Raman Spectroscopic Investigation of the Effect of H₂O on the Molybdenum Surface Species in MoO₃/Al₂O₃ Catalysts[1]

J. M. STENCEL,* L. E. MAKOVSKY,* T. A. SARKUS,* J. DE VRIES,†
R. THOMAS,† AND J. A. MOULIJN†

*Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, Pennsylvania 15236, and †Laboratory
for Chemical Technology, University of Amsterdam, Plantage Muidergracht 30,
1018 TV Amsterdam, The Netherlands

The Raman spectroscopic characterization of a set of MoO₃/Al₂O₃ catalysts containing 3 to 25 wt% MoO₃ is presented. Controlled atmosphere measurements show that the Raman spectra of these catalysts are influenced drastically by the water content of the samples. Catalysts calcined in O₂ at 500°C have spectra very different from previously reported spectra. The Mo=O stretching vibration is at about 1000 cm⁻¹ in calcined samples, whereas in H₂O-exposed samples the frequency is near 950 cm⁻¹. The position of the Mo=O stretching vibration is shown by repeated H₂O exposure, O₂ calcination cycles to be reversible between 950 and 1000 cm⁻¹. Models for the interaction of H₂O with the surface molybdate species are presented and discussed with respect to the Raman data. © 1984 Academic Press, Inc.

INTRODUCTION

Raman spectroscopy has become an important tool for investigating the interaction of molybdenum and tungsten oxides with high surface area supports such as Al₂O₃ and SiO₂. As early as 1977, Brown *et al.* (*1–3*) reported on the Raman spectra from MoO₃/Al₂O₃ hydrodesulfurization catalysts in which crystalline MoO₃ and Al₂(MoO₄)₃ were identified; in addition, a broad asymmetric band located near 950 cm⁻¹, assigned to a vibrational mode associated with monolayer molybdena species interacting with the Al₂O₃ support, was briefly discussed with respect to effects of catalyst drying. Subsequently, a number of studies were conducted on MoO₃/Al₂O₃, CoO-MoO₃/Al₂O₃, and WO₃/Al₂O₃ in which Raman spectroscopy was used to follow the genesis of surface and crystalline species as a function of metal loading, metal impreg-

nation sequence, and method of impregnation (*4–11*).

In general, previous results have shown that the shape and breadth of the Raman band associated with molybdate or tungstate surface species are approximately equal, whereas the frequency of this band is 10–30 cm⁻¹ higher for WO₃/Al₂O₃. Such a frequency difference is in agreement with that for the symmetric tungsten–oxygen stretching vibration in bulk, crystalline molybdates and tungstates (*5, 7, 8*). However, the identification of the surface species producing this "950 cm⁻¹" band is still a matter of debate.

In a Raman study of MoO₃/Al₂O₃, Sombret *et al.* (*6*) showed that the frequency of the band associated with the molybdate surface species increased from 930 to 966 cm⁻¹ as the concentration of MoO₃ was increased from 4 to 24 wt%. As a result of this frequency increase with increasing MoO₃ concentration and of a corresponding growth in intensity of a band near 220 cm⁻¹, the genesis of the molybdate surface species was described in terms of isolated tet-

314

rahedral species at concentrations less than 4 wt% MoO_3; these species are condensed and form distorted octahedral, polymeric species for concentrations above 4 wt% MoO_3. Thomas et al. (11) observed shifts in frequency from 940 to 975 cm^{-1} of a Raman mode for the molybdate surface species as the concentration of MoO_3 was increased from 2 to 20 wt%. However, the surface species causing the shift was described as containing octahedral symmetry. Wang and Hall (9) suggested that the ratio of intensities at 950 and 970 cm^{-1} could be taken as a measure of the ratio of tetrahedrally to octahedrally coordinated molybdenum surface species. This interpretation was based on the comparisons of their spectra, acquired with samples exposed to atmospheric conditions, with previously reported data also acquired with samples exposed to atmospheric conditions (12, 13). The present communication addresses the interpretations of previous publications (1–13) concerning the correlation of Raman frequencies from MoO_3/Al_2O_3 catalysts with those from monomeric and polymeric molybdenum-containing models. This fundamental question is addressed by performing in situ Raman analyses of MoO_3/Al_2O_3 as a function of Mo concentration. The spectra of calcined catalysts will be shown to be fundamentally different than spectra of catalysts exposed to ambient conditions. In particular, the water content of the catalysts will be shown to control the appearance and position of the Raman bands of the molybdate surface species.

