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Characterization of Supported Molybdena Catalysts by SIMS

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Static SIMS was used to characterize SiO_2- and Al_2O_3-supported molybdena catalysts. Changes in dispersion following calcination and water exposure treatments previously observed by UV, ESCA, ISS, and Raman spectroscopies for Mo/SiO_2 were confirmed by the SIMS data. As such dispersion changes were not found by SIMS with Mo/Al_2O_3 catalysts, additional ESCA and UV spectra were recorded for these catalysts after calcination/water vapor exposures cycles. These data essentially confirm the absence of any change in dispersion on Mo coordination. Analysis of both Mo/SiO_2 and Mo/Al_2O_3 catalysts illustrate the sensitivity of the static SIMS technique to structural changes in supported molybdena phases. © 1987 Academic Press, Inc.

INTRODUCTION

Recently we reported (*1*, *2*) that on Mo/SiO_2 catalysts the UV absorption bands characteristic of Mo in octahedral coordination disappear almost completely upon O_2 calcination at low Mo coverage. At higher Mo coverage, however, these bands do not disappear completely although the UV spectra are significantly modified by the calcination treatment. It was also shown that these changes may be reversed by prolonged exposure of the freshly calcined catalysts to air or water vapor at room temperature. (Prolonged air or water vapor exposure caused the UV absorption bands characteristic of octahedrally coordinated Mo that were lost during calcination to reappear). It was tentatively suggested that hydration causes the formation of stable structures similar to those of silicomolybdic acid species on the surface and that these structures collapse upon calcination. Hence the question arose whether indeed silicomolybdic acid species are formed during hydration. If so, the formation of such species on hydration should be accompanied by a decrease in the Mo dispersion, while the Mo dispersion should be increased on calcination if indeed the silicomolybdic acid species are dismantled as suggested. These questions were addressed in detail in a subsequent *in situ* study of Mo/SiO_2 catalysts by ESCA, ISS, and Raman spectroscopy (*2*, *3*). As it was suggested previously (*1*), the Mo dispersion as measured by ESCA and ISS techniques indeed showed a reversible variation as a function of calcination–hydration cycles; i.e., the Mo dispersion is increased upon calcination while it was decreased upon hydration. Raman spectroscopic analysis of these catalysts finally established beyond doubt that indeed the variation in the Mo dispersion as a function of hydration–calcination cycles is accompanied by the appearance and the disappearance of silicomolybdic acid species on the surface.

Similarly, on Mo/Al_2O_3 catalysts calcination–hydration cycles lead to reversible changes in their Raman spectral features (*4*–*7*). Hydration of freshly calcined Mo/Al_2O_3 catalysts, however, does not lead to the appearance of the spectral features of a new phase in the Raman spectra as with Mo/SiO_2 catalysts (*4*–*7*). On Mo/Al_2O_3 catalysts the prominent Raman band observed at 900–1000 cm^{-1} attributed to the Mo=O terminal stretching mode can be reversibly shifted by repeated calcination–hydration treatments (*4*–*7*). This Raman band sensitivity to hydration–calcination treatments

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has been attributed to a variation in the bond order and bond length of Mo═O terminal groups (*5, 6*). Stencel *et al.* (*5, 6*) proposed that this could occur by an increase in the Mo coordination symmetry from tetrahedral to octahedral as a result of water coordination to Mo. This does not appear to be the case, since hydration–calcination treatments had no effect on the UV spectrum of a 0.1 wt% Mo/SiO_2 catalyst, where only the isolated tetrahedral monomers are found (*2*). On Re/Al_2O_3 catalysts the effect of hydration on the Raman band features has been attributed to the hydrolysis of the Al–O–Re bond (*8*). Hall and co-workers (*7*) recently reported an *in situ* Raman study of several γ-Al_2O_3 supported metal oxides. It was suggested that the interaction of water molecules either increases the degree of disorder or changes the symmetry of surface bonding affecting the symmetric Mo═O stretch. The increased disorder was seen as a consequence of non-uniform coordination of water molecules to the surface metal oxide.

These data point to some important differences in the supported molybdena phases stabilized by the two different supports Al_2O_3 and SiO_2 and their sensitivity to hydration–calcination treatments. On Mo/SiO_2 catalysts it is established that hydration leads to the formation of silicomolybdic acid species. On Mo/Al_2O_3 catalysts, however, data are lacking for any definitive conclusion to be made. The effect of hydration on the Raman band features of Mo/Al_2O_3 catalysts is less clear. It is not certain whether the water coordination leads to any change in the coordination symmetry of Mo affecting the charge transfer spectra and whether the modifications to the Raman spectra induced by hydration are related to changes in the structure of the surface molybdates similar to those observed on Mo/SiO_2 catalysts.

The present communication is a result of an attempt to address these questions by a study of the sensitivity of the surface molybdates on supported molybdena catalysts to hydration using the static SIMS technique. Although the surface sensitivity of the static SIMS technique has been recognized (*9, 10*) this technique has rarely been applied in the characterization of supported metal oxide catalysts. Furthermore on Mo/Al_2O_3 catalysts it is yet to be established whether hydration results in any changes in the coordination symmetry of Mo affecting the charge transfer spectra and/or whether hydration induces any change in the Mo dispersion on the surface as was the case for Mo/SiO_2 catalysts.

Therefore in order to understand differences observed in SIMS data of SiO_2- and Al_2O_3-supported Mo catalysts, it appeared necessary to complement our previous works on Mo/SiO_2 catalysts with a study with UV diffuse reflectance spectroscopy and with *in situ* ESCA of the effect of hydration on Mo/Al_2O_3 catalysts.

EXPERIMENTAL

Catalysts

As in previous works (*1–3*) four series of supported molybdena catalysts are used. They were prepared using commercial grade (Fisher S-662) high-surface-area silica gel (surface area 400 m^2/g, pore volume 0.35 cm^3/g, 60–200 mesh) and Norton SA 6473 γ-Al_2O_3 (surface area 195 m^2/g, pore volume 0.5 cm^2/g, 50–140 mesh aggregates).

