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Studies of Supported Hydrodesulfurization Catalysts

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Mo/Titania Catalysts:

Three aspects of titania-supported Mo catalysts have been studied: first, a combined Raman-ESCA quantitative characterization of the surface species, second, correlation between surface species formed on the oxidic catalyst and HDS activity of the sulfided catalyst; third, an ESCA investigation of the oxidation states on reduced Mo-titania catalysts, and correlation between oxidation state and activity for benzene hydrogenation.

Two Mo species, the Mo-interaction species (polymolybdate) and MoO_3 were measured quantitatively for a series of Mo/TiO_2 catalysts. Concentration of the interaction species increased with total Mo loading up to 6 wt%; MoO_3 was detected at 7.5 wt% and increased linearly with additional total Mo. The results from Raman spectroscopy correlated well with measurements by ESCA and XRD on the same catalysts, XRD measuring the MoO_3 and ESCA the interaction species. A Mo phase of uniform and high dispersion exists for catalysts with Mo loadings of 6 wt% MoO_3 or below.

A combination of Raman data and thiophene HDS activity measurements showed that three Mo species are present on the surfaces of oxidic Mo/TiO_2 catalysts. ESCA data showed that two of these are highly dispersed surface species. One of the species was assigned to a tetrahedral surface molybdate species, its concentration increases up to ca. 2.5 wt% MoO_3 . This species is denoted as Mo(t). The second surface Mo species is assigned to a polymolybdate and is formed at higher Mo loadings; it is referred to as Mo(p). Mo(t) accounts for the Raman band at 950 cm^{-1} ; Mo(p) contributes to the background on the low frequency of the Mo(t) peak. The third species is crystalline MoO_3 .

Thiophene HDS Activity of Mo/TiO_2 Catalysts

Figure 1

Thiophene HDS activity was correlated with the total amount of Mo(t) + Mo(p) on the catalyst surface. This plot is shown in Figure 1. The break at 4 wt% MoO_3 shows that only the Mo(t) species correlates with high HDS activity. This clearly establishes that the Mo(t) species on the oxidic catalyst is the precursor to the active HDS species. Although the Mo(t) species has been proposed by others to be the precursor to HDS activity, this is the first quantitative correlation between HDS activity and a surface species.

A 5 wt% $\text{MoO}_3/\text{TiO}_2$ catalyst was reduced at various temperatures to study the Mo oxidation states produced for reduction in the range 200-700 C. It was possible to measure the chemical shifts in the ESCA spectra for Mo oxidation states between +4 and 0, something not accomplished previously. An oxidation state distribution diagram was established; average

Figure 2

Mo/Alumina Catalysts:

Two series of $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts were prepared containing 8 wt% Mo and various amounts of B (0.3-3 wt%) or Ti (1-14 wt%); preparation was by sequential impregnation with B or Ti first. The catalysts were used to study the influence of additives on the structure and reactivity of $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts. The catalysts were first characterized in the oxidic form and then as sulfided catalysts. Correlation with activity was for hydrodesulfurization of thiophene.

ESCA and x-ray diffraction indicated that Mo is highly dispersed in the unmodified catalyst and in both the B- and Ti-modified catalysts. No significant change in dispersion was observed for reduction in hydrogen at 350 C. The reducibility of Mo in hydrogen at 350 C increases with increasing Ti content, and for B contents greater than 0.9 wt% B. ESCA reduction studies correlated well with microbalance measurements. The increased reduction is attributed to formation of reducible Mo-O-Ti and Mo-O-B species. Data were obtained for a minimum of five species on the oxidic catalysts, as shown in Table 1. The $\text{Mo}(t)m$ and $\text{Mo}(t)d$ species could not be distinguished in the oxidic catalysts.

oxidation state as a function of reduction temperature calculated from ESCA data correlated well with similar data obtained by gravimetric analysis. It was possible to correlate catalytic activity for the hydrogenation of benzene with the oxidation state formed on the catalyst as shown in Figure 2. Benzene hydrogenation depended strongly on the extent of reduction and correlated well with $\text{Mo}(+2)$. It is not possible to rule out hydrogenation by $\text{Mo}(0)$, because of structural changes induced in the catalyst by the high reduction temperatures necessary to produce Mo metal.

