

## PROGRESS REPORT

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Research progress to be reviewed here will be in three areas. First, correlation of the distribution of molybdenum oxidation states in reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts with benzene hydrogenation activity. Second, the use of factor analysis curve-fitting to determine the distribution of molybdenum oxidation states in reduced  $\text{Mo}/\text{TiO}_2$  catalysts. Third, quantitative Raman and ESCA characterization of  $\text{W}/\text{TiO}_2$  catalysts.

#### Correlation of Mo Oxidation States with Benzene Hydrogenation Activity.

Direct measurement of the distribution of Mo oxidation states on catalysts can be done using ESCA. We have recently demonstrated this for  $\text{Mo}/\text{TiO}_2$  catalysts (1). The purpose of the present study is to carry out a systematic investigation of the reduction of alumina supported catalysts and to compare with results obtained using titania as a support. The work included measuring the distribution of Mo oxidation states in reduced catalysts, correlation of the average Mo oxidation state measured by ESCA with values derived from oxygen consumption and correlation of the distribution of Mo oxidation states and benzene hydrogenation activity.

The Mo3d envelopes were measured for oxidic and reduced  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts. Curve fitting of the 3d envelopes revealed six different oxidation states depending on the temperature at which reduction was carried out. The binding energy values measured for the oxidation states on alumina are in good agreement with those measured for the  $\text{Mo}/\text{TiO}_2$  system (1). The distribution of Mo oxidation states as a function of reduction temperature was similar to that for the  $\text{Mo}/\text{TiO}_2$  catalysts although for the alumina supported catalysts, it was not possible to achieve complete reduction to  $\text{Mo}(0)$  even at  $900^\circ \text{C}$ .

Variation of the extent of reduction of the Mo phase as a function of reduction temperature was measured by oxygen consumption and the results were compared with the values measured by ESCA. The oxygen consumption and ESCA experiments agreed with each other within experimental error ( $\pm 10\%$ ). Measured variations of the ESCA Mo/Al intensity ratio as a function of reduction temperature indicated that no major changes in catalyst morphology were occurring over the reduction range studied ( $400^\circ$  to  $900^\circ \text{C}$ ).

The catalytic activity for benzene hydrogenation showed a threshold of approximately  $600^\circ \text{C}$  and a nearly linear increase in rate up to  $900^\circ \text{C}$ . Comparison with the distribution of Mo oxidation states shows that  $\text{Mo}(0)$  is the major oxidation state for benzene hydrogenation for Mo on alumina. However, it is clear that  $\text{Mo}(+2)$  must also be active because  $\text{Mo}(0)$  does not appear until a reduction temperature of  $700^\circ \text{C}$ . This result is different than that observed for  $\text{Mo}/\text{TiO}_2$ , although in the latter case the results are somewhat clouded because of morphology changes in the catalyst at the higher reduction temperatures.

#### Factor Analysis for Curve Fitting Mo ESCA Spectra.

Normally, non-linear least-squares curve fitting (NLSCF) routines are used for measuring the oxidation state distribution from Mo3d envelopes (2,3,4). However the major problem with

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NLSCF lies in estimating the number and positions of components under the 3d envelope. Use of "spectroscopic intuition" is necessary because an unconstrained curve fitting routine will relax into a local minimum regardless of whether or not the result is spectroscopically meaningful. Thus, choosing the correct number of components can be a difficult problem. Our work has focused on the use of factor analysis, which is comprised of principal component analysis (PCA) and iterative target transformation factor analysis (ITTFA), to provide an independent estimate of the number, position, and shapes of components required to describe the ESCA Mo3d envelope. PCA involves mathematical transformation of the data matrix into a set of abstract factors related to abstract eigenvectors which describe the variance of the data matrix. The idea is to provide n-abstract eigenvectors for n-spectra; the principal components account for all of the signal and the other secondary components account for the noise. Various statistical criteria must be applied for use of PCA. Once the correct number of principal components has been determined, these abstract components are transformed using ITTFA into components which have spectroscopic meaning. This approach to the analysis of ESCA spectra was applied to data obtained from Mo/TiO<sub>2</sub> catalysts.

A set of Mo3d spectra were obtained for reduction temperatures in the range 117° to 301° C. Statistical tests using PCA showed that only three components were necessary to reproduce the original data with high statistical significance (nine spectra in all), and the other six eigenvectors simply constituted noise. The conclusion was justified by three statistical tests applied to the data. Next we undertook use of ITTFA to transform the three abstract components into true spectroscopic components without making any assumptions about peak shape. The "standard" method predicted vectors representing Mo(+6), Mo(+5) and Mo(+4). Although these components did resemble the normal Mo3d doublet, they had extraneous and negative features. An iterative process was then carried out so that a small portion of the positive signal could be discarded along with the noise which permitted excellent spectra to be produced in full agreement with the normal Mo3d doublet. The major problem remaining is to provide reasonable criteria in for "goodness of fit" which will allow one to decide statistically when to terminate iteration.