The first two series of catalysts were prepared by the pore volume impregnation of SiO_2 and γ-Al_2O_3 with aqueous solutions of ammonium paramolybdate (Anachemia AC-630) with varying Mo content. After impregnation the catalysts were first dried at 120°C for 12 h and then calcined at 500°C for 15 h in air (impregnated catalysts).

The other two series of catalysts were prepared by soaking the SiO_2 and γ-Al_2O_3 in pentane solutions of $Mo(\eta^3\text{-}C_3H_5)_4$ complex with different Mo contents under an inert atmosphere. The supports used were degassed at 200°C to eliminate the physisorbed water prior to catalyst preparation.

After the reaction of $Mo(\eta^3\text{-}C_3H_5)_4$ with the surface hydroxyl groups of the support, the catalysts were washed with pentane to remove the excess of $Mo(\eta^3\text{-}C_3H_5)_4$ and they were dried under vacuum at ambient temperature. The catalysts were then calcined at 500°C for 15 h (fixed catalysts).

Static SIMS

The static SIMS spectra are recorded using a V.G. Scientific SIMS spectrometer. The primary ion beam was Ar^+ of 3 kV energy and the beam current was 0.5 nA with a current density of 5 nA/cm^2. The diameter of the beam was 200 μm. The argon pressure at the target during analysis was 2×10^{-8} Torr and other background gases were below 10^{-10} Torr. The secondary positive and negative ions were mass analyzed in a quadrupole mass filter and detected by a Channeltron multiplier. During analysis the catalyst samples were neutralized using a flood gun of 500 eV energy with a maximum current of 1 μA.

The catalyst samples were analyzed in their original granulometry loaded into stainless-steel cups. SIMS spectra were first obtained for air-stabilized samples (aged at least for 6 months under atmospheric conditions after the first calcination), then for the same samples calcined at 500°C in O_2 for 1 h, and for the calcined samples after exposure to water vapor at ambient temperature for 1 h. The sample pretreatments are performed in a reaction cell located inside the fast entry lock chamber of the spectrometer. Prior to the introduction of O_2 into the cell the sample was heated in air and evacuated at 500°C. O_2 was then introduced at 700 Torr. After 0.5 h of calcination, the cell was evacuated and refilled with new oxygen. This procedure was repeated at the end of the 1-h calcination period. The sample was then cooled to ambient temperature and evacuated before its transfer to the analytical chamber. Following spectral accumulation, the calcined samples were returned to the reaction cell for water vapor exposure. For this treatment, the cell was first evacuated and filled with saturated water vapor at room temperature. The sample was maintained under these conditions for 1 h before it was transferred to the analysis chamber for spectral accumulation.

UV Diffuse Reflectance Spectroscopy

Spectra were recorded using a Perkin–Elmer Model 559 UV-VIS spectrophotometer equipped with a diffuse reflectance attachment B 258. The Mo/Al_2O_3 catalyst samples were studied in the form of 12-mm-diameter, 2-mm-thick pellets prepared by pressing the ground samples. The spectra were recorded under air-exposed conditions in the range 210–500 nm against an Al_2O_3 reference. In order to minimize the effect of rehydration of the calcined catalysts prior to spectral accumulation, the spectra were recorded within 5 min after removal of the pellets from the oven. In all cases the reference sample pellets and the catalyst pellets were subjected to identical pretreatments.

ESCA

The ESCA spectra of Mo/Al_2O_3 catalysts were recorded using a V.G. scientific Microlab system with an hemispherical energy analyzer operated in the constant pass energy mode (20 eV). The spectrometer is equipped with a Mg anode ($MgK\alpha = 1253.6$ eV) operated at 300 mA and 15 kV. The residual gas pressure in the spectrometer during data acquisition was 5×10^{-8} Torr.

The catalyst samples were analyzed in their original granulometry loaded into stainless-steel cups. ESCA spectra were first obtained for air stabilized Mo/Al_2O_3 samples. The spectra of calcined and water vapor-exposed samples were obtained after treatments performed in the reaction cell located inside the fast entry lock chamber of the spectrometer, similar to those described for the SIMS analysis.

RESULTS

Static SIMS

Secondary ion mass spectra of 4 wt% impregnated Mo/SiO_2 and Mo/Al_2O_3 catalysts are given in Figs. 1A and 1B, respectively. It can be seen that both positive and negative SIMS spectra are similar and simple for the two catalysts shown, as only molecular ions containing one Mo atom are observed. The spectra reported in Figs. 1A and 1B are representative of all spectra obtained for catalysts with other Mo loadings. Calcination–hydration treatments did not induce

