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Symposium on Advanced Methods of Catalyst Characterization

(Jointly sponsored by the Materials Research Society and the American Chemical Society)

Chair

K. Klier, Lehigh University

November 1-2, 1982

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SUMMARY

→ The objective of the Symposium was to present, discuss, and evaluate the most advanced state-of-the-art methods that can be used for the characterization of heterogeneous catalysts down to atomic and molecular level.

The 30 presented papers covered applications of very high resolution transmission (TEM) and scanning transmission (STEM) electron microscopy, in situ TEM studies, and high resolution analytical STEM; characterization and preparation of metal clusters and encapsulation of small particles; spectroscopic studies of catalysts and their surfaces, particularly solid state spin-echo and magic angle spinning NMR, Fourier transform infrared, including beam deflection spectroscopy, EXAFS, SIMS, ISS, and Mössbauer spectroscopic investigations. The Symposium program and abstracts are attached in Appendix I. Fifteen full papers will appear, along with the abstracts, in a late 1983 issue of the Journal of Molecular Catalysis. The Symposium was international in scope, with six foreign speakers from the United Kingdom (3), Netherlands (1), and Mexico (2). ← The generous support by the Department of the Navy (ONR), American Chemical Society (PRF) and industrial sponsors listed on the front page was mainly used for travel assistance of the foreign as well as some of the domestic speakers. Financial report is attached in Appendix II.

Among the highlights were the presentations of atomic resolution STEM, solid state NMR studies of zeolite local structures and adsorbate-metal particle interactions, and 2nm resolution analytical STEM of the multiphase, highly inter-dispersed, and concentration gradient containing catalysts. The very active and constructive discussion as well as post-symposium reviews demonstrated the usefulness of the Symposium to the participants as well as to a wider scientific audience. It is evident that the art of catalyst characterization has established a firm and respectable position in the Materials Society programs. Furthermore, as both the electron microscopic and spectroscopic methods undergo a continuous development, the full atomic and molecular structure of a catalyst as well as spacial mapping thereof appears to be in the reach of experimental science.

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APPENDIX I

**SYMPOSIUM K**

**ADVANCED METHODS OF  
CATALYST CHARACTERIZATION**

(Jointly sponsored by the American Chemical Society)

**Chair**

**K. Klier, Lehigh University**

**November 1-2  
Clarendon Room**

***Principal Symposium Support***

**Office of Naval Research (D. Nelson)  
American Chemical Society Petroleum Research Fund**

***Supplemental Support***

**Air Products and Chemicals  
The Badger Company  
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**K**

## SYMPOSIUM K

## ADVANCED METHODS OF CATALYST CHARACTERIZATION

## Chair

K. Klier, Lehigh University, Bethlehem, PA

November 1 - 2, 1982

## Session K1

HIGH RESOLUTION TEM AND STEM, SIMS, EELS, ISS  
Monday Morning, November 1

- 8:30 K1.1 Present and Future STEM Studies of Catalysts at the Atomic Level, Albert V. Crewe, Enrico Fermi Institute and the University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637
- 9:10 K1.2 Characterization of the Surface Structure on Small Metallic Particles, M. José Yacamán, Instituto de Física, U.N.A.M., Apartado Postal 20-364, 01000 México, D.F.
- 9:35 K1.3 Microstructural Transformations of Catalyst Particles, Lanny D. Schmidt, Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455
- 10:00 BREAK
- 10:20 K1.4 In-Situ TEM and ISS Studies of Supported Metal "SMSI" Catalysts, Michael J. Kelley, David R. Short, and Dennis G. Swartzfager, Engineering Technology Laboratory and Central Research Department, DuPont Experimental Station, Wilmington, DE 19898
- 10:45 K1.5 Preliminary Investigation of the Palladium-Tungsten- $\gamma$ Al<sub>2</sub>O<sub>3</sub> Catalyst System by Transmission Electron Microscopy (TEM), H. K. Plummer, Jr., S. Shinozaki, K. M. Adams and H. S. Gandhi, Ford Motor Co., P.O. Box 2053, Dearborn, MI 48121
- 11:10 K1.6 Identification of Small Bimetallic Particles by Controlled Atmosphere Electron Microscopy, R. Terry Baker, Rex D. Sherwood and James A. Dumesic\*, Corporate Research Science Laboratories, Exxon Research and Engineering Co., Linden, N.J. 07036. \*Chemical Engineering Department, University of Wisconsin, Madison, WI 53706
- 11:35 K1.7 Direct Observations of Small Gold Clusters and In Situ Cluster Growth by Scanning Transmission Electron Microscopy, Marilyn A. Listvan and A. V. Crewe, Physics Department and Enrico Fermi Institute of the University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637
- 12:00 LUNCH BREAK

Session K2  
**PREPARATION, CHARACTERIZATION AND ENCAPSULATION OF METAL CLUSTERS**  
 Monday Afternoon, November 1

- 1:30 K2.1 Generation of Supported Metal Clusters of Controlled Size and Composition, R. S. Bowles, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544; S. B. Park, N. Otsuka, and R. P. Andres, School of Chemical Engineering, Purdue University, West Lafayette, IN 47907
- 1:50 K2.2 Supported and Protected Metal Clusters: An Attempt at Characterisation, Peter B. Wells and R. B. Moyes, Department of Chemistry, The University, Hull, England, HU6 7RX, and R. Whyman, ICI New Science Group, Runcorn, England, WA7 4QE
- 2:10 K2.3 Encapsulation, A New Mechanism of Catalyst Deactivation, Bob R. Powell and Shell E. Whittington, Physical Chemistry Department, General Motors Research Laboratories, Warren, MI 48090
- 2:30 K2.4 Interaction of Al<sub>2</sub>O<sub>3</sub> with Rh and Pt Thin Films, J. E. E. Baglin\*, J. A. Cairns\*\*, G. J. Clark\*, and J. F. Ziegler\*, \*IBM Thomas J. Watson Research Center, Yorktown Heights, NY; \*\*AERE Harwell, Oxfordshire, UK
- 2:50 K2.5 An X-Ray Method to Characterize the Structure of Cobalt in CO-ZSM-5 Catalysts, Ashok G. Dhere and Robert J. De Angelis, Department of Metallurgical Engineering and Materials Science, University of Kentucky, Lexington, KY 40506

