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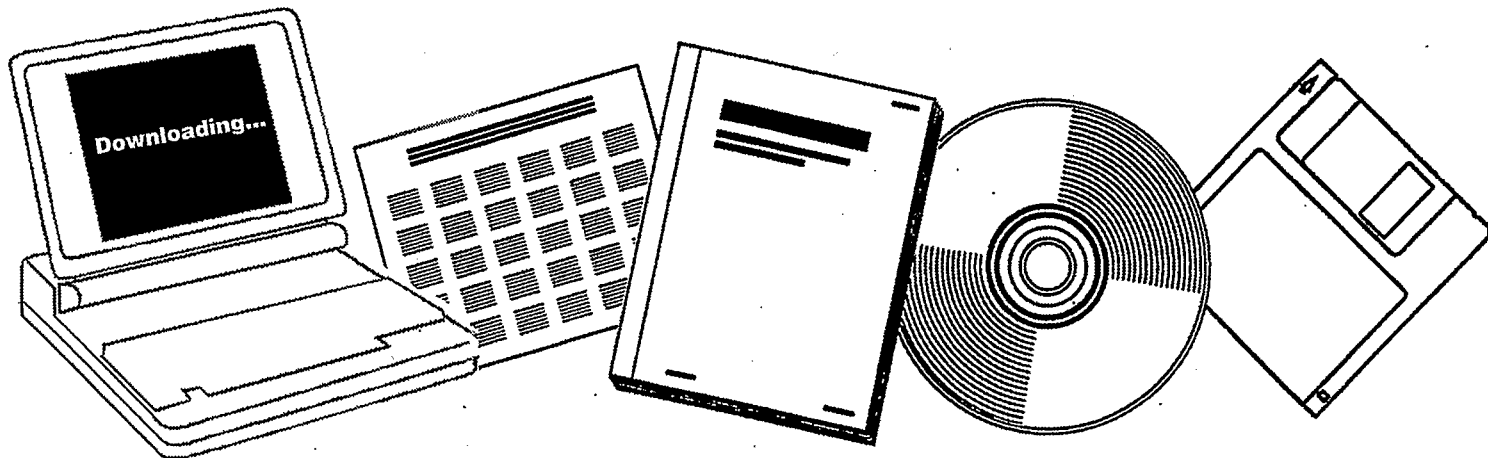
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**CHEMICAL INTERACTIONS IN  
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REPORT, JANUARY 7, 1988--JANUARY 6, 1989**

**NORTHWESTERN UNIV.  
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# CHEMICAL INTERACTIONS IN MULTIMETAL/ZEOLITE CATALYSTS

## PROGRESS REPORT

FOR PERIOD JANUARY 7, 1988 - JANUARY 6, 1989

WOLFGANG M. H. SACHTLER

NORTHWESTERN UNIVERSITY  
EVANSTON, ILLINOIS 60208

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Chemical Interactions in Multimetal/Zeolite Catalysts

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Principal Investigator: W.M.H. Sachtler

Northwestern University, Evanston, IL 60208

Progress Report on Second Year, starting January 07, 1988

Research in the second year focused on the mono- and multimetal/zeolite catalysts Pt/NaY, Pd/NaY, (Pt+Cu)/NaY, (Ni+Mn)/NaY, (Ni+Mn+Pt)/NaY and (Pt+Re)/NaY. Thanks to a supplementary budget provided by DOE in November of 1987, research was started on temperature programmed oxidation of used PtRe catalysts, in order to analyze the hydrocarbonaceous overlayers which are deposited during catalytic conversion of hydrocarbons. These catalysts included Pt and PtRe supported on alumina, silica or NaY. Coke deposition was compared for samples which had or had not been exposed to a 9.4 ppm H<sub>2</sub>S in H<sub>2</sub> in order to pick up sulfur.