EXPERIMENTAL

Sample preparation. The MoO_3/Al_2O_3 catalysts were prepared using Harshaw Al-4104E 1/32-in. γ-Al_2O_3 (Harshaw Chemical Co.) having a surface area of approximately 200 m^2/g. The Al_2O_3 extrudates were ground with a mortar and pestle and then sieved to -100 mesh. Water suspension was used to remove fines from the ground Al_2O_3. The Al_2O_3 was then dried overnight at 120°C. For Mo impregnation, a predeter-mined amount of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Baker, Analyzed Reagent) was dissolved in distilled water, and this solution was used to saturate the dried Al_2O_3 to incipient wetness. Concentrations of Mo above 15% MoO_3 required two-step impregnations. The impregnated samples were allowed to sit at 25°C for 0.5 hr before subsequent drying at 120°C with occasional stirring. The samples were then calcined in air overnight at 500°C.

Raman spectral acquisition. The air-calcined, powdered catalysts were pressed into 13-mm-diameter wafers. These wafered samples were attached to a rotary feedthrough in a sample cell containing a quartz optical flat. This cell could be evacuated, flushed with selected gases, heated in a tubular furnace, and positioned at the entrance optics of the Raman spectrometer. Evacuation was facilitated with ultrahigh vacuum, stainless steel hardware having a turbomolecular pump as the primary pumping station. No vacuum grease or oil is present in this system.

The cell permitted the environment of the catalysts to be controlled before and during spectral acquisition. Typically, a Raman spectrum of the air-exposed catalyst was obtained while the catalyst was in the cell. The cell containing the sample was then evacuated to $\sim 10^{-5}$ Torr, backfilled with 760 Torr of O_2 (Matheson, Research Grade), and then heated at 550°C. During this O_2 calcination, the sample cell was evacuated and backfilled with O_2 at least three times to ensure complete calcination. For catalysts exposed to distilled, deionized H_2O or D_2O (Wilmad, 99.8% D), the cell was evacuated to 10^{-5} Torr and then backfilled to 10–25 Torr with the selected gas while the sample was at 25°C. Similar experimental procedure was used to expose the samples to anhydrous NH_3 (Matheson). The O_2, H_2O, D_2O, or NH_3 was left in the sample cell during spectral acquisition.

The Raman spectra were recorded on a Spex Ramalog spectrometer equipped with holographic gratings. A Spectra Physics

STENCEL ET AL.

Model 165 argon-ion laser was used to sup-
ply 45 mW at 5145 Å to the rotating sample.
The spectral slit width was maintained at 4
cm^{-1} throughout the experiments. Data
handling was facilitated by use of a Spex
Datamate.

RESULTS

Figure 1 shows Raman spectra of the (3–
25) wt% MoO$_3$/Al$_2$O$_3$ catalyst series (6.1 ×
10^{13}–5.5 × 10^{14} Mo/cm^2) acquired while the
catalysts were exposed to atmospheric con-
ditions. The position of the most intense
Raman band varies from 938 to 970 cm^{-1} as
the MoO$_3$ concentration is increased. This
band has been associated with the symmet-
ric Mo=O stretching mode of a molybdate
surface species. Another Raman band can
be observed between 320 and 370 cm^{-1}. It is
observable with as little as 3% MoO$_3$ when
it has maximum intensity at 325 cm^{-1}. At a
loading of 5% MoO$_3$, this peak becomes
asymmetric toward higher wave numbers;
at a loading of 10% MoO$_3$, it becomes a

distinct doublet located at approximately
330 and 360 cm^{-1}. Simultaneous with the
appearance of this doublet is the appear-
ance of a Raman mode at 215 cm^{-1}. The 215
cm^{-1} mode shifts to 208 cm^{-1} at 15% MoO$_3$
loading and concurrently becomes more in-
tense. At 20% MoO$_3$, the 208 cm^{-1} band
appears as an ill-defined doublet located at
205 and 215 cm^{-1}. Also at 20% MoO$_3$, the
intensity of the bands in the 320 to 370 cm^{-1}
region is primarily associated with a band at
365 cm^{-1}. At 25% MoO$_3$ loading, a value in
excess of that needed for monolayer cover-
age (7), peaks are at 377, 820, 997, 1005,
and 1025 cm^{-1}. The frequencies of these
peaks agree with those expected for bulk
MoO$_3$ and Al$_2$(MoO$_4$)$_3$; X-ray diffraction
has confirmed the existence of crystalline
MoO$_3$ and Al$_2$(MoO$_4$)$_3$ in the 25% MoO$_3$/
Al$_2$O$_3$ catalyst. In addition, Raman bands
are at 204, 288, and 968 cm^{-1} for the 25%
MoO$_3$/Al$_2$O$_3$ sample.