3:10 BREAK

Session K3  
 IR AND NMR METHODS

- 3:30 K3.1 Infrared Characterization of Catalyst Surfaces using Beam Deflection Spectroscopy, M. J. D. Low, C. Morterra and A. G. Severdia, Department of Chemistry, New York University, 4 Washington Place, New York, NY 10003
- 3:50 K3.2 N.M.R. Studies of Platinum Catalysts, Harold T. Stokes\*, Claus D. Makowka, Po-Kang Wang, Serge L. Rudaz, Charles P. Slichter, and J. H. Sinfelt\*\*, Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801. \*Present Address: Department of Physical Astronomy, Brigham Young University, Provo, UT 84602, \*\*Exxon Research and Engineering Co., Linden, NJ 07036
- 4:10 K3.3 <sup>29</sup>Si-N.M.R. Characterization of the Structure and Aluminum-Orderings of Zeolites, Janos B. Nagy and Eric G. Derouane, Laboratoire de Catalyse, Facultés Universitaires de Namur, Rue de Bruxelles, 61, B-5000 Namur, Belgium, and Peter A. Jacobs, Centrum voor Oppervlakteskunde en Colloidale Scheikunde, Katholieke Universiteit Leuven, De Croylaan 42, B-3030 Leuven, Belgium
- 4:30 K3.4 FTIR Spectroscopic Characterization of Surface Reactions Occurring on Metal-Impregnated Carbons, R. R. Swardzewski and D. E. Tevault, Chemistry Division, Code 6170, Naval Research Laboratory, Washington, D.C. 20375

Session K4  
Tuesday Morning, November 2

- 8:30 K4.1 New Ways of Studying Catalysts, John M. Thomas, University of Cambridge, Department of Physical Chemistry, Lensfield Road, Cambridge, CB2 1EP, U.K.
- 9:10 K4.2 Observations of Surface Hydrogen during Heterogeneous Catalytic Reactions, M. Mullins and H. Saltsburg, Department of Chemical Engineering, University of Rochester, Rochester, NY 14627

ANALYTICAL STEM

- 9:35 K4.3 Analytical Electron Microscopic Study of the Dispersion and Distribution of Active Species in Oxide and Sulfide Catalysts, F. Delannay, Groupe de Physico-chimie Minérale et de Catalyse, Place Croix du Sud n°1, B-1348 Louvain-la-Neuve, Belgium. Present address: Lawrence Berkeley Lab, MMRD, Bldg 62, University of California, Berkeley, CA 94720
- 10:00 BREAK
- 10:20 K4.4 Characterisation of Supported Catalyst Particles by High Resolution STEM, S. J. Pennycook, University of Cambridge, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, U.K.
- 10:45 K4.5 Microanalysis of Catalysts By Analytical Electron Microscopy, C. E. Lyman, Central Research and Development Department, E. I. duPont de Nemours and Co., Experimental Station, Wilmington, DE 19898
- 11:10 K4.6 Characterization of Cu/ZnO Methanol Catalysts by TEM, AEM and EELS, J. M. Domínguez and G. W. Simmons, Lehigh University, Sinclair Laboratory # 7, CSCR, Bethlehem, PA 18015, \*on leave from Mexican Petroleum Institute (IMP-PEMEX)
- 11:35 K4.7 Electron Microscopy of Solid Catalysts. John W. Geus, University of Utrecht, Department of Inorganic Chemistry, NL 3522 Ad Utrecht, Groesestraat 77a, The Netherlands, and J. Pieters, EMSA, Molecular Cell Biology.
- 12:00 LUNCH BREAK

Session K5  
EXAFS AND MOSSBAUER SPECTROSCOPY OF CATALYSTS  
Tuesday Afternoon, November 2

- 1:30 K5.1 Characterization of Supported Metal Catalysts by X-Ray Absorption Spectroscopy, Farrel W. Lytle and Robert B. Gregor, The Boeing Co., Seattle, WA 98124; John Sinfelt and Grayson H. Via, Exxon Research and Engineering Co., Linden, NJ 07036.
- 1:55 K5.2 EXAFS Study of Model Catalysts of Platinum, Rhodium and Platinum-Rhodium on Gamma Alumina, Robert W. Broach, J. P. Hickey and G. R. Lester, UOP Inc., 10 UOP Plaza, Des Plaines, IL

- 2:20 **KS.3 The Effect of Atmosphere on the Structure of Pt and Pd Catalysts, J. B. Cohen, R. K. Nandi, J. B. Butt and R. L. Burwell, Jr., Ipatieff Catalytic Laboratory and Department of Materials Science and Engineering, The Technological Institute, Northwestern University, Evanston, IL 60201**
- 2:45 **KS.4 Dispersion Effects on Alkane Hydrogenolysis over Rhodium Supported on Titanium Oxide, D. E. Resasco and G. L. Haller, Department of Chemical Engineering, Yale University, P.O. Box 2159 YS, New Haven, CT 06520-2159 (U.S.A.)**
- 3:10 **BREAK**
- 3:30 **KS.5 Structure of Alumina Supported Mo/Co Hydrodesulfurization Catalysts Via EXAFS, S. H. Bauer and N-S. Chiu, Department of Chemistry, Cornell University, Ithaca, NY 14853, and M. F. L. Johnson, Harvey Technical Center, ARCO Petroleum Products Company, Harvey, IL 60426**
- 3:55 **KS.6 Characterization of Iron Particles on Thin-Film and High Surface Area Titania Supports, J. A. Dumesic, J. Santos and B. J. Tatarchuk, Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706**
- 4:20 **KS.7 In Situ Mössbauer Study of Iron Sulfides Interactions with Coal and Model Compounds, P. A. Montano and A. S. Bommanavar, Department of Physics, West Virginia University, Morgantown, WV 26506 U.S.A.**

**K1.1**

**PRESENT AND FUTURE STEM STUDIES OF CATALYSTS AT THE ATOMIC LEVEL.** Albert V. Crewe, Enrico Fermi Institute and the University of Chicago, 5640 S. Ellis Ave, Chicago, Illinois 60637

The Scanning Transmission Electron Microscopy (STEM) has demonstrated its capabilities of imaging small clusters and single atoms. This feature of the STEM is obviously of some importance in the field of catalysis and indeed many of the experimental materials we have used have catalytic properties, for example Platinum on carbon. Some of this work will be discussed together with many possible extensions of the techniques to materials of more direct relevance.