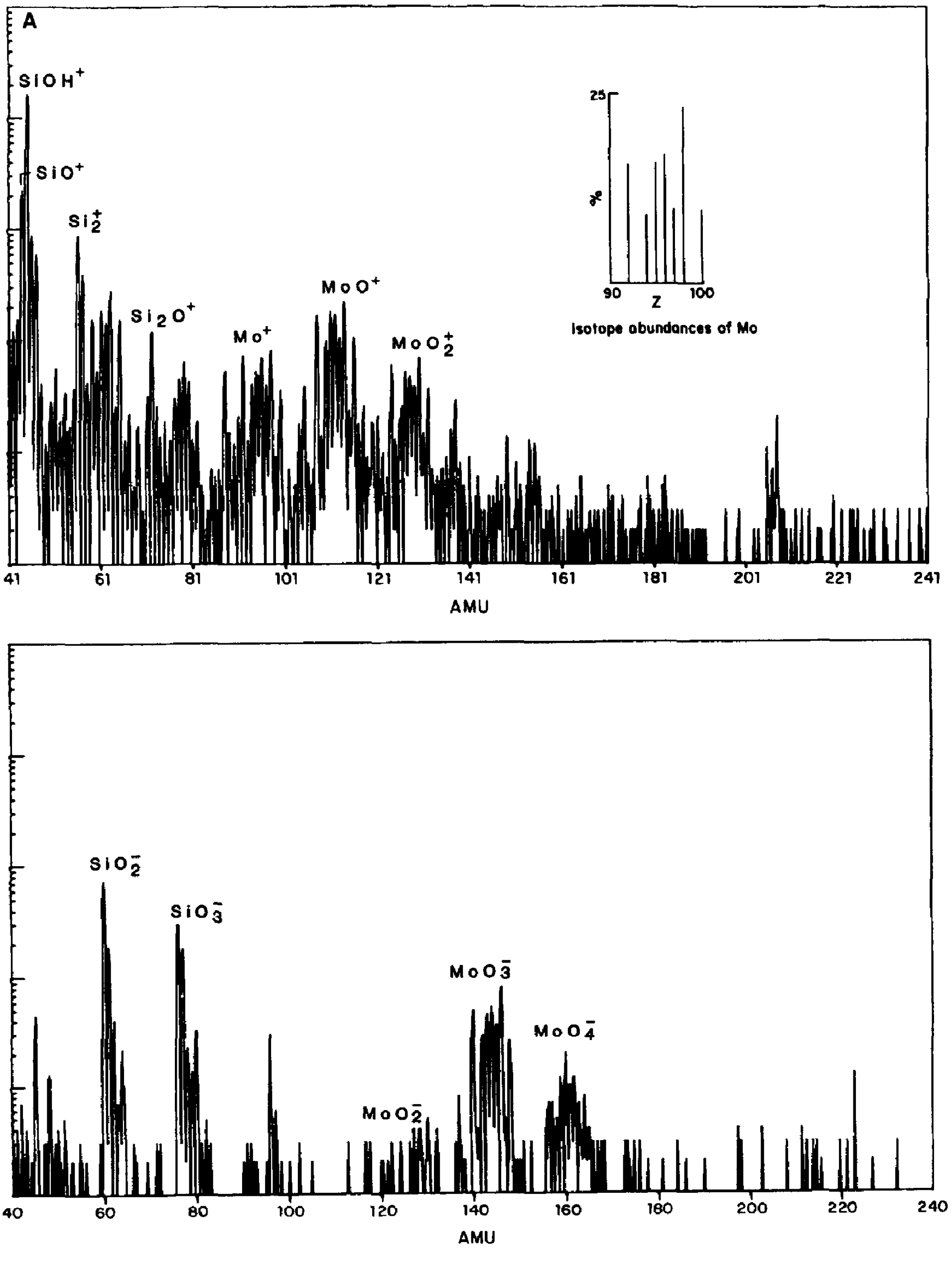

FIG. 1. SIMS spectra of air-stabilized supported molybdena catalysts. (A) Impregnated 4 wt% Mo/SiO_2. (B) Impregnated 4 wt% Mo/Al_2O_3.