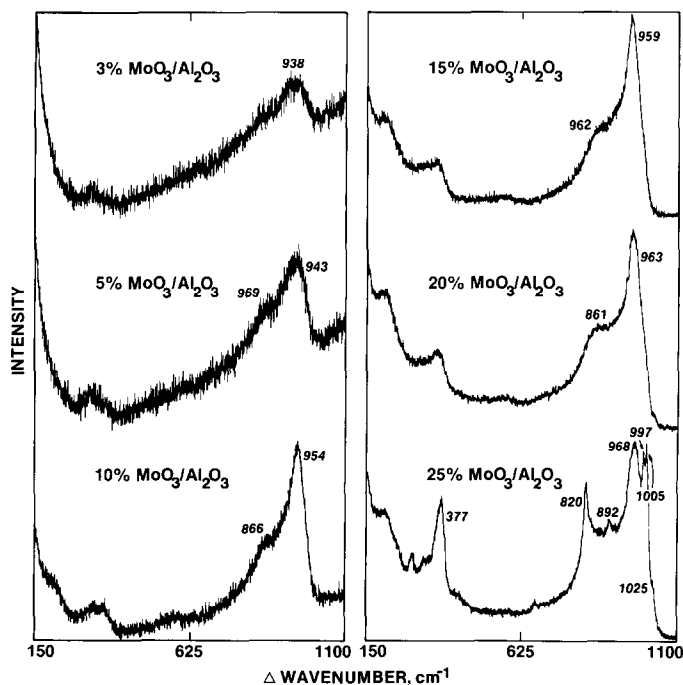The data in Fig. 1 were obtained within
three days of the preparation of the cata-

FIG. 1. Raman spectra of the catalyst series (3–25) wt% MoO$_3$/Al$_2$O$_3$ acquired within 3 days of
catalyst synthesis and with the catalysts exposed to atmospheric conditions.

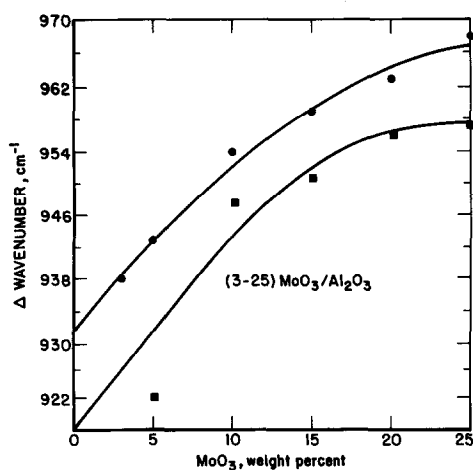lysts and while the sample wafers were exposed to atmospheric conditions during data aquisition. Acquiring Raman data from these catalysts after they had been exposed to atmospheric conditions for another three months produced spectra similar to those shown in Fig. 1 except that the frequency of the stretching mode of the molybdate species decreased 10 to 20 cm^{-1}. This decrease is shown in Fig. 2 and suggests that control of the environment around the sample is important in obtaining accurate and repeatable Raman analyses.

Figure 3a shows a Raman spectrum from 700 to 1100 cm^{-1} of the 15% MoO_3/Al_2O_3 catalyst after extended exposure to atmospheric conditions. Figure 3b shows the Raman spectrum from the same sample after O_2 calcination at 550°C. This spectrum was acquired while an O_2 pressure of 760 Torr was in the sample cell. The O_2 calcination has shifted the peak to 1006 cm^{-1} from its original 951 cm^{-1} position. The cell was then evacuated to 10^{-5} Torr, and with the sample at 25°C, the cell was backfilled with 11 Torr of H_2O vapor. After a 1-hr equilibration, the Raman spectrum of the H_2O-exposed sample (Fig. 3c) is nearly identical

to that from the air-exposed sample (Fig. 3a). This sequence of O_2 calcination and H_2O exposure was repeated again on the same 15% MoO_3/Al_2O_3 sample and showed reversibility in the position of the Raman bands. The lower frequency region from 100 to 700 cm^{-1} (Fig. 4b) for the O_2-calcined catalyst contains a very weak Raman band at 210 cm^{-1} and a broad, ill-defined band in the 250 to 360 cm^{-1} region (Fig. 4a).