**K1.2**

**CHARACTERIZATION OF THE SURFACE STRUCTURE ON SMALL METALLIC PARTICLES.** M. Jose Yacamán, Instituto de Física, U.N.A.M., Apartado Postal 20-364, 01000 Mexico, D.F.

In the present work it is discussed how advanced TEM ultra-high resolution techniques can be used to characterize the surface structure of small metallic particles in the size range between 25-200Å. These techniques include weak beam thickness fringes, single particle electron diffraction, lattice fringes and surface images. It is shown that the particles have rough surfaces which contain steps and irregularities. The number of different types of surface sites is calculated as a function of the particle size. It is shown that an excellent agreement is found between the activity data and the population of surface sites for some reactions.

**K1.3**

**MICROSTRUCTURAL TRANSFORMATIONS OF CATALYST PARTICLES.** L. D. Schmidt, Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455.

Properties of supported catalysts are determined predominantly by structural changes produced in pretreatment, reaction, and regeneration. We describe the use of electron microscopy, X-ray photoelectron spectroscopy, temperature programmed desorption, and secondary ion mass spectrometry to examine the effects of oxidation-reduction cycling and exposure to H<sub>2</sub>S of 10-200Å diameter alloy particles of Pt-Rh and other alloys on planar amorphous SiO<sub>2</sub>. Results for molybdenum oxide particles will also be discussed. Combination of several techniques on the same sample and repeated examination of the same particles before and after various treatments permit a detailed determination of particle shapes, surface enrichment, location and amounts of oxides and sulfides, and sintering and redispersion. Systems and conditions are sufficiently close to those of industrial catalysts to provide direct information on these processes.

K1.4

IN-SITU TEM AND ISS STUDIES OF SUPPORTED METAL "SMSI" CATALYSTS. Michael J. Kelley<sup>+</sup>, David R. Short<sup>+</sup> and Dennis G. Swartzfager<sup>++</sup>, Engineering Technology Laboratory<sup>+</sup> and Central Research Department<sup>++</sup>, DuPont Experimental Station, Wilmington, DE 19898.

The loss of carbon monoxide and hydrogen chemisorption capacity by Pt:TiO<sub>2</sub> reduced above about 400°C is well established as a strong metal-support interaction ("SMSI") effect. In contrast, despite several experimental studies, the underlying physical mechanisms remain a subject of controversy.

We report here studies of the effect of reduction temperature on high purity Pt:TiO<sub>2</sub>. The anatase support was prepared by hydrolyzing titanium isopropoxide; the platinum was applied by ion exchange from the tetramine hydroxide. We reduced this material in-situ in a special cell constructed for a commercial TEM. The instrument is also equipped with high resolution electron energy loss spectrometer (EELS) for elemental and fine structure analysis. We also used ion scattering spectroscopy (ISS) to determine the first monolayer surface composition of externally (ex-situ) reduced materials. These techniques add to our understanding of SMSI, but do not yet give a firm and final insight.

K1.5

PRELIMINARY INVESTIGATION OF THE PALLADIUM-TUNGSTEN- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> CATALYST SYSTEM BY TRANSMISSION ELECTRON MICROSCOPY (TEM). H. K. Plummer, Jr., S. Shinozaki, K. M. Adams and H. S. Gandhi, Ford Motor Company, P.O. Box 2053, Dearborn, MI 48121.

Preliminary studies comparing the morphology and chemical nature of a Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with a Pd-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst have been carried out using transmission electron microscopy. Evidence is presented to indicate that the incorporation of a high concentration of tungsten changes the palladium particle characteristics after calcination in air at 500°C and also after reduction in hydrogen at 550°C.

When Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is calcined in air small palladium particles (<2 nm) are formed in addition to larger palladium oxide particles (<7 nm). Both types of particles are thin, essentially two dimensional, resulting in a high surface to volume ratio. On the other hand, the palladium particles formed during the temperature reduction step contain a narrow size range (~3 to 10 nm) with many particles assuming a three dimensional symmetry thus providing a lower surface to volume ratio.

Pd-W/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, when calcined in air, also produces an essentially two dimensional binodal particle size distribution but in this system the particles are all metallic palladium with no oxides detected. After heating this specimen in hydrogen only a small increase in the particle size range, with a slight decrease in the concentration of small particles, was noted indicating a strong interaction between particles and substrate. Thus a high palladium surface area is retained in this catalyst.

**K1.6**  
**IDENTIFICATION OF SMALL BIMETALLIC PARTICLES BY CONTROLLED ATMOSPHERE ELECTRON MICROSCOPY.** R. Terry K. Baker, Rex D. Sherwood and James A. Dumesic\*, Corporate Research Science Laboratories, Exxon Research and Engineering Co., Linden, NJ 07036. \*Chemical Engineering Dept., University of Wisconsin, Madison, WI 53706

Controlled Atmosphere Electron Microscopy (CAEM) has been used as a microanalytical probe of Pt-Ir particles on single-crystal graphite. The test reactions for this probe were the catalyzed gasification in 5 Torr oxygen and 1 Torr hydrogen. The strategy has been to compare the catalytic behavior of the alloy with that of the pure constituents on the graphite-oxygen and graphite-hydrogen reactions. In the oxidizing environment, the reactivity pattern observed with the alloy paralleled that of Ir, suggesting that the surface of the alloy particles were enriched with Ir. In contrast, the behavior in a hydrogen environment indicated that the Pt component preferentially segregated to the alloy particle surface.

**K1.7**  
**DIRECT OBSERVATIONS OF SMALL GOLD CLUSTERS AND IN SITU CLUSTER GROWTH BY SCANNING TRANSMISSION ELECTRON MICROSCOPY.** Marilyn A. Listvan and A. V. Crewe, Physics Department and Enrico Fermi Institute of the University of Chicago, 5640 South Ellis Avenue, Chicago, IL 60637

We will present studies of in situ growth of cluster size for low coverage gold films. Clean amorphous carbon substrates were coated with low coverage gold films at  $10^{-7}$  torr in the specimen chamber of our high resolution scanning transmission electron microscope (STEM). The specimen was quickly examined at  $10^{-10}$  torr and many small irregular clusters of gold were evident whose average diameter was less than 1.7 nm. After remaining 15 hours at room temperature and high vacuum ( $10^{-10}$  torr) the cluster size had increased by greater than a factor of 2, and the distribution of clusters was significantly changed with no additional deposition and no evidence of contamination. Some evidence of crystallite formation and coalescence of clusters was evident at this stage of growth. Studies to characterize the growth rate and microstructure of the crystallites and the cluster boundaries will be discussed.