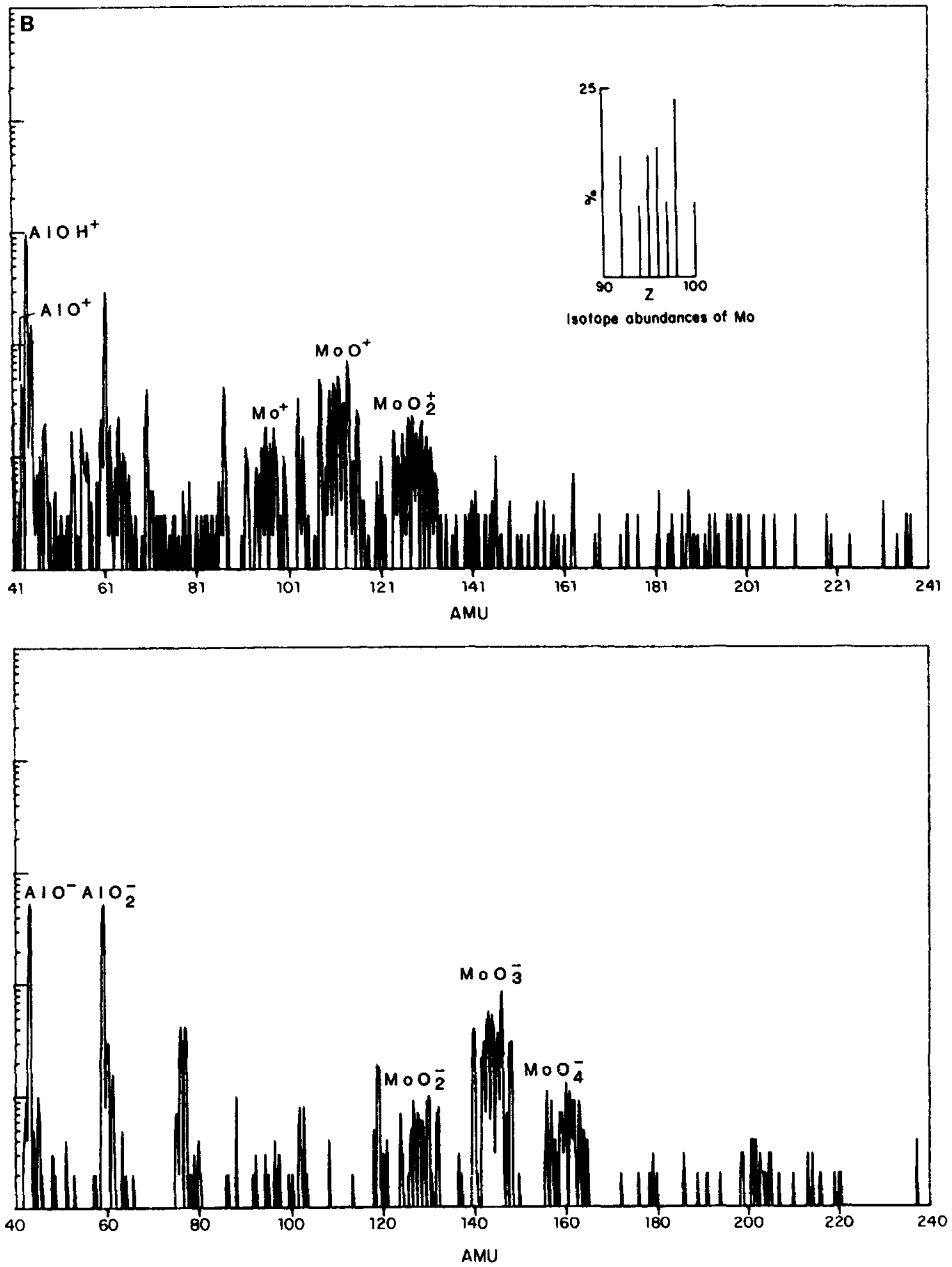

FIG. 1—*Continued.*

changes in the nature of the ions observed in the SIMS spectra. It was shown previously that water vapor- and air-exposed Mo/SiO_2 catalysts contain tridimensional polymolybdate clusters such as silicomolybdic acid species (*1–3*). It was expected that these differences in the structure of surface molybdates on calcined and air- or water vapor-exposed catalysts may lead to some detectable differences in the nature of the molecular ions seen by SIMS. These expectations were not fulfilled by the experiments. Although qualitatively the SIMS spectra remained unaltered with these different pretreatments, the relative intensities of various molecular ions were, however, seen to be sensitive to these treatments for the Mo/SiO_2 catalysts.

The relative intensities of various molecular ions of Mo with respect to SiO^+ (m/e = 44) are given in Figs. 2 and 3 as a function of loading for both impregnated and fixed air-stabilized Mo/SiO_2 catalysts. These ratios show an increase with loading for both types of catalysts. Such behavior is an indication of the surface sensitivity of the SIMS technique. More important, it can be readily noted that the magnitude of these ratios is three to five times higher for impregnated Mo/SiO_2 catalysts than for fixed Mo/SiO_2 catalysts. From ESCA dispersion measurements reported elsewhere (*11*) we have shown that Mo is surface segregated on impregnated Mo/SiO_2 catalysts, while Mo is well dispersed on fixed Mo/SiO_2 catalysts. Thus, the higher intensity ratios obtained for impregnated Mo/SiO_2 catalysts reflect the higher local Mo concentration at the external surface of the impregnated catalysts. These data follow trends very similar to those observed for the ESCA intensity ratio ($I_{Mo\ 3d}/I_{Si\ 2p}$) for the same catalysts (*11*).

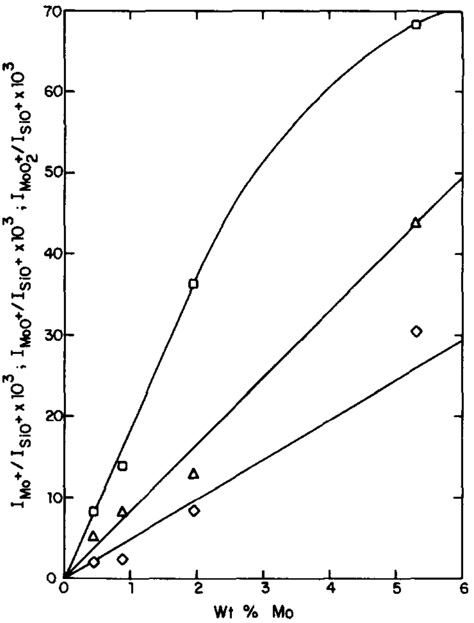

FIG. 3. SIMS relative intensity ratios for fixed Mo/SiO_2 catalysts as a function of Mo coverage. △, I_{Mo^+} (98)/I_{SiO^+} (44); □, I_{MoO^+} (114)/I_{SiO^+} (44); ◇, $I_{MoO_2^+}$ (130)/I_{SiO^+} (44).

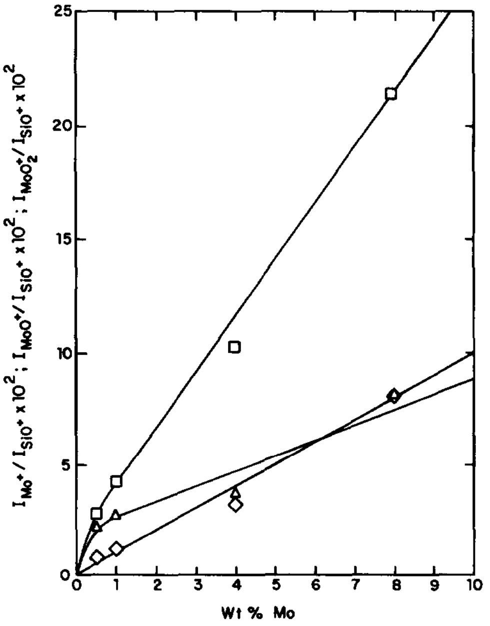

FIG. 2. SIMS relative intensity ratios for impregnated Mo/SiO_2 catalysts as a function of Mo coverage. △, I_{Mo^+} (98)/I_{SiO^+} (44); □, I_{MoO^+} (114)/I_{SiO^+} (44); ◇, $I_{MoO_2^+}$ (130)/I_{SiO^+} (44).