After two sequences of O_2 calcination and H_2O exposure, the cell containing the 15% MoO_3/Al_2O_3 catalyst was evacuated for 2 days to a final pressure of 1×10^{-6} Torr. During this 25°C evacuation, the catalyst turned to a dark-brown color; attempts to obtain a Raman spectrum from this sample failed because of an intense fluorescent background. Exposure of this brown sample to O_2 while it was at 550°C changed the sample color to a pale yellow, as previously observed for the dried catalyst. Addition-
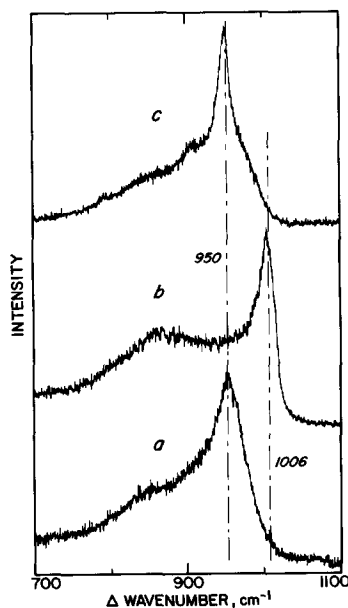

FIG. 3. Raman spectra of 15% MoO_3/Al_2O_3 for (a) the catalyst exposed to atmospheric conditions for three months, (b) the catalyst calcined in 760 Torr O_2 at 550°C for 1 hr with O_2 in the sample cell during spectral acquisition, and (c) the catalyst after exposure to 11 Torr of H_2O vapor at 25°C for 1 hr subsequent to O_2 calcination.
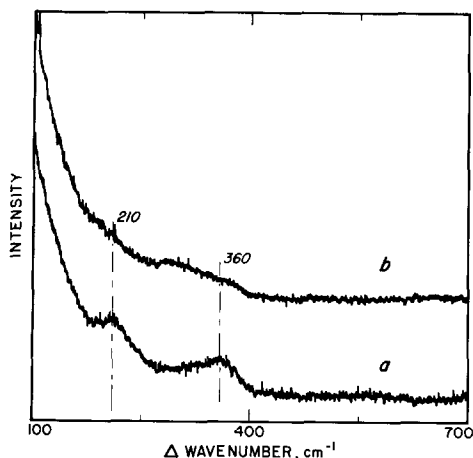
FIG. 4. The Raman spectra from 100 to 700 cm^{-1} for 15% MoO$_3$/Al$_2$O$_3$ for (a) the catalyst exposed to atmospheric conditions and (b) after calcination in O$_2$ at 550°C with the catalyst in a controlled-O$_2$ environment during spectral acquisition.

ally, Raman spectra of good quality were again easily obtained and had structure identical to that in Figs. 3b and 4b.

After calcination, the O$_2$ was evacuated and then the catalyst was exposed to 11 Torr of D$_2$O for 1 hr at 25°C. The Raman spectrum obtained from this D$_2$O-exposed sample was identical to that shown in Fig. 3c, with the frequency of the most intense Raman band at 950 cm^{-1}. Such a result indicates that the frequency of this Raman band is not dependent on a mass effect; instead, an electronic effect is possibly causing the observed frequency shift.

The relative importance of the contribution of H$_2$O to the frequency shifts shown in Figs. 1 to 3 versus the contribution of structural polymerization of the molybdate surface species was investigated by obtaining Raman spectra of a 5% MoO$_3$/Al$_2$O$_3$ sample as a function of O$_2$–H$_2$O treatment cycles. These spectra are shown in Fig. 5. The position of the 922 cm^{-1} band (Fig. 5a) for this catalyst shifted to 985 cm^{-1} (Fig. 5b) after O$_2$ calcination at 550°C. Subsequent exposure of the sample to 20 Torr H$_2$O or D$_2$O for 1 hr shifted the band down to 965 cm^{-1} (Fig. 5c). With an extended 3-day exposure

of the catalyst to 20 Torr H$_2$O or D$_2$O at 25°C, the 965 cm^{-1} band was slowly replaced by a band at 922 cm^{-1}, a position in agreement with that for the original air-exposed sample. Thus, although 5% MoO$_3$/Al$_2$O$_3$ does not react as fast to H$_2$O or D$_2$O, it does show reversibility in the band position of the Mo=O stretching mode.