**K2.1**  
**GENERATION OF SUPPORTED METAL CLUSTERS OF CONTROLLED SIZE AND COMPOSITION.** R. S. Bowles, Department of Chemical Engineering, Princeton University, Princeton, NJ 08544; S. B. Park, N. Otsuka, and R. P. Andres, School of Chemical Engineering, Purdue University, West Lafayette, IN 47907.

Important parameters in determining the performance of supported metal catalysts are the size and composition of the metal clusters. We describe a method of generating small metal clusters by condensation from the vapor phase. The clusters are formed as an aerosol supported in an inert gas flow. They can be used to produce model catalysts by expansion of the flow through an orifice into a vacuum region and impingement of the clusters on a clean substrate. The advantages of such a procedure are:

1. It allows one to produce extremely small clusters.
2. The clusters have an extremely sharp size distribution.
3. The chemical composition of the metal vapor, which is easily controlled, is frozen into the small clusters.

Clusters of Cu, Ag, Au, and Ni have been produced and supported on thin carbon films. TEM micrographs of these particles are presented. Although the smallest clusters cannot be resolved in our electron microscope, experiments performed on the cluster beam before it impinges on the substrate show that the mean cluster size can be controlled from a few atoms to several hundred atoms. Diffraction patterns from 8Å - 16Å diameter Ag and Au clusters have been obtained. Preliminary results on the crystal structure, thermal stability, and melting temperature of these clusters are presented.

#### K2.2

SUPPORTED AND PROTECTED METAL CLUSTERS: AN ATTEMPT AT CHARACTERISATION. Peter B. Wells and R. B. Moyes, Department of Chemistry, The University, Hull, England, HU6 7RX, and R. Whyman, ICI New Science Group, Runcorn, England, WA7 4QE

Small clusters of metal atoms (say, <25) when suitably stabilised against sintering, and supported so as to make them simple to handle under realistic reaction conditions, provide an intriguing form of metal catalyst and a major challenge for characterisation procedures. Such supported and protected metal clusters (SUPROMECLERS) have been prepared in this laboratory by (i) impregnation of osmium cluster compounds (e.g.  $\text{Os}_3(\text{CO})_{12}$  and  $\text{Os}_5(\text{CO})_{18}$ ) onto carefully preconditioned traditional supports (silica, alumina, titania) and (ii) suitable thermal activation. This procedure gives supported clusters having a nuclearity of about 12. These species are completely protected against sintering to temperatures in excess of 250°C by an almost complete adlayer of ligand-CO and ligand-C and are chemically bound to the support surface. Yet they have the ability to chemisorb hydrogen, carbon monoxide, carbon dioxide, and hydrocarbons, and to catalyse hydrogenations and hydrogenolyses.

The claims made above have been established by use of, *inter alia*, electron probe microanalysis, high resolution electron microscopy, infra-red and u.v./visible diffuse reflectance spectroscopies, measurements of chemisorption and of temperature-programmed desorption (using isotopically labelled materials), and EXAFS.

The fine details of the compositions of the SUPROMECLERS are determined by the supports used.

#### K2.3

ENCAPSULATION, A NEW MECHANISM OF CATALYST DEACTIVATION. Bob R. Powell and Shell E. Whittington, Physical Chemistry Department, General Motors Research Laboratories, Warren, MI 48090

Silica-supported platinum model catalysts show evidence of encapsulation when annealed at 1200 K and 1375 K. The 100 nm Pt particles become partially immersed in the  $\text{SiO}_2$  surface with concurrent formation of a  $\text{SiO}_2$  ridge around the base of the Pt particles. A model of these processes has been developed which predicts this behavior based on the reduction of the surface free energy of the Pt/ $\text{SiO}_2$  system. Partial Pt encapsulation at lower temperatures and in more highly dispersed Pt catalysts is discussed and is shown to be a possible and as yet unreported mechanism of deactivation.

K2.4  
 INTERACTION OF  $Al_2O_3$  WITH Rh AND Pt THIN FILMS. J.E.E. Baglin,<sup>1</sup> J. A. Cairns,<sup>\*\*</sup>  
 and J. F. Ziegler,<sup>2</sup> <sup>1</sup>IBM Thomas J. Watson Research Center, Yorktown Heights, NY;  
<sup>\*\*</sup>AERE Harwell, Oxfordshire, UK.

Rutherford backscattering (RBS), scanning Auger spectrometry and SEM have been applied to the study of a strong metal-support interaction between Pt or Rh thin films and substrates of  $Al_2O_3$  at high temperatures. In the case of Rh(2000Å)/ $Al_2O_3$ , extended heat treatment in inert gas (He or  $N_2$ ) at 1000°C leads to a partial coating of the metal surface with a thin layer containing Rh, Al and O. This layer can be recognized readily from 'surface' peaks in the RBS profiles, and from surface Auger signals. Evidently,  $Al_2O_3$  'wets' Rh, perhaps forming a ternary of the  $\beta$ -alumina type. Similar behavior was found for the Rh/ $TiO_2$  system. Such a coating must impair the activity of a thin catalytic Rh film, independently of the presence of reactive gases.

For the case of Pt(2000Å)/ $Al_2O_3$ , no coating was observed after heat treatment in He. Heating in forming gas (10% $H_2$ , 90% $N_2$ ) at 1000°C led to the formation of Pt islands, each island surrounded by etched 'troughs' in the substrate. We surmise that the active atomic hydrogen generated in the vicinity of the Pt is capable of reducing the  $Al_2O_3$ , with consequent physical loss of Al. Upon re-heating in  $O_2$  at 1000°C, the Pt islands became coated with a continuous layer of  $Al_2O_3$ .

It is difficult to reconcile these observations with the kind of reactivation cycle cited by Tauster et al.<sup>1,2</sup> for Pt or Rh on  $TiO_2$ . It is clear, however, that the diffusional coating of the grains of Pt and Rh films on  $Al_2O_3$  and  $TiO_2$  substrates presents a significant hazard to the life of such catalyst surfaces.

<sup>1</sup>S.J. Tauster, S.C. Fung and R.L. Garten, J. Amer. Chem. Soc. 100, 170 (1978).

<sup>2</sup>S.J. Tauster, S.C. Fung, R.T. Baker and J.A. Horsley, Science 211, 1121 (1981).