The effect of calcination/water vapor exposure treatments on the SIMS intensity ratios Mo^+/SiO^+, MoO^+/SiO^+, and MoO_2^+/SiO^+ is shown in Figs. 4 and 5 for impregnated and fixed Mo/SiO_2 catalysts, respectively. Calcination of the air-stabilized catalysts leads to an increase in these intensity ratios and water vapor exposure caused these ratios to decrease, tending back toward the initial value for air-stabilized samples. UV, Raman, ESCA, and ISS data reported previously (*2*, *3*) indicate similar reversible changes. These data were interpreted in terms of the collapse of the tridimensional polymolybdate clusters including silicomolybdic acid species present on the air-stabilized samples, thus leading to an increase in the Mo dispersion on the support during calcination. From UV and Ra-

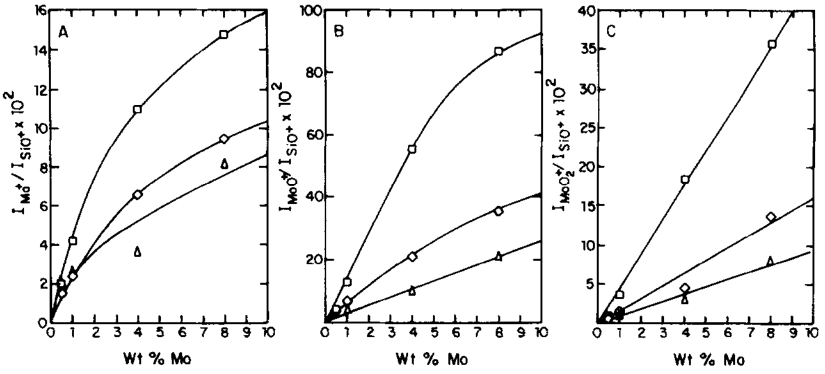

FIG. 4. SIMS relative intensity ratios for impregnated Mo/SiO_2 catalysts as a function of Mo coverage and pretreatment. (A) I_{Mo^+} (98)/I_{SiO^+} (44). (B) I_{MoO^+} (114)/I_{SiO^+} (44). (C) $I_{MoO_2^+}$ (130)/I_{SiO^+} (44). △, air stabilized (6 months); □, calcined *in situ* (500°C/O_2/1 h); ◇, water vapor exposed (25°C/10 Torr/1 h).

man spectroscopic analyses (*2*, *3*) it was shown unambiguously that these clusters are rebuilt upon exposure to water vapor with a subsequent decrease in the Mo dispersion. Thus, the variation in the SIMS intensity ratios as a function of calcination/water vapor treatments also reflects these reversible changes in the Mo dispersion on the support.

The above analysis of the SIMS data obtained with Mo/SiO_2 catalysts shows the sensitivity of the SIMS intensity ratios to the variations in the Mo dispersion on the support. Thus the results reported in Figs. 4 and 5 illustrate the ability of the static SIMS technique to detect changes in the dispersion of the active elements in a supported-oxide catalyst.

The effect of calcination–hydration treatments on the SIMS intensity ratios MoO^+/Mo^+ and MoO_2^+/Mo^+ as a function of loading is reported in Fig. 6, for impregnated Mo/SiO_2 catalysts. These ratios also show a reversible increase with calcination–hydration treatments. These data suggest that the static SIMS technique is sensitive not only to the dispersion of Mo on the surface but also to the detailed structure of the surface molybdates. Presently, however, these variations in the secondary ion yields of Mo as a function of calcination–hydration treatment cannot be interpreted unambigu-

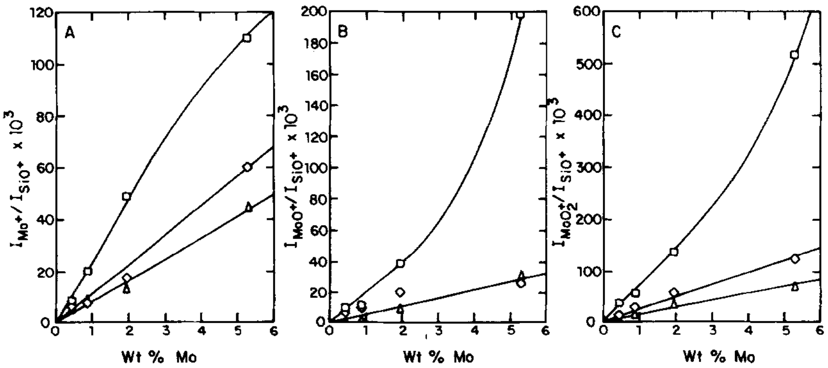

FIG. 5. SIMS relative intensity ratios for fixed Mo/SiO_2 catalysts as a function of Mo coverage and pretreatment. (A) I_{Mo^+} (98)/I_{SiO^+} (44). (B) I_{MoO^+} (114)/I_{SiO^+} (44). (C) $I_{MoO_2^+}$ (130)/I_{SiO^+} (44). △, air stabilized (6 months); □, calcined *in situ* (500°C/O_2/1 h); ◇, water vapor exposed (25°C/10 Torr/1 h).

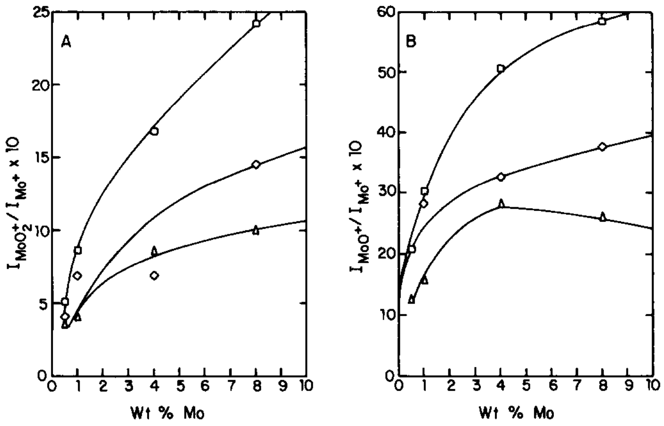

FIG. 6. The variation in the I_{MoO^+} (114)/I_{Mo^+} (98) and $I_{MoO_2^+}$ (130)/I_{Mo^+} (98) SIMS relative intensity ratios for impregnated Mo/SiO_2 catalysts as a function of Mo coverage and pretreatment. (A) $I_{MoO_2^+}$ (130)/I_{Mo^+} (98). (B) I_{MoO^+} (114)/I_{Mo^+} (98). △, air stabilized (6 months); □, calcined *in situ* (500°C/O_2/1 h); ◇, water vapor exposed (25°C/10 Torr/1 h).

ously. Such an interpretation would require a complete understanding of the process of secondary ion formation, which is far from the present situation. However, it is interesting to note that the increase in dispersion associated with calcination is accompanied by an increase in the relative yield of formation of the oxygen-bearing Mo ions. This suggests a higher resistance to reduction of the dispersed phase. However, low Mo reducibility is usually associated with species in strong interaction with the support. Therefore the species present on Mo/SiO_2 at very low loading should yield higher values for the relative yields of oxygen-bearing Mo ion formation. It is the reverse situation which is actually observed experimentally (Fig. 6), which indicates that reducibility is not the only factor affecting these relative yields. They may also be influenced by the oxygen coordination of the Mo species.

