Mo Oxidation State - Catalytic Activity Relationships

Work on Mo oxidation state - catalytic activity relationships has centered around measuring the distribution of Mo oxidation states on reduced Mo/Alumina and Mo/Titania catalysts, and correlating catalyst activity with Mo oxidation states. In addition, factor analysis has been developed as a protocol for quantitatively measuring Mo oxidation state distributions on reduced catalysts. Four papers have been published in this area and one has been submitted.

1. J. Phys. Chem. (1990), 94, 1520-1526

A 5 Wt % MoO3/TiO2 catalyst was reduced in hydrogen at various temperatures to produce a surface with average Mo oxidation states between +6 and 0. The changes in molybdenum oxidation states as a function of reduction temperature were monitored by gravimetric analyses and X-ray photoelectron spectroscopy (XPS, ESCA), and the results were correlated with benzene hydrogenation activity. Non-linear least squares curve fitting was used to obtain oxidation state distributions. ESCA Mo 3d5/2 binding energy values for the various Mo oxidation states on a 5 Wt % MoO3/TiO2 catalyst show a shift of 5.1 eV between Mo+6 (232.7 eV) and Mo0 (227.6 eV). The benzene hydrogenation activity was found to depend strongly on the extent of reduction of the Mo phase. When the catalyst was reduced at temperatures of ≤350°C (average Mo oxidation state ≥4), the benzene hydrogenation rate was very low (<0.2 mmol of cyclohexane/(h g of MoO3)). The rate increased sharply for reduction temperatures of 400-500°C and reached a maximum of ~6 mmol of cyclohexane/(h g of MoO3) after 500-550°C reduction. A sharp decline in benzene hydrogenation activity was observed when the catalyst was reduced at temperatures >550°C. A correlation between benzene hydrogenation rate and reduction temperature is shown in Figure 1. Comparison of benzene hydrogenation activity with the distribution of Mo oxidation states determined by ESCA suggests that molybdenum ions with an oxidation state of +2 are the most active species, but this may be an artifact due to blocking of Mo metal active sites by Ti moieties following high (>600°C) temperature reduction.

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This study expanded the one reported above to reduced Mo/Alumina catalysts. The distribution of Mo oxidation states in reduced Mo/Al₂O₃ catalysts (8 wt % Mo) was determined by ESCA using non-linear least-squares curve fitting analysis. The results show that Mo oxidation states ranging from +6 to 0 are produced on reduction in the range 500-900°C. The Mo 3d binding energy values obtained for various Mo oxidation states were the same as those for the Mo/TiO₂ catalysts. The full widths at half-maxima for all Mo 3d peaks were larger than those for the corresponding Mo/TiO₂ system. The average Mo oxidation state estimated from ESCA for a reduced catalyst agrees with that obtained by measuring the O₂ consumption on reoxidation. The benzene hydrogenation activity was measured for all reduced catalysts. Significant conversion occurs only for reduction temperatures >600°C. The onset of catalytic activity coincides with Mo³⁺ formation. However, comparison of the Mo oxidation state distribution determined by ESCA with catalytic activity indicates that Mo metal is the most active species.

This paper, a study on correlation between Mo oxidation states and catalytic activity, is a preliminary communication of research described, in greater detail, in No. 4. The distribution of Mo oxidation states in reduced Mo/Al₂O₃ catalysts (8 wt% Mo) was determined by ESCA and curve fitting. The results showed that Mo oxidation states ranging from +6 to 0 are produced on reduction between 200°C and 900°C. The catalytic activity of the reduced Mo/Al₂O₃ catalysts for propene hydrogenation and propane hydrogenolysis was measured as a function of the reduction temperature. The variation of catalytic activity of the reduced catalysts was compared with the distribution of Mo oxidation states obtained from ESCA. The results indicated that Mo oxidation states ≤ +4 are required for propene hydrogenation. Propane hydrogenolysis required a more severe reduction pretreatment. The catalytic activity correlated with the change in abundance of Mo metal, suggesting that Mo metal is the most active species for propane hydrogenolysis.

The catalytic activity of reduced Mo/Al₂O₃ catalysts (8% Mo) for propane hydrogenolysis was measured as a function of the reduction temperature. The variation of catalytic activity in the reduced catalysts was compared with the distribution of Mo oxidation states obtained from ESCA using non-linear least squares curve fitting. The results indicated that both Mo²⁺ and Mo metal are active for propane hydrogenolysis. However, Mo metal exhibits much higher intrinsic activity than Mo²⁺. If one assumes that Mo⁰ is four-times as active as Mo²⁺, a good linear correlation is found, as seen in Figure 2.