Table 1. Species Observed on Mo/Al₂O₃ Catalysts

Species	Chemical Description	350 C Reduction	350 C Sulfidation \
Mo(t)m	Tetrahedral monomer	not reducible	reduces to +5
Mo(t)d	Tetrahedral dimer	not reducible	sulfides to +4
Mo-Al-O	Octahedral monomer	not reducible	reduces to +5
Mo-O-Mo	Octahedral polymer	reduces to +5	sulfides to +4
Mo-O-Ti	Octahedral Mo-O-Ti	reduces to +4	sulfides to +4
Mo-O-B	Octahedral Mo-O-B	reduces to +4	sulfides to +4

Figure 3

Sulfidation of the catalysts with thiophene in hydrogen at 350 C produced no significant change in Mo dispersion. An increase in sulfidability was observed for Ti-modified catalysts and for B-modified catalysts with loadings greater than 0.9 wt% B. By comparison with the oxidic catalysts, it was possible to show that the increased sulfidability was due to formation of Mo-O-Ti and Mo-O-B in the oxidic catalysts. Distinction between Mo(t)m and Mo(t)d was possible by studying catalysts leached with aqueous ammonia. The behavior of all species is summarized in Table 1.

The HDS activity for thiophene was determined to be a function of added Ti or B; Ti was an activator and B a poison. Changes in HDS activity for the modified catalysts were correlated with formation of Mo-O-X (X=Ti,B) on the oxidic catalysts. This is shown in Figure 3. Assuming that

MoS₂ is produced in all cases, the conclusion is that MoS₂ produced from Mo-O-Mo species has average activity, that from Mo-O-Ti superior activity and that from Mo-O-B poor activity. The explicit reason for this behavior is not apparent; the effect could be structural or electronic.

Absorption of Metal Oxyanion on Alumina:

A comparative study of ISS and ESCA was performed to evaluate the two techniques for studying surface coverage of heterogeneous catalysts. The dispersion of the Mo phase of a series of Mo/Alumina catalysts, prepared by equilibrium adsorption, was studied as a function of Mo loading. Theoretical models were compared for plots of I(Mo)/I(Al) as a function of surface coverage for both ISS and ESCA. It was shown that plots of I(Al)/I(Mo) vs. 1/(Mo loading) for ISS were linear and that extrapolation to zero intensity yielded coverage equal to a monolayer. Similar studies were performed using I(Al)/I(O) ISS intensity ratios. Both methods yielded monolayer coverages of 4.7×10^{12} and 5.5×10^{12} Mo atoms/cm² for calcined and dried catalysts, respectively.

The adsorption of perrhenate, permanganate, molybdate, tungstate, and chromate on alumina was studied at $\text{pH} = 4.5$. Two types of interactions between metal oxyanions and alumina were observed. Permanganate and perrhenate adsorb on alumina primarily through electrostatic interactions. The amounts of permanganate and perrhenate which adsorb on alumina are directly proportional to the fraction of anions present in solution as MnO_4^- or ReO_4^- . This was studied by diluting the amounts of these anions with nitrate. Calculated maximum amounts of MnO_4^- and ReO_4^- which adsorb agree with predicted amounts, based on the alumina surface charge measured by potentiometric titration.

Electrostatic interactions between MoO_4^{2-} , WO_4^{2-} , or CrO_4^{2-} and the alumina surface occur, but some other mechanism is also operative. Adsorption of MoO_4^{2-} and WO_4^{2-} occurs on two types of sites to yield tightly- and loosely-bound surface species based on EXAFS measurements and ratios of adsorbed MoO_4^{2-} to WO_4^{2-} , both species are polymeric anions. Two types of basic alumina hydroxyl groups are suggested as adsorption sites for the loosely- and tightly-bound species.

The isoelectric point (IEP) of γ -alumina was modified by the addition of various amounts of fluoride. The modified aluminas were used as supports for Mo-based catalysts prepared by equilibrium adsorption at $\text{pH} = 6.5$. Adsorption of molybdate on supports containing various amounts of fluoride was also studied as a function of pH of the adsorbing solution. The amount of Mo adsorbed on the fluoride-modified aluminas decreased as the IEP of the carrier decreased. The trend was explained by an electrostatic adsorption model and the Mo species present in solution.

The use of fluoride as an additive leads to a decrease in dispersion of dried Mo- and W-Alumina catalysts. This effect is due to loss of basic hydroxyl groups by fluoride addition. Calcination causes the dispersion to increase; the dispersion of calcined catalysts is similar to that of unmodified alumina. Calcination leads to loss of fluoride, the increase in dispersion involves site-substitution for fluoride. The use of magnesium as a modifier leads to larger dispersion for the uncalcined modified catalyst than for the unmodified catalyst. The larger dispersion is retained after calcination. The increased dispersion is due to the increase in basic hydroxyl groups in the Mg-modified catalyst.