#### Quantitative Raman and ESCA Characterization of W/TiO<sub>2</sub> Catalysts.

Although much research has focused on W/Al<sub>2</sub>O<sub>3</sub> and W/SiO<sub>2</sub> catalysts, few studies of W/TiO<sub>2</sub> catalysts have appeared. The net summary of the literature results show that it is not entirely clear how many and what species are present on these catalyst surfaces. We have used the methodology developed in our laboratories, based on the combination of Raman and ESCA for Mo/TiO<sub>2</sub> catalysts, and have applied this to the W/TiO<sub>2</sub> system. This has permitted us to determine the number of species and to estimate their amount quantitatively on catalyst surfaces.

Raman spectroscopy revealed a W-TiO<sub>2</sub> "interaction species" on the catalysts that has a peak at 970cm<sup>-1</sup> analogous to comparable Mo/TiO<sub>2</sub> catalysts. Raman spectroscopy also revealed the presence of WO<sub>3</sub> for all catalysts having greater than 6.7 wt% WO<sub>3</sub> loadings. The Raman results were confirmed by x-ray diffraction data. A calibration curve for WO<sub>3</sub> was constructed and showed that Raman spectroscopy will be an excellent tool for quantitation of WO<sub>3</sub> on these catalysts.

The presence of a third W species was indicated primarily by ESCA data. A uniformly dispersed W phase was indicated by ESCA up to 6.7 wt%  $WO_3$ . This deviated significantly from a comparable plot of Raman intensity. The conclusion was that a third species was present and that this is a disordered W species. Raman spectroscopy monitors both the W interaction species and  $WO_3$  as a function of W loading quite well. Because of the apparent low Raman scattering cross-section of the disordered W species it does not show up in the Raman spectra. We were able to determine the distributions as a function of loading. Up to about 5% only the W interaction species is present.  $WO_3$  begins to appear on the catalyst at approximately 6% and increases linearly with low slope up to about 15%  $WO_3$  at which point the slope increases. The disordered W species appears at about 10% loading and increases linearly with  $WO_3$  loading.

#### References.

1. R. B. Quincy, M. Houalla, A. Proctor and D. M. Hercules, *J. Phys. Chem.* 1990, **94**, 1520.
2. R. C. Ng and G. Horlick, *Spectrochim. Acta.*, 1981, **36B**, 529.
3. E. O. Brigham "The Fast Fourier Transform", Prentice-Hall, Englewood Cliffs, N.J., 1974.
4. D. P. Hoffmann, A. Proctor and D. M. Hercules, *Anal. Chem.* 1989, **61**, 898.

### List of Publications for Period

The following publications acknowledged DOE support. Some are from the prior grant. They were listed as "in press" in the report and are included here for completion. Reprints are attached.

1. S. W. Ho, M. Houalla and D. M. Hercules, "Effect of Particle Size on CO Hydrogenation Activity of Silica Supported Cobalt Catalysts", J. Phys. Chem., 1990, **94**, 6396-99.
2. M. A. Stranick, M. Houalla and D. M. Hercules, "The Influence of  $TiO_2$  on the Speciation and Hydrogenation Activity of  $Co/Al_2O_3$  Catalysts", J. Catal., 1990, **125**, 214-26.
3. F. M. Mulcahy, M. Houalla and D. M. Hercules, Ion Scattering and Electron Spectroscopic Study of Catalysts Prepared by Adsorption of Molybdate on Alumina, " Anal. Chem., 1990, **62**, 2232-36.
4. M. Yamada, J. Yasumaru, M. Houalla and D. M. Hercules, "Distribution of Molybdenum Oxidation Studies in Reduced  $Mo/Al_2O_3$  Catalysts. Correlation with Benzene Hydrogenation Activity", J. Phys. Chem. 1991, **95**, 7037-42.

## PLANS FOR UPCOMING YEAR

Research for the next year will focus in four areas. First, measuring the distribution of supported species in Mo-based catalysts. Second, studying the reduction of supported molybdenum catalysts. Third, a study of model compounds used for preparation of molybdenum based catalysts. Fourth, correlation of spectroscopic measurements with catalytic activity.