K2.5  
 AN X-RAY METHOD TO CHARACTERIZE THE STRUCTURE OF COBALT IN CO-ZSM-5 CATALYSTS.  
 Ashok G. Dhare and Robert J. De Angelis, Department of Metallurgical Engineering  
 and Materials Science, University of Kentucky, Lexington, KY 40506.

Impregnated 9.5% Co-ZSM-5 catalysts produced in the calcined state( $Co_3O_4$ ) were investigated by X-ray diffraction using a diffractometer equipped with a "in-situ" high temperature environmental controlled X-ray camera. The catalysts were reduced at 350°C under hydrogen for times up to 24 hrs. Following reduction the catalysts were exposed to (H/CO=1) a carburizing gas mixture at 280°C, 300°C and 320°C for 24 hrs. Following carburization the catalysts were regenerated by calcining in oxygen at 350°C and re-reduced under hydrogen at 350°C.

Intensities as a function of two theta were recorded in the 30° to 100° range after each stage of the treatment by step scanning in (1/30)° of 2θ. The ZSM-5 spectrum was unfolded from the 9.5% Co-ZSM-5 spectrum using a Fourier spectrum unfolding technique. The cobalt spectrum that resulted from the unfolding contained the (100), (002), (101) and (110) hexagonal Bragg reflection. These profiles were analyzed to obtain metallic particle size, particle size distributions and the average stacking fault density that existed in the Co particles.

The particle sizes determined from X-ray profiles ranged from 10Å to 150Å and the stacking fault probability is about 0.1. These results will be discussed with the particle size distribution calculated from the Fourier analysis of the shape of the X-ray diffraction profile.

One of the authors (A.G.D.) acknowledges STI/MIC of the Brazilian Government for financial support. This work was partially supported by Pittsburgh Energy Technology Center of D.O.E. on Contract No. DE-AC22-81PC41760.

### K3.1

**INFRARED CHARACTERIZATION OF CATALYST SURFACES USING BEAM DEFLECTION SPECTROSCOPY.**  
M. J. D. Low, C. Morterra and A. G. Severdia, Department of Chemistry, New York University, 4 Washington Place, New York, NY 10003.

The new technique of infrared (IR) photothermal beam deflection spectroscopy (PDS) is outlined, and measurements of IR spectra over the range 3950-450  $\text{cm}^{-1}$  made with an interferometer coupled with a detector which senses the photothermal effect by the deflection of a He/Ne laser beam are described. PDS is a general technique and requires no sample preparation. All that is needed is some simple mechanical device to hold the solid sample at the IR focus. The sample must have a flat spot about 2 mm in diameter accessible to the IR and laser probe beams. As no sample cells per se are required, the solid to be examined may be very large (at present the limitation in size is 20 x 20 x 6 cm high) so that selected areas on the surface of an entire large catalyst pellet can be examined.

IR spectra can also be recorded of adsorbed species at sub monolayer coverage and, significantly, this can be done under the rigorously controlled conditions usually employed in surface studies. Adsorbents and catalysts which scatter and/or absorb IR strongly can be studied, e.g., catalysts with heavy metal loadings, carbons and chars, and carbon-supported metal catalysts. Such materials would be impossible to examine by the conventional IR absorption techniques. Examples are given, such as the spectra of CO chemisorbed on 50 weight percent Fe supported on carbon.

### K3.2

**NMR STUDIES OF PLATINUM CATALYSTS\*** Harold T. Stokes\*\*, Claus D. Makowka<sup>†</sup>, Po-Kang Wang, Serge L. Rudaz, Charles P. Slichter, and J. H. Sinfelt\*\*\*, Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL 61801. \*\*Present address: Dept. of Physics and Astronomy, Brigham Young University, Provo, UT 84602, \*\*\*Exxon Research and Engineering Co., Linden, NJ 07036, <sup>†</sup>Present Address: IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, NY 10598

We present NMR studies of alumina-supported platinum catalysts. For the samples studied the dispersion (fraction of Pt atoms on the surface) ranged from 4% to 76%. The  $^{195}\text{Pt}$  absorption lineshapes exhibit dramatic differences between samples, and we have been able to assign certain features of these lineshapes to various kinds of Pt sites in the Pt particles. In samples with adsorbed CO ( $^{13}\text{C}$  enriched), we used  $^{13}\text{C}$ - $^{195}\text{Pt}$  double resonance to resolve that part of the Pt lineshape which arises from surface Pt bonded to the CO molecules. We have also studied  $^{13}\text{C}$  absorption lineshapes and relaxation times in these samples. We compare our results with NMR data taken on Pt carbonyls.

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## K3.3

**<sup>29</sup>Si-N.M.R. CHARACTERIZATION OF THE STRUCTURE AND ALUMINUM-ORDERINGS OF ZEOLITES.** Janos B. Nagy and Eric G. Derouane, Laboratoire de Catalyse, Facultés Universitaires de Namur, Rue de Bruxelles, 61, B-5000 Namur, Belgium and Peter A. Jacobs, Centrum voor Oppervlaktescheikunde en Colloidale Scheikunde, Katholieke Universiteit Leuven, De Croylaan 42, B-3030 Leuven, Belgium.

High resolution magic-angle-spinning (HRMAS) solid state <sup>29</sup>Si-n.m.r. was applied to characterize various zeolites among which ZSM 5, ZSM 11, ZSM 34, ZSM 39, offretite, erionite, ferrierite . . . Structural information was inferred from the <sup>29</sup>Si-n.m.r. chemical shifts and line intensities. Silicon-aluminum orderings have been assessed for zeolites characterized by a low Si/Al ratio. Finally, the use of cross-polarization (CP) n.m.r. pulse sequences has enabled us to obtain proton-enhanced (PE) HRMAS-<sup>29</sup>Si spectra, which, in turn, provide unambiguous information on the silanol ( $\equiv$  Si-OH) groups the presence of which is linked to defects in the zeolite lattice.

## K3.4

**FTIR SPECTROSCOPIC CHARACTERIZATION OF SURFACE REACTIONS OCCURRING ON METAL-IMPREGNATED CARBONS.** R. R. Smardzewski and D. E. Tevult, Chemistry Division, Code 6170, Naval Research Laboratory, Washington, D.C. 20375.