![Figure 2](image-url)

This represents development of new methodology for estimating the number and percentages of components in an ESCA data set for a catalyst system. The motivation was to eliminate as much as possible the assignment of arbitrary characteristics for doing curve fitting analysis. This study shows that principal component analysis (PCA) in conjunction with iterative target transformation factor analysis (ITTFA) is able to provide an independent estimate of the number, position and, to a certain extent, the shape of spectral components required to describe the Mo 3d envelope as monitored by XPS in reduced Mo/TiO_2 catalysts. Three components were required to reproduce the original data set. Abstract components obtained from PCA were transformed through ITTFA into components which have spectroscopic meaning. ITTFA was able to predict the positions and basic shapes of three spectral components and thus give an estimate of their relative contribution to each spectrum. The three spectral components were attributed to Mo^{4+}, Mo^{5+} and Mo^{4+}. Results from factor analysis (FA) were used in conjunction with non-linear least-squares curve fitting (NLLSCF), to provide a detailed description of the Mo 3d envelope during reduction of the Mo/TiO_2 catalysts.

Influence of Preparation on Catalytic Activity:


Two series of silica supported cobalt catalysts were prepared by incipient wetness impregnation, one by varying the calcination temperature (200-400°C, 3 wt % Co) and the other by changing the cobalt loading (1-10 wt % Co). Examination by ESCA, XRD, and H_2 chemisorption showed that Co_3O_4 is the main cobalt phase in the oxidic catalysts. The cobalt phase is reduced to cobalt metal at 400°C. The cobalt particle sizes obtained from ESCA correlated well with those derived from H_2 chemisorption and XRD line broadening. The turnover frequency of Co/SiO_2 for CO hydrogenation was invariant with cobalt dispersion in the range of 6-20% dispersion.


The adsorption of perrhenate, permanganate, molybdate, tungstate, and chromate on alumina was studied at pH 4.5. The effect of nitrate in the impregnating solution on the adsorption of these ions was examined as well as the effect of washing the freshly prepared catalysts. The uptake of perrhenate and permanganate decreased with increasing nitrate in the impregnation solution; the uptake of molybdate, tungstate, and chromate was unaffected. Washing the catalysts almost completely removed perrhenate, permanganate, and chromate, but allowed a significant amount of molybdate and tungstate to remain on the alumina. It is concluded that tungstate and molybdate adsorb on two types of surface sites, producing loosely and tightly bound surface species. From the amounts of molybdate and tungstate adsorbed, and from EXAFS results from washed and unwashed Mo/Al_2O_3 samples, it was found that both loosely and tightly bound molybdate and tungstate are polymeric in nature. Two types of interactions occur between oxynitons and alumina. Permanganate and perrhenate adsorb primarily through electrostatic interactions; the amount that adsorbs is proportional to the fraction of anions present in solution. Other anions adsorb through an acid-base reaction on two types of sites.

The influence of TiO₂ on the distribution of supported species in 3 wt% Co/Al₂O₃ catalysts has been examined by X-ray diffraction, X-ray photoelectron spectroscopy (ESCA), Raman spectroscopy, and gravimetric (microbalance) analysis. The results show that for unmodified catalysts with low Ti loadings (<4 wt% Ti) the Co phase is present primarily as Co₃O₄ with lesser amounts of surface octahedral and tetrahedral cobalt [Co(o); Co(t)]. For catalysts having high Ti contents, Co₃O₄ formation is suppressed with increasing Ti loadings in favor of a CoTiO₃-like surface phase. The effect of Ti/Al on the Co₃O₄ content is shown in Figure 3. Benzene and CO hydrogenation activity measurements indicate that Ti addition decreases the catalytic activity for both reactions. This has been attributed primarily to site blocking which results from the migration of reduced Ti species.


Two series of Mo/Al₂O₃-B and Mo/Al₂O₃-Ti catalysts containing a constant loading of Mo (8 wt% Mo) and various amounts of B (0.3-3 wt% B) and Ti (1-14 wt% Ti) were prepared by sequential impregnation (B or Ti first). The catalysts were characterized by x-ray diffraction, ESCA, ISS, and gravimetric analysis to determine the influence of additives on the structure of Mo/Al₂O₃ catalysts. ESCA and x-ray diffraction indicate that molybdenum is highly dispersed on the surfaces of both boron and titania modified alumina. Molybdenum dispersion is unaffected by the presence of boron or titania in the range of additive loadings studied. Molybdenum also remains well dispersed following reduction in hydrogen at 350°C. Modification of the alumina support by titania causes an increase in molybdenum reducibility at 350°C with increasing titania loading. Low loadings of boron had no effect on molybdenum reducibility, while boron loadings in excess of 0.9 wt% B resulted in increased reducibility. The increase in molybdenum reducibility was greater for titania modified catalysts than for boron modified catalysts. The increase in molybdenum reducibility with increasing titania loading and high boron loadings can be rationalized by formation of octahedral Mo-O-Ti and Mo-O-B species, respectively.