Particle Size Effects for Co/Silica Catalysts:

The effect of particle size on CO hydrogenation activities has been studied for a variety of Group VIII metals. Supported cobalt catalysts show strong dependence of activity on particle size over a wide range of dispersions (6-80%). However, catalysts studied often used supports which exhibit strong SMSI effects. Thus, the "particle-size effect" is convolved with other factors. To overcome this problem, two series of silica-supported cobalt catalysts were prepared by incipient wetness impregnation by varying calcination temperature and cobalt loading. The dominant phase was Co_3O_4 which is completely reduced to the metal at 400 C. Cobalt particle sizes were measured by ESCA, x-ray diffraction and H_2 chemisorption; good agreement was observed among techniques. No particle size effect on CO hydrogenation turnover frequency was observed in the cobalt dispersion range of 6-20%.

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 Mo/TiO₂ catalysts. 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 Mo/Al₂O₃ 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 Mo/TiO₂ system. The distribution of Mo oxidation states as a function of reduction temperature was similar to that for the Mo/TiO₂ catalysts although for the alumina supported catalysts, it was not possible to achieve complete reduction to Mo(0) even at 900° 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° to 900° C).

The catalytic activity for benzene hydrogenation showed a threshold of approximately 600°C and a nearly linearly increase in rate up to 900°C. Comparison with the distribution of Mo oxidation states shows that Mo(0) is the major oxidation state for benzene hydrogenation for Mo on alumina. However, it is clear that Mo(+2) must also be active because Mo(0) does not appear until a reduction temperature of 700°C. This result is different than that observed for Mo/TiO₂, 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. However the major problem with 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/TiO₂ 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/TiO₂ Catalysts:

Although much research has focused on W/Al₂O₃ and W/SiO₂ catalysts, few studies of W/TiO₂ 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/TiO₂ catalysts, and have applied this to the W/TiO₂ 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-TiO₂ "interaction species" on the catalysts that has a peak at 970cm⁻¹ analogous to comparable Mo/TiO₂ catalysts. Raman spectroscopy also revealed the presence of WO₃ for all catalysts having greater than 6.7 wt% WO₃ loadings. The Raman results were confirmed by x-ray diffraction data. A calibration curve for WO₃ was constructed and showed that Raman spectroscopy will be an excellent tool for quantitation of WO₃ 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% WO₃. 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 WO₃ 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. WO₃ begins to appear on the catalyst at approximately 6% and increases linearly with low slope up to about 15% WO₃ at which point the slope increases. The disordered W species appears at about 10% loading and increases linearly with WO₃ loading.

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Figure 3

Sulfidation of the catalysts with thiophene in hydrogen at 350 C produced no significant change in Mo dispersion. An increase in sulfidability was observed for Ti-modified catalysts and for B-modified catalysts with loadings greater than 0.9 wt% B. By comparison with the oxidic catalysts, it was possible to show that the increased sulfidability was due to formation of Mo-O-Ti and Mo-O-B in the oxidic catalysts. Distinction between Mo(t)m and Mo(t)d was possible by studying catalysts leached with aqueous ammonia. The behavior of all species is summarized in Table 1.

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MoS₂ is produced in all cases, the conclusion is that MoS₂ produced from Mo-O-Mo species has average activity, that from Mo-O-Ti superior activity and that from Mo-O-B poor activity. The explicit reason for this behavior is not apparent; the effect could be structural or electronic.

Absorption of Metal Oxyanion on Alumina:

A comparative study of ISS and ESCA was performed to evaluate the two techniques for studying surface coverage of heterogeneous catalysts. The dispersion of the Mo phase of a series of Mo/Alumina catalysts, prepared by equilibrium adsorption, was studied as a function of Mo loading. Theoretical models were compared for plots of I(Mo)/I(Al) as a function of surface coverage for both ISS and ESCA. It was shown that plots of I(Al)/I(Mo) vs. 1/(Mo loading) for ISS were linear and that extrapolation to zero intensity yielded coverage equal to a monolayer. Similar studies were performed using I(Al)/I(O) ISS intensity ratios. Both methods yielded monolayer coverages of 4.7×10^{12} and 5.5×10^{12} Mo atoms/cm² for calcined and dried catalysts, respectively.