In our opinion, research on the above topics was quite successful; a considerable number of papers has been prepared and submitted for publication, of which the first ones have appeared in print or are accepted by the journals. A list of 16 papers, written after July 1987 is attached. The principal investigator reported orally on the progress of this work at the DOE Meeting in Gaithersburg on Oct. 15, 1987 and at several other meetings. In the present brief report the following highlights are mentioned:

1. For Pt/NaY catalysts our analysis of the mechanism of metal particle formation has enabled us to produce at will samples which contain either the majority of the Pt particles in supercages, without filling these cages completely, or the Pt particles bulge into neighboring cages. The catalytic selectivity is distinctly different for these preparations, in the former case molecules can enter a supercage which is partially filled by the Pt cluster, in the second case adsorption takes place through the cage window.
2. Applying the same principles of catalyst preparation to bimetallic catalysts enables us to produce PtCu particles in supercages of NaY, which contain, initially a Pt core, surrounded by a Cu mantle.
3. Earlier we had found that Ni ions migrate into hexagonal prisms during calcination of Ni/NaY; this process can be partially suppressed by first filling these prisms with Mn or Cr ions. In more recent work we found that addition of Pt strongly lowers the temperature of Ni reduction. Part of the Ni ions is reduced by hydrogen while still inside the smaller cages. This reduction process is, however, reversible; at elevated temperature and in an inert atmosphere protons re-oxidize the Ni atoms and dihydrogen gas is developed. In this way it seems possible to count the Ni atoms in small cages.
4. Our "chemical anchoring" model for Pt + Fe in NaY or NaHY was further supported by Moessbauer results obtained by professor Dumesic, University of Wisconsin, with our samples.

5. The calcination stage in the preparation of zeolite supported metals has been studied in considerable detail for Pd/NaY. The Pd is introduced as a tetrammin complex; during calcination the ammine ligands are successively oxidized. Once three ammine ligands are destroyed, the Pd ions which carry only one ligand, surprisingly jump from the supercages to the sodalite cages. The metal dispersion after reduction is controlled by the calcination program; highest dispersion is obtained if all Pd ions are in the supercages as di-ammino complexes. Dispersion is very low, if reduction is started while Pd is still present as a tetrammine complex, and a moderate dispersion is obtained by reducing naked Pd ions in sodalite cages.

6. Zeolite supported PtRe catalysts cannot be prepared by simple ion exchange of common salts in aqueous solution, because Re forms a perrhenate anion which cannot be exchanged against positive cations. We have explored a number of alternative paths to solve this problem and obtained excellent catalysts by the following procedure: Pt was first incorporated in the zeolite by exchange, followed by calcination at 360°C and temperature programmed reduction. Then gaseous di-rhenium decacarbonyl is sublimed onto the sample, and the deposit is decomposed by temperature programmed reductive decomposition in flowing hydrogen. Catalytic tests of cyclopentane hydrogenolysis and temperature programmed reduction (TPR) of the oxidized samples suggest a very high degree of formation of bimetallic PtRe clusters.

7. New equipment has been designed for temperature programmed oxidation (TPO) with on-line analysis by mass spectrometry and GLC. This technique has been applied to mono and bimetallic supported Pt, Re or PtRe samples which had been subjected to a catalytic test of hexane conversion for 22 hours. During TPO the consumption of oxygen and the production of CO<sub>2</sub> were continuously monitored quantitatively. After each TPO run the samples were reduced by TPR in order to measure the degree of metal oxidation. From the three measured data of (1) total oxygen consumption, (2) CO<sub>2</sub> formation, and (3) metal oxidation it is possible to calculate the number of carbon and oxygen atoms in the hydrocarbonaceous overlayer. These measurements were repeated for sulfur-free and presulfided catalyst. It was found, that the amount of deposited coke is smaller for the presulfided catalyst. Even more remarkable is, however, a second result: the "coke" formed on the sulfur-free samples is almost hydrogen-free, i.e. presumably graphitic; however on the presulfided samples a hydrogen-rich coke is deposited. This finding supports our earlier model, that S atoms, linked to Re atoms, inhibit the reorganization of "soft coke" to "hard-coke" and thus improve the activity maintenance of these catalysts.

A lecture on these results was given by Dr. S.M. Augustine before the group of Dr. Wayne Goodman in Los Alamos, in view of plans to continue this work as a joint program of both groups. The principal investigator also reported on these results before the 9. International Congress on Catalysis in Calgary.