To provide more information concerning the origin of shifts in Raman band positions, the Raman spectra of a 15% MoO$_3$/Al$_2$O$_3$ catalyst after calcination in O$_2$ and exposure to NH$_3$ were obtained. Figure 6a shows the spectrum of the 500°C calcined catalyst, and Fig. 6b shows the spectrum after exposure of the catalyst to 20 Torr anhydrous NH$_3$. The frequency of the Mo=O stretching mode shifts from 1006 to 975 cm^{-1} with a 1-hr equilibration to NH$_3$ vapor. At an exposure of 50 Torr NH$_3$ for 1 hr, the frequency of this band is further shifted to 958 cm^{-1}. In the 100 to 700 cm^{-1}
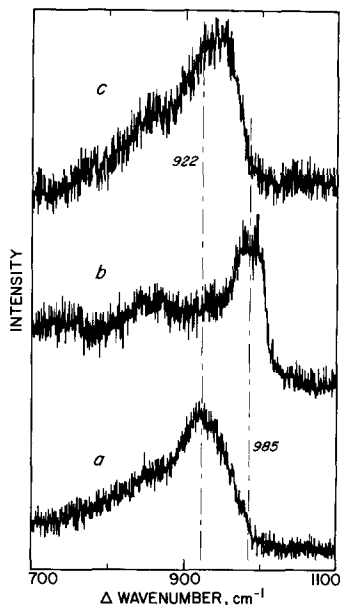

FIG. 5. Raman spectra of 5% MoO$_3$/Al$_2$O$_3$ for (a) the catalyst exposed to atmospheric conditions for 3 months, (b) the catalyst calcined in 760 Torr O$_2$ at 550°C for 1 hr with O$_2$ in the sample cell during spectral acquisition, and (c) the catalyst after exposure to 40 Torr H$_2$O vapor at 25°C for 3 days subsequent to O$_2$ calcination.
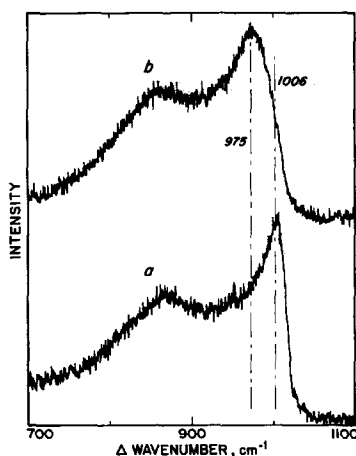
FIG. 6. Raman spectra of 15% MoO_3/Al_2O_3 (a) after O_2 calcination at 550°C and (b) after exposure to 20 Torr anhydrous NH_3 at 25°C for 1 hr.

region the spectral characteristics of the NH_3-exposed catalyst do not differ from those of the O_2-calcined precursor. Hence, only the Mo=O stretching vibrational mode is affected by NH_3 exposure in a manner similar to H_2O or D_2O exposure.

DISCUSSION

Most Raman spectroscopic characterization studies of catalysts in their oxidic state have not addressed the effect that adsorbed H_2O may have on the spectral characteristics of the catalysts. Recently, Wang and Hall (14) showed that the adsorption of H_2O onto calcined rhenia-alumina catalysts caused a substantial decrease in the frequency of a band attributed to a Re=O stretching vibration. This information on rhenia-alumina is the only data that the authors are aware of that explicitly show reversibility in the Raman band structure of highly dispersed, supported metal oxides during O_2 calcination–H_2O exposure cycles. However, Kasztelan et al. (15) do allude to changes in the frequency of the stretching vibration of the molybdate surface species that accompany hydration of MoO_3/Al_2O_3 catalysts. In addition, Kasztelan et al. (15) briefly discuss interpretation difficulties that subsequently arise when

comparing Raman spectra of MoO_3/Al_2O_3 catalysts with those of model compounds. In the present discussion, the data in Fig. 2 provide an explanation for the differences in frequency that have been observed from supposedly identical MoO_3/Al_2O_3 catalysts. Thomas et al. (11) determined that the most intense Raman band for a 4% MoO_3 concentration was located at 940 cm^{-1}, while Sombret et al. (6) measured 933 cm^{-1}. At a concentration near 15% MoO_3, Thomas and co-workers found 975 cm^{-1}, while Sombret's spectra showed 956 cm^{-1}. Hence, the frequency of the most intense Raman peak in Thomas's spectra was consistently larger than that from Sombret's spectra. Such a result can be expected for two sets of catalysts exposed to atmospheric conditions for different lengths of time. Hence, the Raman spectroscopic characterization of MoO_3/Al_2O_3 catalysts is sensitive to the extent of interaction or surface coverage with atmospheric constituents that has involved the surface molybdate species.