The mechanisms of gas-solid reactions occurring on various carbons or carbon-supported metal catalysts are examined by Fourier Transform Infrared (FTIR) spectroscopic techniques. In one series of experiments, reactant-air mixtures are passed through a temperature-ramped carbon bed. Desorption and/or combustion products are characterized and quantified downstream by real-time analysis of the effluent vapors in a rapid-scanning FTIR spectrometer. Lower concentration components are collected via condensation onto a cryogenic IR-transmitting crystal and subsequently analyzed by FTIR methods.

These techniques applied to combustion studies in dynamic air streams have demonstrated the catalytic effects of various metal ions in carbon beds in (a) lowering the spontaneous ignition temperature and (b) altering the relevant surface chemistry. In other experiments, cryogenic methods have been used to investigate the hydrolytic reactions of methyl iodide (CH<sub>3</sub>I) and other organic adsorbents/impregnants on moist carbons in flowing air streams.

## K4.1

**NEW WAYS OF STUDYING CATALYSTS.** John M. Thomas, University of Cambridge, Department of Physical Chemistry, Lensfield, Cambridge, CB2 1EP, U.K.

Traditional techniques, such as IR spectroscopy and X-ray diffraction can, by appropriate adaptation, be utilized to study heterogeneous catalysts under in situ conditions. So also may other, more recently available ones such as neutron scattering and EXAFS. There are however, a number of new techniques, which, although they cannot be used in situ, afford fresh insights into the structural features of a wide range of catalytic materials and their precursors. Amongst these are magic-angle-spinning NMR, high resolution and scanning transmission electron microscopy and extended, electron-energy-loss fine structure

(EXELFS). The lecture will illustrate examples of the advantages offered by all the techniques mentioned above and assess the potential and applicability of a few other, as yet, largely untried ones. Typical categories of catalysts encompassed will include transition metal chalcogenides (for hydrodesulphurization), ternary oxides (for selective oxidation of hydrocarbons) zeolites (for cracking, hydrocracking syntheses and isomerization), supported oxides, graphitic materials and metal-exchanged clays which are nowadays studied as potentially more efficient catalysts for the syntheses of a range of organic chemicals such as esters, ethers, and secondary amines.

#### K4.2

OBSERVATIONS OF SURFACE HYDROGEN DURING HETEROGENEOUS CATALYTIC REACTIONS. M. Mullins and H. Saltsburg, Department of Chemical Engineering, University of Rochester, Rochester, NY 14627.

A common problem in discussions of the reaction networks describing heterogeneous catalytic reactions is a result of the inability, readily, to observe catalytically active species under reaction conditions (e.g. atmospheric pressure and elevated temperatures). Using a solid state electrolyte, a concentration cell has been utilized to make such measurements for surface hydrogen. The technique is similar to that used in the study of surface oxygen under similar reaction conditions. With this probe the failure of the assumption of equilibrium between gas phase and surface phase hydrogen has been demonstrated for both the platinum catalysed hydrogenation of ethylene and, under some conditions, the adsorption of hydrogen on a partially covered but non-reacting surface.

#### K4.3

ANALYTICAL ELECTRON MICROSCOPIC STUDY OF THE DISPERSION AND DISTRIBUTION OF ACTIVE SPECIES IN OXIDE AND SULFIDE CATALYSTS. F. Delannay, Groupe de Physico-chimie Minérale et de Catalyse, Place Croix du Sud n°1, B-1348 Louvain-la-Neuve, Belgium.

Analytical electron microscopy (AEM) has been applied to the characterization of a large number of supported catalysts for HDS and selective oxidation reactions. The active species (oxides or sulfides of Mo, Co, Ni, Fe, Te) were usually contained within several different phases. The major informations gained from the AEM study are:

- (1) the distinction between supported particles and surface compounds;
- (2) the atomic and, possible, crystalline nature of supported particles down to a size of about 10 nm;
- (3) in conjunction with XPS measurements, the dispersion of the various species;
- (4) the distribution of these species within the porous structure of the support.

Modifications of these features as a function of both preparation conditions and use of various additives were carefully investigated. Prospects and present limitations of AEM for this type of study will be discussed.

**R4.4**  
**CHARACTERISATION OF SUPPORTED CATALYST PARTICLES BY HIGH RESOLUTION STEM.** S. J. Pennycook, University of Cambridge, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.

A variety of signals are available on a STEM to facilitate microanalysis at spatial resolution down to 1 nm which is required for the characterisation of industrial supported catalysts. Firstly, a reliable high resolution image is required to locate the particles. This may either be a standard phase contrast image, or an incoherent dark field image produced from an annular detector. An efficient high angle annular detector has been constructed which is useful for locating all of the catalyst particles, particularly in thicker regions and on crystalline supports.

Chemical analysis is provided by the X-ray, electron energy loss, and micro-diffraction signals which, when taken together, can provide a complete description of the composition and structure of the particles<sup>(1)</sup>. Possible techniques for studying the surfaces of individual particles will be discussed briefly.

Examples of the techniques applied to various industrial catalysts will be presented. A detailed study of three Rh cluster catalysts prepared in different ways has shown up differences between the particles produced, which can begin to be correlated with their differing catalytic activity.

(1) S. J. Pennycook, J. Microscopy 124, 15-22, (1981).

**R4.5**  
**MICROANALYSIS OF CATALYSTS BY ANALYTICAL ELECTRON MICROSCOPY.** C. E. Lyman, Central Research and Development Department, E. I. duPont de Nemours and Co., Experimental Station, Wilmington, DE 19898.

Analytical electron microscopy of individual catalyst particles provides much more information than particle size and shape. The scanning transmission electron microscope with analytical facilities allows chemical analysis and electron diffraction patterns to be obtained from areas on the order of 10 nm in diameter.

Examples of imaging, microdiffraction, and chemical analysis by X-ray emission spectroscopy will be drawn from studies of supported metal, bismuth molybdate and zeolite catalysts. Qualitative analysis of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts revealed small concentrations of impurity elements as well as the major components. Phase analysis of bismuth molybdates by quantitative analysis and convergent beam electron diffraction provided rapid identification of phases present within single particles. Quantitative analysis of zeolite crystals revealed gradients in composition across some types of zeolite crystals. For small ZSM-5 crystals with Si:Al=10, the particles had either a surface enriched in Si or a nearly homogeneous composition across the particle. For large particles with Si:Al=40, the particles had more Al near the surface than in the interior.

