is really the Fe which catalyzes the benzene oxidation,.not some acid center as has been proposed by other authors. For this purpose we used hydrogen sulfide to selectively poison the Fe sites, without deactivating the acidic sites. In addition we could show that the hydrothermal treatment of catalysts prepared by

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technique (4) is essential to transform iron ions in the zeolite lattice to "*ex lattice ions*" in guest positions. That line of the work required very careful experimentation, because a hydrothermal treatment of a zeolite containing Fe ions in its cavities can also lead to agglomeration of such ions to nano -particles of iron oxide which lowers the selectivity for the desired formation of phenol.

This part of the program showed convincingly that indeed Fe is responsible for the benzene oxidation catalysis. The results and conclusion of this work, including the comparison of different catalysts, was published in a number of papers in the scientific literature, listed in the attached list. In these papers also our analysis of the reaction orders and the possible mechanism of the used test reaction are given.

Publications W.M.H. Sachtler, acknowledging DOE support 2002-2004

1. "Identification of Highly Active Iron Sites in N_2O-Activated Fe/MFI," J. Jia, Q. Sun, B. Wen, Lin X, Chen, W M.H. Sachtler, *Cat Lett* 82 (**2002**) 7-11.

2 "Spectroscopic Evidence for a Nitrite Intermediate in the Catalytic Reduction of NO_x with Ammonia on Fe/MFI," Qi Sun, Zhi-Xian Gao, Bin Wen and Wolfgang M. H. Sachtler *Cat. Lett.* 78 **2002**, 1-5.

3. "Synergism of Cobalt and Palladium in MFI Zeolites of Relevance to NO_x Reduction with Methane," B. Wen, Jifei Jia, Sh. Li, T.Liu, Lin X. Chen,W.M.H. Sachtler, *Phys. Chem. Chem. Phys.* 4 **2002** 1983-1989

4. "Characterization by EXAFS of Co/MFI Catalysts Prepared by Sublimation," V. Schwartz, R. Prins, X. Wang, W.M.H. Sachtler *J. Phys Chem.* B 106 (**2002**) 7210-7217.

5. "Chemical Anchoring of Palladium by Fe-oxo ions in Zeolite ZSM-5," Bin Wen, Jifei Jia, Wolfgang. M. H. Sachtler *J. Phys. Chem.* B 106 (**2002**) 7520-7523.

6. "Identification by Isotopic Exchange of Oxygen Deposited on Fe/MFI by Decomposing N_2O," Jifei Jia, Bin Wen, and Wolfgang M.H. Sachtler, *J.Catal.* 210 (2002) 453-459.

7. "NO_x reduction from diesel emissions over a non-transition metal zeolite catalyst effect of water in the feed," Bin Wen, Young Hoon Yeom, Eric Weitz, Wolfgang M. H. Sachtler, *Appl Catal. B* 48. (**2004**) 125-134

8. "Mn/MFI catalyzed Reduction of NO_x with Alkanes," Qi Sun, Wolfgang M. H. Sachtler *Appl Catal. B* 42 **2003** 393-401

9. "Activity enhancement for catalytic NO_x reduction and selective oxidation by structural changes in Co/MFI and Fe/MFI," Bin Wen , Qi Sun, Jifei Jia, Wolfgang M.H. Sachtler Abstract for 18th meeting North Amer. Cat. Soc., meeting Cancun) June 1-6, **2003**.

10. "One-step Oxidation of Benzene to Phenol with Nitrous Oxide over Fe/MFI Catalysts," Jifei Jia, Krishnan S. Pillai, and Wolfgang M. H. Sachtler, *J. Catal.*, 221 (**2004**) 119-126.

11. "Effect of Steaming on One-step Oxidation of Benzene to Phenol with Nitrous Oxide over Fe/MFI Catalysts," Krishnan S. Pillai, Jifei Jia, and Wolfgang M. H. Sachtler, *Appl. Catal. A.* (**2004**) 119-126

12. "NO_x reduction from diesel emissions over a non-transition metal zeolite catalyst effect of water in the feed," Bin Wen, Young Hoon Yeom, Eric Weitz, Wolfgang M. H. Sachtler, *Appl Catal. B* 48. (**2004**) 125-134

13. "NO reduction by CH4 over Pd/Co-sulfated zirconia catalysts" L. F. Córdoba, W. M. H. Sachtler, C. Montes de Correa, Appl. Catal. (submitted)

14 ."NO_x reduction from diesel emissions over a non-transition metal zeolite catalyst. A Mechanistic study using FTIR spectroscopy," Young Hoon Yeom,, Bin Wen, W.M.H. Sachtler, Eric Weitz. *J. Phys. Chem.* (**2004**) (in press).

15 "Characterization of iron catalysts prepared by chemical vapor deposition on non-zeolitic supports," J. D. Henao, B. Wen, W. M. H. Sachtler, *J. Phys. Chem.* (Submitted)

16 "Mechanism of Nitrogen Oxide Reduction with Acetaldehyde in Simulated Diesel Emissions over Zeolite-based Catalysts," Bin Wen, Young-Hoon Yeom, Eric Weitz, Wolfgang M. H. Sachtler Abstract for 13. ICC, Paris, July **2004**.

17. "Reduction over zeolite-based catalysts of nitrogen oxides in emissions containing excess oxygen-Unraveling the Reaction mechanism," Hay-Ying Chen, Qi Sun, Bin Wen, Young-Hoon Yeom, Eric Weitz, Wolfgang M. H. Sachtler; *Catalysis Today* (subm.)

18 "Catalysis of Metal Nano-Particles and Multimuclear Oxo-Ions in Zeolites" W.M.H. Sachtler, Abstract Invited Lecture Symposium "*Nanotechnology in Catalysis*, 228th ACS Nat'l Meeting Philadelphia, **2004**