Cotton and Wing (16) have shown that a smooth, monotonic relationship exists between the bond orders, the stretching-force constants, and the bond lengths for molybdenum–oxygen compounds. Hence, it may be expected that as the bond order of Mo=O decreases, the Raman frequency associated with this bond vibration should also decrease. For example, it is known that the Raman frequency of the Mo=O stretching mode in crystalline ammonium molybdates is sensitive to the coordination of the molybdenum (17). This contribution to the change in Raman frequencies for MoO_3/Al_2O_3 has been discussed previously (4–13) without careful analysis of the effect of equilibration with atmospheric H_2O on the MoO_3/Al_2O_3 catalysts. In crystalline tungstates, the frequency of the W=O stretching mode in WO_4 units increases in going from pure WO_4 units to alternating WO_4–WO_6 units, possibly as a result of decreasing W=O bond length (18). Within the MoO_3/Al_2O_3 catalysts discussed here, this argument of changing bond orders and/

or lengths may in part provide an explanation for the frequency shifts of the Raman band in the 920 to 1000 cm^{-1} region as a function of molybdena concentration and O_2–H_2O exposure cycles.

In addition to bond order and/or length changes, a concentration-dependent degree of hydration may also provide a simple explanation for the frequency shifts in the Raman spectra. However, reducibility studies have shown that the intrinsic reactivity of the surface molybdate is highly dependent on the Mo concentration (19–21). Hence, the chemical nature of the Mo may be a function of the Mo concentration. This concentration dependency could be the result of (a) having the degree of aggregation of the molybdate surface species dependent on the Mo concentration and (b) having the interaction of the molybdate surface species with the Al_2O_3 dependent on the Mo concentration. It is not possible to present a definitive conclusion; both of the above factors could be true, affecting Raman frequencies in the same or opposite direction. However, the effect of H_2O on the frequency of the molybdate stretching mode does offer insight into possible models of the molybdate surface species.

Studies of MoO_3/Al_2O_3 catalysts have suggested that the Mo is tetrahedrally coordinated when the MoO_3 concentration is less than 7 wt% and that the amount of octahedrally coordinated Mo increases at concentrations greater than 7% MoO_3 (7). However, assuming no change in the coordination of the Mo as a consequence of H_2O exposure or O_2 calcination, a simple model of the interaction of H_2O with a tetrahedral species could be as follows:

$$(1)$$
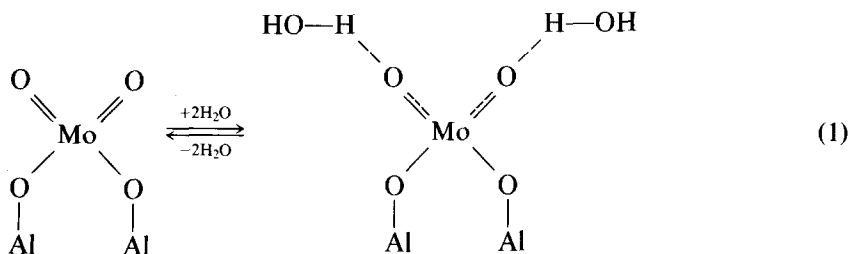
Such an interaction of H_2O with the terminal oxygen in the Mo=O bond decreases its bond order. The association of the OH is not known; indeed, the alumina surface may help to stabilize such a configuration. As a result of this hydration, the frequencies in the Raman spectra of the H_2O-exposed catalysts should tend to agree with those observed for polymolybdates (5, 17). The interaction of H_2O could also occur in the Mo–O–Al or in bridging Mo–O–Mo bonds. However, such an interaction would not be expected to affect the Mo=O vibrational mode as much as direct interaction with the terminal oxygen. In addition, the frequency of Mo–O–Mo stretching modes would be expected to be in the 700 to 900 cm^{-1} region, whereas the spectra of dried, H_2O-exposed, or D_2O-exposed catalysts have similar band structures in this region.
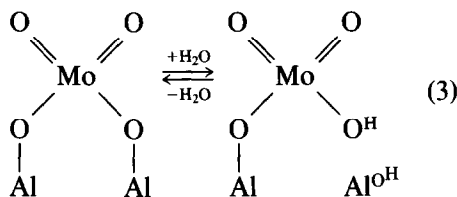
Another model able to define the interaction of H_2O with the molybdate species and to cause shifts in Raman frequencies could be the following:

$$(2)$$
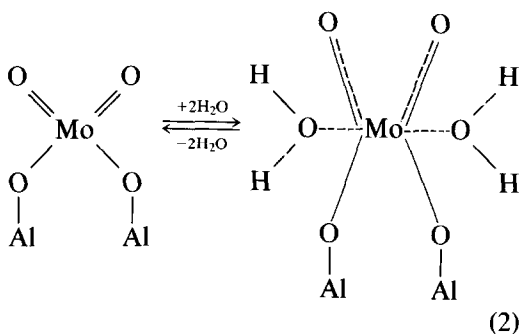
This model would imply increased coordination of the Mo and a change in symmetry from tetrahedral to octahedral. Simultaneously, the order of the terminal Mo=O bonds would be decreased, causing a decrease in the stretching frequency of the molybdate surface species and providing agreement between band positions of H_2O-exposed MoO_3/Al_2O_3 and polymolybdates. In addition, this model agrees with a Brønsted-site model proposed to explain enhanced sulfiding of MoO_3/Al_2O_3 in the presence of H_2O (22).

Finally, a possible model of the H_2O interacting with Mo–O–Al bonds could also occur, as shown in (3):

$$
\begin{array}{c}
\overset{O}{\underset{Al}{\overset{\diagdown}{\underset{\diagup}{\text{Mo}}}}} \quad \overset{O}{\overset{\diagup}{}} \quad \xrightarrow[-H_2O]{+H_2O} \quad \overset{O}{\underset{Al}{\overset{\diagdown}{\underset{\diagup}{\text{Mo}}}}} \quad \overset{O}{\overset{\diagup}{}}
\end{array} \tag{3}
$$

Hydrolysis of a Mo–O–Al bond may occur during exposure of the calcined catalysts to H_2O; indeed, an interpretation that was proposed to explain the effect of H_2O on the Raman band structure of rhenia-alumina catalysts involved hydrolysis of Re–O–Al bonds (14). Also, this model does explain Brønsted-site assisted sulfidation. However, it is not obvious, considering the stability of the molybdate surface layer, how such a model would affect the terminal Mo=O bond length and/or order.

Features of the Raman spectra of the MoO_3/Al_2O_3 catalysts in the 100 to 700 cm^{-1} region as a function of O_2 calcination, H_2O or D_2O exposure, and NH_3 exposure also provide direction for deciding between models (1), (2), or (3). Since D_2O- and H_2O-exposed catalysts have identical spectral characteristics in this region, the bands at 210 and 360 cm^{-1} are not expected to involve significant motion of the hydrogen or deuterium. The extremely weak 210 cm^{-1} band in O_2-calcined and NH_3-exposed catalysts may suggest that this mode is symme-

try-sensitive to the presence of H_2O-like species. It is possible that the 210 cm^{-1} band in the H_2O-exposed catalyst is the result of a O···Mo···O symmetric stretching mode in a sixfold coordinated Mo. Such an assignment is somewhat contrary to previous assignments in that the presence of the 210 cm^{-1} band would be directly dependent on the presence of water instead of on the degree of cross-linking in the molybdate species. The absence of this band with MoO_3 concentrations below 10 wt% could be a result of the weak intensity associated with the O···Mo···O stretching mode and/or a result of a low concentration of such scattering centers. Alternately, the effect of H_2O may be to help bridge near-by Mo surface units to create what has frequently been referred to as polymeric structures. However, the use of Raman spectra acquired without controlled sample environments to discern between such polymeric or monomeric species is questionable since the data in Fig. 2 clearly shows that interpretations based only on band positions may be dependent upon previous H_2O exposure.

The 1006 cm^{-1} position of the Mo=O stretching frequency for O_2-calcined 15% MoO_3/Al_2O_3 versus the 985 cm^{-1} position for O_2-calcined 5% MoO_3/Al_2O_3 suggests that previous interpretations (4–13) concerning aggregate size- or symmetry-dependent frequency shifts may still be realistic. However, the mode of interaction between H_2O and the surface molybdate is still not understood; its elucidation will provide impetus for discerning between the three models and will possibly provide fundamental insight into the interaction of metal oxides with Al_2O_3 supports.