### 1. Distribution of Supported Species in Mo-Based Catalysts.

The major thrust in this area will be to use ESCA valence band measurements for characterizing Mo-based catalysts. Because of the involvement of valence bands in chemical bonding, they exhibit subtle changes as a function of atomic environment. Valence band spectra can be predicted from  $x\alpha$  calculations (1) and also should be sensitive to the symmetry of oxy anions and their degree of aggregation. For example, it should be possible to tell monomeric tetrahedral molybdate species from heptamolybdate species and both from polymeric octamolybdate species. We will therefore expand our use of the multi-technique approach for catalyst characterization to include measurement of the valence band. This should allow quantitative analyses of the distribution of oxidic species and positive identification of the exact nature of the species on the catalyst surface. This combined with the PCA based factor analysis should represent a powerful methodology for catalyst characterization.

### 2. Reduction of Supported Mo Catalysts.

We will continue our studies on the use of principal component analysis for characterization of Mo3d spectra on a variety of supported Mo catalysts. As stated in the progress report, it is necessary to establish cut-off criteria for the iterative method which we have developed. We will also apply the methodology to catalysts which are reduced at higher temperatures. For these catalysts, the distribution of oxidation states is more complex and therefore more challenging to the data analysis methodology.

### 3. Study of Model Compounds Containing Discrete Mo Oxidation States.

Yermakov and Iwasawa (2,3) have synthesized Mo based catalysts which presumably contain a discrete oxidation state. The preparation involves reaction between a molybdenum allyl-based metal complex and hydroxyl groups on the catalyst surface to form a bidentate molybdenum complex with the surface. Subsequent treatment of the catalyst presumably produces a single species having an Mo(+2) oxidation state. According to the literature this species can be reversibly oxidized to Mo(+4) and Mo(+6) and subsequently reduced. We are currently in the process of preparing allyl based Mo catalysts having monomeric, dimeric and polymeric molybdenum species anchored to the surface. We have carried out preliminary measurements on the catalyst prepared exactly according to Iwasawa's specifications and the ESCA data indicate the presence of primarily of one oxidation state which appeared to be Mo(+2). However, preliminary experiments on oxidation and re-reduction of the catalyst indicated that there are complications in the cyclic process. Our goal for the year is to prepare catalysts having exactly defined species (according to synthetic criteria) and then to carry out ESCA and reduction experiments on these.

Kazansky and co-workers described a simple procedure for the synthesis of Mo based catalysts which contain a single Mo oxidation state presumably Mo(+4) (4). This is done by UV irradiation of Mo catalysts containing low Mo loadings (1%) in a CO atmosphere at room temperature. We have initiated a collaboration with Dr. Kazansky and during the next year we will check the stoichiometry of photoreduced Mo catalysts using ESCA. Our preliminary results indicate the presence of two oxidation states rather than a single one. We will prepare various photoreduced samples which will be transferred to the ESCA spectrometer using our sealable probe technique so that we can insure catalysts are examined without air oxidation.

#### Correlation Between Mo Oxidation States and Catalytic Activity.

Because of our ability to measure accurately the distribution of Mo species in reduced Mo catalysts, it will be possible to correlate the activity of molybdenum catalysts for various probe reactions with the oxidation state present on the surface of the Mo catalysts. We have selected three probe reactions. These are summarized below.

**Propene Hydrogenation**-Literature data indicate that Mo(+4) is the active oxidation state for this reaction (5). We will measure the propene hydrogenation activity of reduced Mo/Alumina and Mo/Titania catalysts prepared by equilibrium adsorption and pore volume impregnation. We will use both methods because our preliminary ESCA results indicate that exclusively Mo(+6) and Mo(+5) are formed on reduction at low temperatures using pore volume impregnation. This will allow a good test of the hypothesis that Mo(+4) is the active oxidation state.

**Propene Metathesis**-Propene metathesis to ethylene and butene has been extensively studied (6). Literature data indicate that Mo(+4) is the most active oxidation state for this catalytic reaction. This will be elucidated by measuring the distribution of Mo oxidation states and correlating the results with propene metathesis activity. Mo carbonyl based catalysts will be studied for this reaction, given that they presumably yield Mo(+4).

**Hydrogenolysis of Propane**-It has been indicated that Mo(0) (metal) is the active form of molybdenum for this reaction. We will investigate the reactivity of both alumina and titania based Mo catalysts for propane hydrogenolysis.

#### References.

1. I. D. Welsh and, P. M. A. Sherwood, Phys. Rev. 1989, **B40**, 6836.
2. Y. I. Yermakov, Catal. Rev. Sci. Cry. 1976, **13**, 77.
3. Y. Iwasawa, H. Ichinose, and S. Agasawana, J. Chem. Soc. Faraday Trans. I, 1981, **77**, 1763.
4. I. V. Elev, B. N. Shelimor and V. B. Kazinsky, J. Catal. 1988, **113**, 256.
5. R. L. Burwell and J. S. Chung, React. Kinet. Catal. Lett. 1987, **35**, 381.
6. E. A. Lombardo, M. L. LaJacono and W. K. Hall, J. Catal. 1980, **64**, 150.

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