The only H-containing ions showing a clear evolution with calcination–water exposure treatments are $SiOH^+$ and $AlOH^+$ in SiO_2- and Al_2O_3-supported catalysts, respectively. No $MoOH^+$, MoO_2H^+, or MoO_3H^- ions are observed in either the calcined samples or the water vapor-exposed samples.

Although a complete interpretation of these results is not yet possible, they indicate the possibility that the SIMS technique may be used to study supported oxides and in particular to sense differences in dispersion and in oxide–support interactions.

SIMS results obtained on Mo/Al_2O_3 catalysts are summarized for a 4 wt% Mo/Al_2O_3 catalyst in Fig. 7. The figure shows the various SIMS intensity ratios as a function of the pretreatment conditions. It can be readily noticed that calcination–hydration treatments do not lead to significant changes in the various SIMS intensity ratios reported. This indicates that calcination–hydration treatments do not cause variations in the Mo dispersion on Mo/Al_2O_3 catalysts. However, as discussed in the introduction such calcination–hydration treatments have been shown to cause pronounced changes in the Raman spectra of Mo/Al_2O_3 catalysts. In light of the SIMS data reported above, it may be concluded that the Raman band sensitivity to calcination–hydration treatments observed on Mo/Al_2O_3 catalysts is not accompanied by variations in the Mo dispersion on these catalysts. These results clearly demonstrate that the phenomena associated with the hydration of Mo/SiO_2 catalysts are not present on Mo/Al_2O_3 catalysts. In order to further verify these aspects, Mo/Al_2O_3 catalysts were analyzed by UV diffuse reflectance spectroscopy and

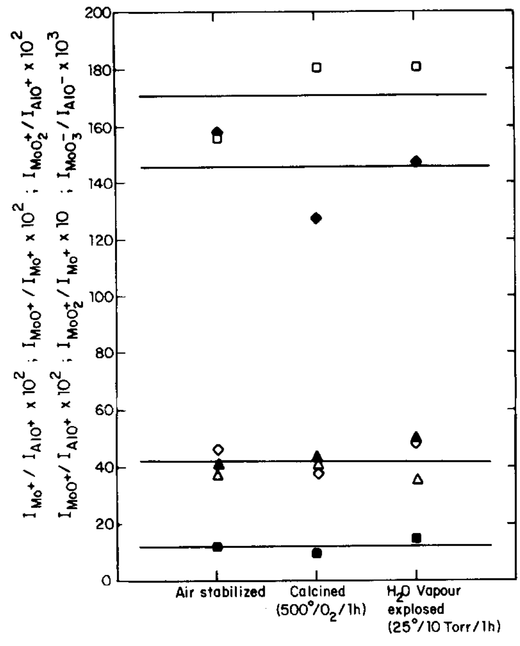

FIG. 7. Various SIMS relative intensity ratios for a 4 wt% Mo/Al$_2$O$_3$ impregnated catalyst as a function of pretreatment. △ I_{Mo^+} (98)/I_{AlO^+} (43); □ I_{MoO^+} (114)/I_{AlO^+} (43); ◇, $I_{MoO_2^+}$ (130)/I_{AlO^+} (43); ▲ I_{MoO^+} (114)/I_{Mo^+} (98); ■, $I_{MoO_2^+}$ (130)/I_{Mo^+} (98); ◆, $I_{MoO_3^-}$ (146)/I_{AlO^-} (43).

in situ ESCA as a function of calcination–hydration treatments. The results obtained by these techniques are discussed below.

UV Diffuse Reflectance Spectroscopy of Mo/Al$_2$O$_3$ Catalysts

The UV diffuse reflectance spectra of air-stabilized and calcined impregnated Mo/Al$_2$O$_3$ catalysts are given in Figs. 8A and 8B. The spectra obtained for fixed Mo/Al$_2$O$_3$ catalysts are very similar to those of impregnated catalysts and for this reason they are not reported here, but they are available elsewhere (*2*).

In agreement with data published previously for Mo/SiO$_2$ catalysts (*1*, *2*), the dominant species on these catalysts appear to be Mo in octahedral coordination as in polymolybdates. The presence of an intense 310-nm band even at very low coverage indicates the dominant presence of polymeric molybdena species.

Calcination of Mo/Al$_2$O$_3$ catalysts at 500°C did not lead to the important spectral changes (Fig. 8B) as observed with Mo/