W.M.H. Sachtler, Publications written after 7/1/1987

1. "Catalytic Evidence for the Formation of Mixed Metal Ensembles in Supported PtRe Catalysts" S.M. Augustine, M.S. Nacheff, C. M. Tsang, J.B. Butt and W.M.H. Sachtler, CATALYSIS 1987, Proc. 10th North Am. Meeting Catalysis Society, San Diego, CA, 17-22 May 1987, J.W. Ward Editor; Volume 38 of "Studies in Surface Science and Catalysis, Elsevier, Publ. p. 1-10.
2. "Formation and Growth Mechanisms of Pt Particles in Y Zeolites", M.S. Tzou, W.M.H. Sachtler, CATALYSIS 1987, Proc. 10th North Am. Meeting Catalysis Society, San Diego, CA, 17-22 May 1987, J.W. Ward Editor; Volume 38 of "Studies in Surface Science and Catalysis, Elsevier, Publ. p. 233-241;
3. "Dehydrocyclization Controlling Site in Bifunctional Reforming Catalysts. - Reply to Letter by Margitfalvi and GLOBOLLOS", V.K. Shum, J.B. Butt, W.M.H. Sachtler, Applied Catalysis 36 (1988) 337-9.
4. "Genesis and Characterization of Transition Metal Clusters in Y Zeolites" M. S. Tzou, H.J. Jiang, W.M.H. Sachtler, Solid State Ionics 26 1988 71-76
5. "Promoting Effect of Preadsorbed Sulfur in Ethylene Hydroformylation Reaction on Supported Rhodium Catalysts", Yasuo Konishi, Masaru Ichikawa, Wolfgang M.H. Sachtler, Shokubai 1987.
6. "Bimetallic Cluster Formation in supported PtRe Catalysts; Characterization and Activity of Multi-atomic Sites on Supported PtRe Catalysts" Steve M. Augustine, Maurena S. Nacheff, C. Mark Tsang, John B. Butt, and Wolfgang M. H.Sachtler, Catalysis: Theory to Practice, Proceedings Intern. Congr. Catalysis, 9th, Calgary, Canada, 1988, M.J. Phillips. M. Ternan, Eds. (Chem. Inst. Canda, Ottawa, CDN 1988) Vol. 3, p.1190-1197.
7. "Formation of Pt Particles in Y Type Zeolites; The Influence of

- Co-Exchanged Metal Cations" M. S. Tzou, B. K. Teo, W.M.H. Sachtler, J. Catal. (accepted)
8. "Hydrogen Release from Ni/Faujasite Catalysts" H.J. Jiang, M.S. Tzou, W.M.H. Sachtler, Catalysis Letters 1988 1, 99-107
  - 9 "Fischer-Tropsch Revisited; Product Control Circumventing Schulz-Flory," W.M.H. Sachtler, Proceedings NATO Workshop on Heterogeneous Catalysts for Carbon Monoxide Conversion, Nieuwpoort, Belgium, April 17-22, 1988 (in print)
  10. "On the Mechanism for the Platinum Catalyzed Reduction of Rhenium in PtRe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>", S.M. Augustine, W.M.H. Sachtler, J. Catal. (submitted May 1988)
  11. "Synthesis and Characterization of Bimetallic PtRe<sub>x</sub> Clusters Prepared by Sublimation of Re<sub>2</sub>(CO)<sub>10</sub> onto Pt/NaY" C. Mark Tsang, Steven M. Augustine, John B. Butt and Wolfgang M.H. Sachtler, (submitted to Applied Catalysis)
  12. "Elementary Steps in the Formation of Highly Dispersed Palladium in NaY; Part I Chemical Processes During Calcination" S.T. Homeyer W.M. H. Sachtler, J. Catalysis (submitted)
  13. "Moessbauer Spectroscopy Studies of PtFe/NaY Zeolite" Vijay R. Balse, W.M.H. Sachtler, J.A. Dumesic, Catalysis Letters (submitted)
  14. "Characterization and Catalysis of Pt-Cu Clusters in NaY" Giuliano Moretti, W.M.H. Sachtler, J. Catalysis (submitted)
  15. "Geometric Causes of the Methylcyclopentane Selectivity over Pt/NaY Catalysts, Giuliano Moretti, Wolfgang M.H. Sachtler, J. Catalysis (submitted)
  16. "The Effect of Re, S, and Cl on the Deactivation of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Reforming Catalysts" S.M. Augustine, G. N. Alameddin, and W.M.H. Sachtler J. Catalysis (submitted)