**K4.6**  
**CHARACTERIZATION OF Cu/ZnO METHANOL SYNTHESIS CATALYST BY TEM, AES, AND EELS.**  
 J. M. Domínguez\* and G. W. Simmons, Lehigh University, CSCR, Sinclair Lab #7,  
 Bethlehem, PA 18015 USA. \*On leave from Mexican Petroleum Institute (IMP-PEMEX)

The combination of high resolution imaging, microdiffraction and energy dispersive analysis techniques is a powerful tool for determination of the spatial distribution of phases and elements in finely dispersed multiphase catalysts. The present work deals with the bi-phase Cu/ZnO methanol synthesis catalyst, for which earlier studies demonstrated that physical and chemical interactions of the two components give rise to high specific activities at low temperatures and low pressure conditions.

The chemical composition analyses were carried out by EDS using probe diameters of 2 to 10 nm. It is shown that reliable elemental analysis can be obtained in volumes containing  $10^{-20}$  g of matter. Experiments were designed to avoid interference caused by spurious radiation, backscattering and X-ray fluorescence from neighbor particles. Thus, in a catalyst of nominal composition 67/33 - Cu/ZnO where particles of each phase are morphologically distinct, an average and uniform copper content of about 2% was found in isolated ZnO crystallites. The presence of Cu in the ZnO phase offers a possible explanation for the high activity in methanol synthesis. Similar investigations are being extended to the 30/70 - Cu/ZnO catalyst which is the most active one for methanol synthesis and which presents a more difficult problem for analysis because both components are interdispersed in a scale of 1 to 10 nm. Consequently, analysis of EELS in addition to EDS is being applied to determine the amount of copper present in the ZnO phase of the catalyst.

**K4.7**  
**ELECTRON MICROSCOPY OF SOLID CATALYSTS.** J. W. Geus and J. Pieters\*, Department of Inorganic Chemistry, University of Utrecht, Netherlands.

After dealing with the need to utilize thermostable, highly porous supports in the production of most solid catalysts, it is argued that the performance of solid catalysts strongly depends on:

- the dimensions of the catalyst tablets or particles;
- the pore-size distribution of the loaded support;
- the distribution of the active material within the tablets or particles;
- the particle size and particle size distribution of the active component(s);
- the composition and shape of the active particles.

Combined with macroscopical techniques electron microscopy is of paramount importance to determine the above properties.

To investigate catalysts at small to intermediate magnifications a conventional scanning electron microscope equipped with a back-scattered electron detector and apparatus to analyze the emitted X-ray photons is very useful. Preparation of suitable specimens offers generally no problems. With highly porous materials, however, it can be difficult to endow the specimens with a sufficiently high electrical conductivity. Control of the bias voltage of the secondary detector can be used to get good micrographs from less well conducting specimens.

Many solid catalysts contain active particles with dimensions down to about 1 nm. To investigate these particles transmission microscopy is a prerequisite. Some remarks are made about the preparation of specimens. Transmission electron

microscopy can provide information about the size and size-distribution of the active particles. To this end combined bright and dark-field microscopy is very useful. Dark-field microscopy is especially appropriate to display the distribution of the particles of the active material within the support. The use of scanning transmission electron microscopy (STEM) to assess the distribution of active particles inside thicker particles of the support is dealt with. The shape and dimensions of small pores in loaded supports can be established very well by combining secondary electron scanning (SEM) and transmission electron microscopy. Some results about the attack of the support by the precursor of the active component are shown.

Problems in the determination of the chemical composition of very small particles are reviewed. Generally very intense electron sources, such as field emission guns, are required to analyze successfully small particles. The most promising technique seems to be determination of the characteristic energy losses of transmitted electrons. To assess the structure of small particles, lattice imaging can be useful, but the support generally presents difficulties. It is argued that it is also difficult to get good diffraction patterns from very small particles.

Determination of the shape of small particles present on a support may suffer from effects of interaction with foreign molecules and/or the electron beam. Results obtained by using both infrared spectroscopy of adsorbed molecules and electron microscopy are presented.

\* EMSA, Molecular Cell Biology.

**KS.1**  
**CHARACTERIZATION OF SUPPORTED METAL CATALYSTS BY X-RAY ABSORPTION SPECTROSCOPY.**  
 Farrel W. Lytle\* and Robert B. Gregor\*, The Boeing Co., Seattle, WA 98124;  
 John Sinfelt and Grayson H. Via, Exxon Research and Engineering Co., Linden, NJ  
 07036.

We have used the near edge (XANES) and extended X-ray absorption fine structure (EXAFS) to characterize single and bi-metallic supported catalysts. Results will be reported on the micromorphology of the metal clusters including bond distances, coordination number, thermal and static disorder, type of near neighbor (in bimetallic clusters) and interaction with the support. Inferences will be made concerning the significance of these parameters on catalytic performance.

\*Research supported in part by NSF Grant CHE 7918084.

**KS.2**  
**EXAFS STUDY OF MODEL CATALYSTS OF PLATINUM, RHODIUM AND PLATINUM-RHODIUM ON GAMMA ALUMINA.** Robert W. Broach, J. P. Mickey and G. R. Lester, UOP Inc.,  
 10 UOP Plaza, Des Plaines, IL 60016.

Measurements of extended X-ray adsorption fine structure (EXAFS) at the platinum L edge and/or the rhodium K edge were made for a series of model catalysts including Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Pt/Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after the catalysts had been treated at various temperatures under different atmospheres including vacuum, air and H<sub>2</sub>. The EXAFS results are analyzed to determine the best estimates of the composition, coordination number and distance of the lower coordination shells around both the platinum and rhodium atoms; this information leads to some important conclusions relative to the chemical and physical forms of these elements after the several treatments.

## K5.3

THE EFFECT OF ATMOSPHERE ON THE STRUCTURE OF Pt AND Pd CATALYSTS. J. B. Cohen, R. K. Nandi, J. B. Butt and R. L. Burwell, Jr., Ipatieff Catalytic Laboratory and Department of Materials Science and Engineering, The Technological Institute, Northwestern University, Evanston, IL 60201.

Combined X-ray and EXAFS studies have been made of Pd/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> catalysts with particle sizes from 14Å to 100 Å, using rotating anode and synchrotron sources. Pd hydride is produced during reduction, or during hydrogenolysis, and this conversion varies with size. These results explain the differences in catalytic activity when Pd is cooled in He or H<sub>2</sub>. When these catalysts are stored in air, crystalline Pt<sub>3</sub>O<sub>4</sub> or PdO forms, particularly when the size is small. Catalytic activity seems to correlate with mean-square amplitude of vibration. Emphasis will be placed on the techniques developed to carry out these studies on supported metals, with sizes and loading corresponding to commercial catalysts.