The adsorption of perrhenate, permanganate, molybdate, tungstate, and chromate on alumina was studied at pH = 4.5. Two types of interactions between metal oxyanions and alumina were observed. Permanganate and perrhenate adsorb on alumina primarily through electrostatic interactions. The amounts of permanganate and perrhenate which adsorb on alumina are directly proportional to the fraction of anions present in solution as MnO_4^- or ReO_4^- . This was studied by diluting the amounts of these anions with nitrate. Calculated maximum amounts of MnO_4^- and ReO_4^- which adsorb agree with predicted amounts, based on the alumina surface charge measured by potentiometric titration.

Electrostatic interactions between MoO_4^{2-} , WO_4^{2-} , or CrO_4^{2-} and the alumina surface occur, but some other mechanism is also operative. Adsorption of MoO_4^{2-} and WO_4^{2-} occurs on two types of sites to yield tightly- and loosely-bound surface species based on EXAFS measurements and ratios of adsorbed MoO_4^{2-} to WO_4^{2-} , both species are polymeric anions. Two types of basic alumina hydroxyl groups are suggested as adsorption sites for the loosely- and tightly-bound species.

The isoelectric point (IEP) of γ -alumina was modified by the addition of various amounts of fluoride. The modified aluminas were used as supports for Mo-based catalysts prepared by equilibrium adsorption at pH = 6.5. Adsorption of molybdate on supports containing various amounts of fluoride was also studied as a function of pH of the adsorbing solution. The amount of Mo adsorbed on the fluoride-modified aluminas decreased as the IEP of the carrier decreased. The trend was explained by an electrostatic adsorption model and the Mo species present in solution.

The use of fluoride as an additive leads to a decrease in dispersion of dried Mo- and W-Alumina catalysts. This effect is due to loss of basic hydroxyl groups by fluoride addition. Calcination causes the dispersion to increase; the dispersion of calcined catalysts is similar to that of unmodified alumina. Calcination leads to loss of fluoride, the increase in dispersion involves site-substitution for fluoride. The use of magnesium as a modifier leads to larger dispersion for the uncalcined modified catalyst than for the unmodified catalyst. The larger dispersion is retained after calcination. The increased dispersion is due to the increase in basic hydroxyl groups in the Mg-modified catalyst.

Particle Size Effects for Co/Silica Catalysts:

The effect of particle size on CO hydrogenation activities has been studied for a variety of Group VIII metals. Supported cobalt catalysts show strong dependence of activity on particle size over a wide range of dispersions (6-80%). However, catalysts studied often used supports which exhibit strong SMSI effects. Thus, the "particle-size effect" is convolved with other factors. To overcome this problem, two series of silica-supported cobalt catalysts were prepared by incipient wetness impregnation by varying calcination temperature and cobalt loading. The dominant phase was Co_3O_4 which is completely reduced to the metal at 400 C. Cobalt particle sizes were measured by ESCA, x-ray diffraction and H_2 chemisorption; good agreement was observed among techniques. No particle size effect on CO hydrogenation turnover frequency was observed in the cobalt dispersion range of 6-20%.

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 Mo/TiO₂ catalysts. 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 Mo/Al₂O₃ 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 Mo/TiO₂ system. The distribution of Mo oxidation states as a function of reduction temperature was similar to that for the Mo/TiO₂ catalysts although for the alumina supported catalysts, it was not possible to achieve complete reduction to Mo(0) even at 900° 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° to 900° C).

The catalytic activity for benzene hydrogenation showed a threshold of approximately 600°C and a nearly linearly increase in rate up to 900°C. Comparison with the distribution of Mo oxidation states shows that Mo(0) is the major oxidation state for benzene hydrogenation for Mo on alumina. However, it is clear that Mo(+2) must also be active because Mo(0) does not appear until a reduction temperature of 700°C. This result is different than that observed for Mo/TiO₂, 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. However the major problem with 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/TiO₂ 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/TiO₂ Catalysts:

Although much research has focused on W/Al₂O₃ and W/SiO₂ catalysts, few studies of W/TiO₂ 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/TiO₂ catalysts, and have applied this to the W/TiO₂ 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-TiO₂ "interaction species" on the catalysts that has a peak at 970cm⁻¹ analogous to comparable Mo/TiO₂ catalysts. Raman spectroscopy also revealed the presence of WO₃ for all catalysts having greater than 6.7 wt% WO₃ loadings. The Raman results were confirmed by x-ray diffraction data. A calibration curve for WO₃ was constructed and showed that Raman spectroscopy will be an excellent tool for quantitation of WO₃ 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% WO₃. 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 WO₃ 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. WO₃ begins to appear on the catalyst at approximately 6% and increases linearly with low slope up to about 15% WO₃ at which point the slope increases. The disordered W species appears at about 10% loading and increases linearly with WO₃ loading.

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