Samples containing 8% Mo and 15% W supported on magnesium- and fluoride-modified aluminas were prepared by incipient wetness impregnation and examined in the dried and calcined states using X-ray photoelectron spectroscopy (XPS, ESCA). The presence of...
fluoride as an additive decreased the dispersion of the Mo and W phases for dried samples due to replacement of hydroxyl groups by fluoride. The opposite effect was observed for dried Mg-modified samples. The effects of F and Mg addition largely disappeared when the samples were calcined. The results are interpreted in terms of the interactions between Mo and W species and the basic hydroxyl groups of the alumina. The dispersion of Mo and W supported on fluoride modified alumina increases, yielding dispersions observed for unmodified alumina. This effect is due to greater mobility for Mo and W species on the modified alumina. No such effect is observed for magnesium-doped catalysts.

Organometallic Precursors:


Stoichiometric redox measurements and X-ray photoelectron spectroscopy (XPS or ESCA) studies were performed on an allyl-based Mo/SiO₂ catalyst (1.7 wt % Mo) obtained by the sublimation of Mo(η³-C₆H₅)₄ onto SiO₂ at 40°C. The average oxidation state estimated from stoichiometric measurements correlated well with those reported in the literature. ESCA results indicated that reduction of the Mo/SiO₂ catalyst at 550°C primarily led to the formation of Mo⁴⁺. Also, the results were consistent with the reported reversibility of the redox cycle. However, the reported formation of discrete Mo⁶⁺ by oxidation of the reduced catalyst at room temperature could not be substantiated. The scheme shown in Figure 4 has been proposed to explain behavior of allyl-based Mo catalysts. ESCA results shown in Figure 5a support the structure proposed and the formation of an Mo(+2) oxidation state. The results in 5b show a mixture of oxidation states and not a unique species as suggested by Fig. 4. Complete oxidation yields Mo(+6) as proposed.
Tungsten Catalysts:


The distribution of supported species in a series of W/TiO₂ catalysts (1.8 - 28 wt% WO₃) has been determined by Raman and X-ray photoelectron spectroscopy (XPS, ESCA). The results show that three tungsten species are present on oxidic W/TiO₂ catalysts. A tungsten interaction species is formed almost exclusively for catalysts with W loadings lower or equal to 6.7 wt% WO₃. WO₃ is observed above 6.7 wt% WO₃. For W loadings higher than 10 wt%, a disordered W species (Wds) is also present. The amounts of Wds and WO₃ increase with increasing W content above 10 wt% WO₃. Relative intensity data for ESCA and Raman spectroscopy correlate well in the region below 10% WO₃; both indicate highly-dispersed species. Measurement of WO₃ by x-ray diffraction and Raman correlates well over the range of 6-30% WO₃.

Nickel Catalysts:


A modified ESCA method, which accounts for both difference in particle size among surface species of supported catalysts and metal sintering, is applied to measurement of the reactivity of supported Ni catalysts. The extent of Ni reduction and sulfidation measured by the modified ESCA method correlated well with data obtained by gravimetric analysis and by chemical extraction. The reducibility and sulfidability of the catalysts were different for low Ni loadings (<5%) but the same for higher loadings. The reducibility data were used to measure Ni metal particle size in the reduced catalysts by ESCA. Increasing Ni loading caused the Ni particle size in the reduced catalysts to increase from 0.6 to 2.6 mm. Correlations were established with catalyst activity for benzene hydrogenation. The turnover frequencies (TOF’s) of reduced Ni/Al₂O₃ catalysts for benzene hydrogenation were little affected by the Ni metal particle size in the dispersion range 38 to 100%.

Methodology for Studying Catalysts:

Part of our program has been devoted to developing methodology, mostly spectroscopic, for studying catalysts. These studies include development of low-energy ion scattering, exploring the quantitative aspects of EXAFS, using ESCA valence bands to determine site symmetry, and the effect of solution parameters on catalyst preparation. These will be discussed in some detail below.