CONCLUSIONS

The Raman spectroscopic studies of calcined MoO_3/Al_2O_3 catalysts using controlled environmental conditions during data acquisition have shown that the Mo=O vibrational mode is 50 to 60 cm^{-1} above the positions previously reported for

this mode. For calcined 5% MoO_3/Al_2O_3, this mode is at 985 cm^{-1}, while for calcined 15% MoO_3/Al_2O_3, the position is 1006 cm^{-1}. This 20 cm^{-1} frequency difference could be the result of symmetry and coordination differences between the Mo in the 5% MoO_3/Al_2O_3 and 15% MoO_3/Al_2O_3 catalysts. In addition, such a frequency difference could be the result of a frequency dependence on the size of the Mo aggregates and/or on the extent of interaction of the Mo with the Al_2O_3 surface. Upon atmospheric or controlled H_2O exposure, the Mo=O bond is weakened, thereby causing a downshift in frequency to positions that have been reported previously in the literature. Controlled D_2O or NH_3 exposure of the calcined catalysts also causes frequency shifts to lower positions. Catalysts with lower concentrations of Mo react more slowly to hydration than do catalysts with near-monolayer Mo coverage of the Al_2O_3.

ACKNOWLEDGMENTS

REFERENCES

1. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50**, 162 (1977).
2. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50**, 385 (1977).
3. Brown, F. R., Makovsky, L. E., and Rhee, K.H., *Appl. Spectrosc.* **31**, 563 (1977).
4. Medema, J., van Stam, C., de Beer, V. H. J., Konings, A. J. A., and Koningsberger, D. C., *J. Catal.* **53**, 386 (1978).
5. Jeziorowski, H., and Knözinger, H., *J. Phys. Chem.* **83**, 1166 (1979).
6. Sombret, B., Dhamelincourt, P., Wallart, F., Muller, A. C., Bouquet, M., and Grosmangin, J., *J. Raman Spectrosc.* **9**, 291 (1980).
7. Zingg, D. S., Makovsky, L. E., Tischer, R. E., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84**, 2898 (1980).
8. Salvatti, L., Makovsky, L. E., Stencel, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85**, 3700 (1981).
9. Wang, L., and Hall, W. K., *J. Catal.* **66**, 251 (1980).
10. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60**, 276 (1979).
11. Thomas, R., Mittelmeyer-Hazeleger, M. C., Kerkhof, F. P. J. M., Moulijn, J. A., Medema, J., and de Beer, V. H. J., in "Proc. 3rd International Conference on Chemistry Uses of Molybdenum, 1979" (H. F. Barry and P. C. Mitchell, Eds.), pp. 85–91. Climax Molybdenum Co., Ann Arbor, Michigan.
12. Giordano, N., Bart, J. C. J., Vaghi, A., Castellan, A., and Martinotti, G., *J. Catal.* **36**, 81 (1975).
13. Iannibello, A., Marengo, S. L., Trifiro, F., and Villa, P. L., in "Preparation of Catalysts. II. Scientific Basis for the Preparation of Heterogeneous Catalysts," Proceedings of the Second International Symposium, Louvain-la-Neuve, September 4–7, 1978 (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 65. Elsevier, Amsterdam, 1978.
14. Wang, L., and Hall, W. K., *J. Catal.* **82**, 177 (1983).
15. Kasztelan, S., Grimblot, J., Bonnelle, J. P., Payen, E., Toulhoat, H., and Jacquin, Y., *Appl. Catal.* **7**, 91 (1983).
16. Cotton, F. A., and Wing, R. M., *Inorg. Chem.* **4**, 867 (1965).
17. Aveston, J., Anacker, E. W., and Johnson, J. S., *Inorg. Chem.* **3**, 735 (1964).
18. Knee, F., and Condrate, R. A., Sr., *J. Phys. Chem. Solids* **40**, 1145 (1979).
19. Thomas, R., de Beer, V. H. J., and Moulijn, J. A., *Bull. Soc. Chim. Belg.* **90**, 1349 (1981).
20. Arnoldy, P., de Jonge, J. L. M., Wimmers, O. J., and Moulijn, J. A., to be published.
21. Massoth, F. E., *J. Catal.* **30**, 204 (1973).
22. Arnoldy, P., van den Heijkant, J. A. M., de Bok, G. D., and Moulijn, J. A., to be published.