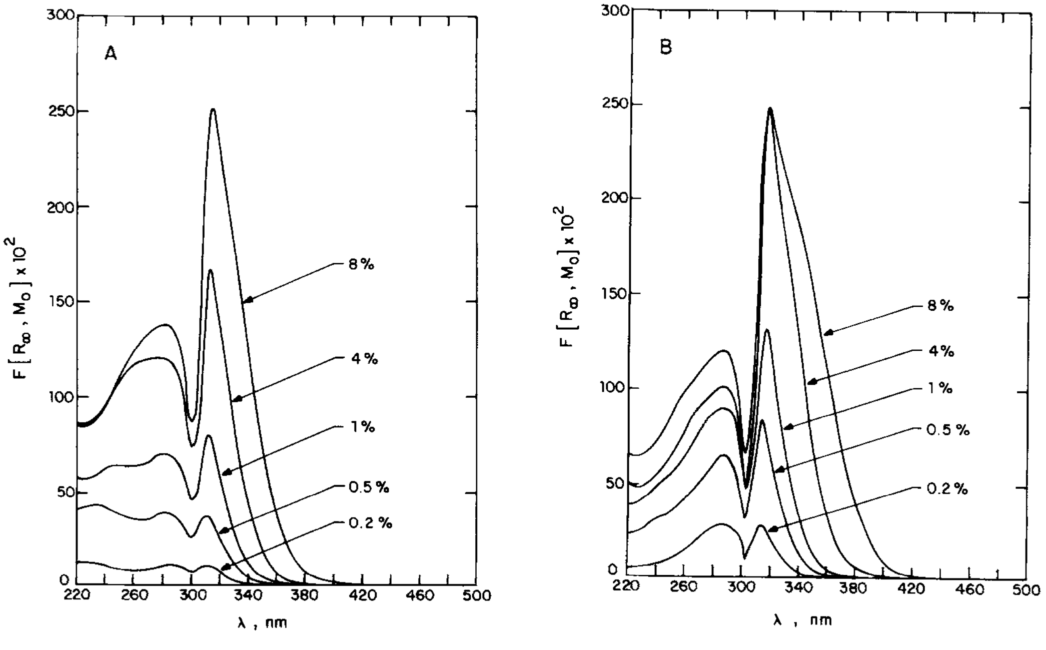

FIG. 8. UV diffuse reflectance spectra of impregnated Mo/Al$_2$O$_3$ catalysts (A) Air stabilized (6 months). (B) Calcined (500°C/air/1 h).

SiO_2 catalysts (*1*). The basic UV spectral features of Mo/Al_2O_3 remained unaltered upon calcination. The only change noted is a moderate increase in the band intensities for some of the spectra. These data indicate that for Mo/Al_2O_3 catalysts calcination does not induce the very important changes in the coordination symmetry of Mo in the surface molybdates, observed for Mo/SiO_2 catalysts. As a consequence, the reversible changes in the Mo/Al_2O_3 Raman spectra upon calcination–hydration discussed in the introduction should not result from changes in the coordination symmetry of Mo species.

The only possible argument against this conclusion would be that rehydration could have occurred during the less than 5 min of air exposure of the catalyst pellet between its calcination and the recording of the UV spectrum. However, from *in situ* Raman spectroscopic studies, Stencel *et al.* (*5*) have shown that although the rehydration of calcined Mo/Al_2O_3 catalysts is fast at high Mo coverages, it is extremely slow at low Mo coverages. Using the hydration-dependent Raman band shift as a measure of the degree of hydration, it was shown that on a 5 wt% MoO_3/Al_2O_3 catalyst after calcination, a complete rehydration of the surface in an atmosphere of water vapor at ambient temperature is achieved only after 3 days (*5*). If this is any indication as to the rate of surface rehydration of Mo/Al_2O_3 catalysts, the changes in the coordination symmetry of Mo as a result of calcination should have manifested in the UV spectra at least at low Mo coverage, although the experimental conditions used in the present study are not ideally suited for such studies. Thus, it may be concluded that the sensitivity of the Raman band features of Mo/Al_2O_3 catalysts to calcination–hydration treatments is not associated with any modification in the coordination symmetry of Mo that affects the charge transfer spectra of the catalysts.

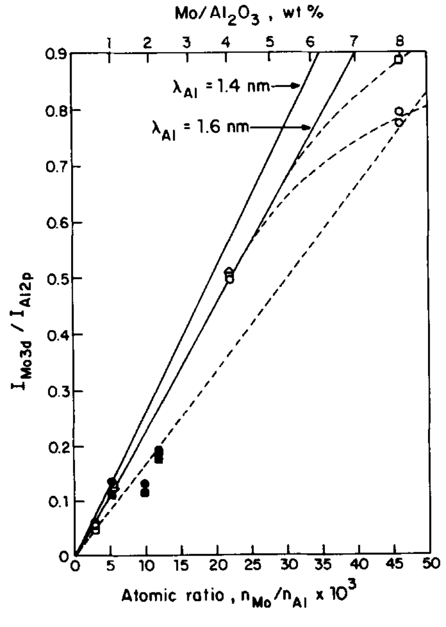

FIG. 9. $I_{Mo\ 3d}/I_{Al\ 2p}$ ESCA intensity ratio as a function of the overall atomic ratio n_{Mo}/n_{Al} for impregnated and fixed Mo/Al_2O_3 catalysts. ○,●, air stabilized (6 months); □,■, calcined (500°C/O_2/1 h); △ water vapor exposed (25°C/10 Torr/1 h). open symbols, impregnated catalysts; solid symbols: fixed catalysts.

ESCA of Mo/Al_2O_3 Catalysts

The ESCA intensity ratios ($I_{Mo\ 3d}/I_{Al\ 2p}$) as a function of calcination–hydration treatments are reported in Fig. 9. The two continuous lines represent the theoretical curves calculated by the Kerkhof–Moulijn model for monolayer dispersion (*12*) for two different values of the escape depth λ_{Al}. This model is based on earlier suggestions of Defosse *et al.* (*13*). The two λ_{Al} values were computed by the procedures proposed by Penn (*14*) and Chang (*15*).

A comparison of the experimental data with theoretical values indicate the presence of a highly dispersed phase of molybdena species on these catalysts at low Mo coverage (<4 wt% Mo). The leveling off of the experimental values at high Mo coverage probably indicates the formation of larger aggregates of Mo and/or crystalline MoO_3. Deviations of the ESCA data from these theoretical curves have been discussed previously for Mo/SiO_2 and Mo/Al_2O_3 catalysts (*3, 11*).

O_2 calcination of Mo/Al_2O_3 catalysts at 500°C and their subsequent exposure to water vapor (10 Torr) at ambient temperature had no influence on the measured I_{Mo}/I_{Al} ratios at low Mo coverage (<4 wt% Mo/Al_2O_3) (Fig. 9). This absence of variation in the measured I_{Mo}/I_{Al} ratio as a function of calcination–hydration treatments indicates the absence of any changes in the structure of surface molybdates leading to modifications in the Mo dispersion on these catalysts. These results are thus in excellent agreement with the static SIMS data. On 8 wt% Mo/Al_2O_3 catalyst, calcination resulted in a slight increase in the measured I_{Mo}/I_{Al} ratio. This increase probably would have been caused by some decomposition of large aggregates or from a surface segregation of Mo during calcination.