A series of Mo/Al₂O₃ catalysts was prepared by using an equilibrium adsorption method. The dispersion of the molybdenum phase and coverage of the alumina surface by Mo species as a function of Mo loading were monitored by ion scattering spectroscopy (ISS) and X-ray photoelectron spectroscopy (XPS, ESCA). By modeling changes in the ISS Mo/Al intensity ratio as a function of molybdenum coverage, it is shown that, for Mo/Al₂O₃ catalysts prepared by equilibrium adsorption, coverage of the alumina surface
should be complete at a loading of $47 \times 10^{13}$ Mo atoms/cm$^2$ for calcined catalysts and $55 \times 10^{13}$ Mo atoms/cm$^2$ for dried catalysts. These values agree with those obtained from modeling of the ISS Al/O intensity ratio as a function of Mo loading. The results are interpreted in terms of solution equilibria at the alumina interface. This study emphasizes the intrinsic surface sensitivity of ISS as opposed to ESCA, shown in Figure 6. An experimental verification of the effect of surface coverage on ISS is shown in Figure 7.

![Figure 6](image)

**Figure 6.** Theoretical plots of absolute ESCA and ISS Al intensity as a function of surface coverage.

![Figure 7](image)

**Figure 7.** Variation of ISS Al/Mo intensity ratio as a function of $1/(\text{Mo loading})$ for dried (O) and calcined (Q) catalysts.


EXAFS spectroscopy has been used to examine the effect of boron on the structure of Co/Al$_2$O$_3$ catalysts. The EXAFS results from unmodified Co/Al$_2$O$_3$ catalysts indicated that Co$_3$O$_4$ was formed at Co loadings of 1.5 wt % Co and higher. The lowest-loading (0.7 wt % Co) catalyst showed evidence of both tetrahedral and octahedral Co surface species. Modification of the Co/Al$_2$O$_3$ catalysts with 3 wt % B completely suppressed the formation of Co$_3$O$_4$ for Co loadings of 6 wt % Co and lower. In the absence of Co$_3$O$_4$, the Co species formed on the 3 wt % boron modified catalysts were in a highly disordered state with large first shell Co-O coordinations and large Co-O nearest-neighbor distances. Results from a constant Co loading series (3 wt % Co) indicated that Co$_3$O$_4$ formation decreased as the boron loading increased. The distribution of supported Co species determined by EXAFS was compared with previous characterization by ESCA and gravimetric measurements; good agreement was found. This is shown in Figure 8. A two-phase procedure was used to analyze the EXAFS data from the

![Figure 8](image)

**Figure 8.** Content of Co$_3$O$_4$ in mg Co$_3$O$_4$/g Al$_2$O$_3$ for unmodified Co/Al$_2$O$_3$ catalysts from EXAFS (O), ESCA (II), and gravimetric (O) measurements, versus Co loading.
Co/B/Al₂O₃ catalysts. This two-phase analysis considered both the fraction of Co EXAFS from bulk Co oxide (Co₃O₄) and the remaining fraction from Co surface species. This allowed the amount of Co₃O₄ to be determined quantitatively and enabled structural information to be obtained about the Co surface phase.


X-ray photoelectron spectroscopy (XPS, ESCA) valence band spectra were used to infer information about the molybdenum phase in standard Mo compounds such as sodium molybdate and ammonium heptamolybdate and in Mo/Al₂O₃ catalysts prepared by equilibrium adsorption and incipient wetness impregnation methods. ESCA valence band measurements can distinguish between tetrahedrally coordinated Mo (sodium molybdate) and octahedrally coordinated Mo (ammonium heptamolybdate). Key to these measurements is the use of derivative spectra which significantly enhances spectral features, an example for a catalyst prepared by incipient wetness is shown in Figure 9. The top and bottom spectra are for tetrahedral and octahedral species, respectively. The catalyst clearly shows features of both, but mostly octahedral species. Mo ESCA valence band results show that Mo/Al₂O₃ catalysts prepared by equilibrium adsorption at pH 2.2 and Mo/Al₂O₃ catalysts prepared by incipient wetness impregnation contain primarily octahedral Mo.


This paper summarizes the methodology which we have developed for measuring the distribution of oxidation states in reduced catalysts. The adopted approach is based on curve fitting the X-ray Photoelectron Spectroscopy (ESCA,XPS) envelope using a Non-Linear Least Squares Curve Fitting (NLLSCF) routine. The procedure was applied to study the reduction of Mo/TiO₂ and Mo/Al₂O₃ catalysts. The distribution of Mo oxidation states obtained by ESCA was corroborated by chemical measurements and correlated with catalytic activity. The limitations of the NLLSCF approach are discussed. It is shown that the uncertainties inherent in curve fitting methods can be minimized by the use of Factor Analysis (FA). This data analysis technique provides an independent estimate of the number, positions, and shapes of components required to describe the Mo 3d envelopes in the reduced catalysts.
Personnel:

The following personnel have been supported by and/or contributed to our DOE funded research program.

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Publications for 1990-1993:

The following is a list of publications which have resulted from research funded by the DOE grant.

A. Papers Published


B. Papers Submitted and In Press


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