## K5.4

DISPERSION EFFECTS ON ALKANE HYDROGENOLYSIS OVER RHODIUM SUPPORTED ON TITANIUM OXIDE, D. E. Resasco and G. L. Haller, Department of Chemical Engineering, Yale University, P.O. Box 2159 YS, New Haven, CT 06520-2159 (U.S.A.)

Ethane, n-butane, and cyclohexane hydrogenolysis have been investigated as a function of dispersion (percentage exposed) on Rh/TiO<sub>2</sub> catalysts. Reduction at 773K caused a depression in hydrogenolysis activity (ethane > n-butane >> cyclohexane) relative to reduction at 473K. At the low temperature reduction, the hydrogenolysis activity for ethane and n-butane increases as dispersion is increased, while following high temperature reduction activity decreases with dispersion. These results indicate that a metal-support interaction exists after both low and high temperature reduction, and the effect is most apparent for the smallest particles. Our results are interpreted in terms of charge transfer to the metal after high temperature reduction where the degree of destabilization of the intermediate varies with the kind of bond to the Rh surface. Physical characterization of the metal-support interactions has included XPS, EXAFS, and infrared probe of molecules.

## K5.5

STRUCTURE OF ALUMINA SUPPORTED Mo/Co HYDRODESULFURIZATION CATALYSTS VIA EXAFS. S. H. Bauer and M-S. Chiu, Department of Chemistry, Cornell University, Ithaca, NY 14853, and M. F. L. Johnson, Harvey Technical Center, ARCO Petroleum Products Company, Harvey, IL 60426

A modified procedure was developed for reducing K-edge EXAFS spectra which minimizes the background noise level in the deduced radial functions. Examination of the Fourier transform of synthetic  $k^3\chi(k)$  functions lead to an explanation as to why low values are generally deduced for coordination numbers in structurally disordered materials. Use of an appropriate calibration curve based on data for known structures which cover a range of structural disorders allow one to obtain reliable values for coordination numbers.

The above procedure was applied to EXAFS spectra obtained on a graded sequence of Mo/Co catalysts both at the Mo and Co K-edges for the calcined oxides and for the reduced-sulfided states. Dependence of the structures of the oxides and sulfides on molybdenum and cobalt content as well as on the degree of reduction

was established, and the role of the promoter was clearly identified. The structural data will be correlated with other physical characterizations of these catalyst preparations, and with reactivity tests.

#### IS.6

**CHARACTERIZATION OF IRON PARTICLES ON THIN-FILM AND HIGH SURFACE AREA TITANIA SUPPORTS.** J. A. Dumesic, J. Santos and B. J. Tatarchuk, Department of Chemical Engineering, University of Wisconsin, Madison, WI 53706

Iron supported on titania has been characterized using conversion electron Mössbauer spectroscopy, X-ray photoelectron spectroscopy, transmission electron microscopy, transmission Mössbauer spectroscopy, CO chemisorption and ammonia synthesis kinetics studies. The first three techniques were applied to samples composed of iron on thin films (ca. 50 nm) of titania, and the latter three techniques were used to study iron on high surface area titania supports. Upon reduction in hydrogen at ca. 700K, metallic iron particles are formed that behave spectroscopically and chemically like bulk metallic iron. When the reduction temperature is raised to ca. 800 K, these particles become thinner and they lose their ability to chemisorb CO at 300 K. The apparent activation energy for iron-catalysed ammonia synthesis also increases. During reduction at temperatures higher than 875 K iron diffuses into the titania support and the partial reduction at  $Ti^{4+}$  to lower valence states takes place.

#### IS.7

**IN SITU MOSSBAUER STUDY OF IRON SULFIDES INTERACTIONS WITH COAL AND MODEL COMPOUNDS.** P. A. Montano and A. S. Bommanavar, Department of Physics, West Virginia University, Morgantown, WV 26506 U.S.A.

*In situ* Mössbauer spectroscopy was used to study the transformations of iron bearing minerals during coal liquefaction. The sulfides play the most important role of all the iron bearing minerals in coal. The presence of pyrite in a coal tends to enhance the production of lower viscosity liquids. Detailed knowledge about the decomposition of pyrite, the effect of hydrogen and hydrogen sulfide and the type of solvent used is necessary to understand all the factors controlling the rate of decomposition and the type of products formed during coal liquefaction. The iron disulfide (mainly pyrite) particle size is one of the major factors controlling the rate of decomposition. The presence of  $H_2$  or hydrogen donor solvents accelerates the decomposition of pyrite above 300°C. The runs were made in a specially designed high temperature and pressure reactor. The behavior of iron sulfides at high temperatures in four well characterized coals was studied. A strong interaction between the pyrrhotites and the coal constituents was observed. The effect of coal, solvent, hydrogen, and mineral additives was studied as a function of temperature and residence time in the reactor. The stoichiometries of the pyrrhotites formed in different runs were determined and a correlation was observed between the total amount of sulfur in the coal and the iron deficiency in the pyrrhotites, suggesting that the partial pressure of  $H_2S$  in the reactor is the principal factor determining the  $Fe_{1-x}S$  stoichiometry. A series of model compounds was selected to study the catalytic behavior of iron sulfides ( $FeS_2$ ,  $Fe_7S_8$ ) at temperatures comparable to those used in direct coal liquefaction. The measurements were carried out in an inert as well as in a hydrogen atmosphere. There was strong evidence of interaction of the iron sulfides with a number of model compounds. The results are discussed in view of the catalytic role of iron sulfides in coal liquefaction.

**APPENDIX II**

FINANCIAL REPORT

MRS SYMPOSIUM

1982 Annual Meeting  
November 1-4, 1982

**INCOME**

Department of the Navy (ONR)	\$ 5,000
ACS-PRF Grant (ACS)	2,550
Industrial Contributions	4,200
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<b>TOTAL</b>	<b>\$11,750</b>

**EXPENSES**

Foreign Speakers' Support	\$ 6,439
Symposium Registration Fee for speakers	1,445
Chairpersons expense	1,572.49
Postage, mailing, printing, telephone, etc.	437.61
Clerical Services	1,047.85
Supplies & Equipment	58.05
Post-meeting expenses (publication, etc.)	750.00
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<b>TOTAL</b>	<b>\$11,750.00</b>

*Karl Flier*

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Symposium Chairman (PI)

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