DISCUSSION

The nature of the supported molybdena phases stabilized by various supports and the coordination symmetry of Mo in surface molybdates have not been completely resolved in the literature. As discussed in the introduction the nature of the supported molybdena species on Mo/SiO_2 catalysts depends on the degree of hydration. On fully hydrated catalysts, depending on the Mo coverage, the various molybdena species present include isolated tetrahedral monomers, silicomolybdic acid species, isopolymolybdates, and crystalline MoO_3 (*2, 3*). On calcination the tridimensional structures such as silicomolybdic acid species collapse. This process is accompanied by changes in the coordination symmetry of Mo and by an increase of the dispersion of Mo on the surface (*1–3*). Static SIMS data obtained with Mo/SiO_2 catalysts are in excellent agreement with the above model. Thus static SIMS data add further support to the conclusions derived from other spectroscopic techniques.

Static SIMS data obtained on Mo/Al_2O_3 catalysts indicate that the Mo dispersion on these catalysts is independent of the degree of hydration of the surface. Measurements of ESCA intensity ratio indicate that Mo dispersion on Mo/Al_2O_3 catalysts is essentially not changed upon calcination–hydration treatment, a result in perfect agreement with the SIMS data. Furthermore UV spectroscopic data indicate the absence of any influence of hydration on the coordination symmetry of Mo in the surface molybdates. According to these data calcination–hydration treatments do not cause any changes in the structure of surface molybdates on Mo/Al_2O_3 catalysts. In this respect the nature of the surface molybdates on Al_2O_3 is different from those on SiO_2. On Mo/Al_2O_3 catalysts the surface molybdates are stable toward calcination–hydration treatments and do not undergo structural reorganizations as found on Mo/SiO_2 catalysts. This may very well be a consequence of very strong Mo–O–Al bonding interactions compared with Mo–O–Si interactions. Thus, the well-documented sensitivity of the Raman bands on Mo/Al_2O_3 catalysts to hydration should be attributed, either as suggested by Stencel *et al.* (*5*), to water coordination via hydrogen bonding to terminal oxygens of Mo═O bonds without an apparent increase in the Mo coordination symmetry or to a non-uniform coordination of water molecules to Mo increasing the degree of disorder of surface bonding affecting the Mo═O stretch as suggested by Hall and co-worker (*7*). In this last model, water coordination to Mo should be viewed as a change in the Mo coordination symmetry. In this case our UV spectroscopic data strongly suggest that this change would have no influence on the charge transfer spectra of these catalysts.

CONCLUSIONS

It was demonstrated that static SIMS can be used as a spectroscopic technique for the characterization of supported oxide catalysts. The reversible variation of the MoO^+/Mo^+ and Mo^+O_2/Mo^+ ratios on Mo/SiO_2 catalysts as a function of calcination–hydration treatments indicates that static

SIMS is sensitive to the variations in the structure of surface molybdates. The relation of these variations in the secondary ion yields of Mo to the structure of the surface molybdates is presently not understood. A comparison of results obtained on Mo/SiO_2 and Mo/Al_2O_3 catalysts as a function of calcination–hydration treatments indicate important differences in the nature of supported molybdena species stabilized by these supports. On Mo/Al_2O_3 catalysts the structures of supported molybdena species are stable while they undergo drastic modifications as a function of calcination–hydration treatments on Mo/SiO_2 catalysts.

REFERENCES

1. Marcinkowska, K., Rodrigo, L., Kaliaguine, S., and Roberge, P. C., *J. Mol. Catal.* **33,** 189 (1985).
2. Rodrigo, L., Ph.D. thesis, Laval University, Quebec (1986).
3. Stencel, J. M., Diehl, J. R., D'Este, J. R., Makovsky, L. E., Rodrigo, L., Marcinkowska, K., Adnot, A., and Roberge, P. C., *J. Phys. Chem.* **90,** 4739 (1986).
4. Kasztellan, S., Grimblot, J., Bonnelle, J. P., Payen, E., Toulhoat, H., and Jacquin, Y., *Appl. Catal.* **7,** 91 (1983).
5. Stencel, J. M., Makovsky, L. E., Sarkus, T. A., De Vries, J., Thomas, R., and Moulijn, J. A., *J. Catal.* **90,** 314 (1984).
6. Stencel, J. M., Makovsky, L. E., Finseth, D. H., and Diehl, J. R., paper presented before the 9th Canadian Symposium on Catalysis, Quebec, P. Q., September, 1984.
7. Chan, S. S., Wachs, I. E., Murrell, L. L., Wang, L., and Hall, W. K., *J. Phys. Chem.* **88,** 5831 (1984).
8. Wang, Li, and Hall, W. K., *J. Catal.* **82,** 177 (1983).
9. McHugh, J. A., *in* "Methods of Surface Analysis" (A. W. Czanderna, Ed.), p. 223. Elsevier, Amsterdam, 1975.
10. Winograd, N., *Prog. Solid State Chem.* **13,** 285 (1982).
11. Rodrigo, L., Marcinkowska, K., Adnot, A., Roberge, P. C., Kaliaguine, S., Stencel, J. M., Makovsky, L. E., and Diehl, J. R., *J. Phys. Chem.* **90,** 2690 (1986).
12. Kerkhof, F. P. J. M., and Moulijn, J. A., *J. Phys. Chem.* **83,** 1612 (1979).
13. Defosse, C., Cannesson, P., Rouxhet, P. G., and Delmon, B., *J. Catal.* **51,** 269 (1978).
14. Penn, D. R., *J. Electron Spectrosc. Relat. Phenom.* **9,** 29 (1976).
15. Chang, C. C., *Surf. Sci.* **48,** 9 (1975).