JOURNAL OF CATALYSIS **105**, 445–454 (1987)

Interactions of Molybdenum Oxide with Various Oxide Supports: Calcination of Mechanical Mixtures

SHARON R. STAMPFL, YI CHEN,[1] J. A. DUMESIC, CHUNMING NIU,[1]
AND C. G. HILL, JR.

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706

Received June 26, 1986; revised January 26, 1987

Laser Raman and Fourier transform infrared spectroscopies as well as X-ray diffraction were used to study the interactions of MoO_3 with various metal oxide supports. Intimate mechanical mixtures containing an amount of MoO_3 corresponding to less than a monolayer were calcined at 720 K. In the cases where the supports were TiO_2, SnO_2, Al_2O_3, and MgO surface molybdate species were formed on calcination via thermally induced spreading of the bulk MoO_3 phase. Interactions between the support and the MoO_3 were sufficiently strong in these cases that no bulk MoO_3 could be detected in the calcined mixture. A weaker interaction occurs in the case of SiO_2. Raman results from the calcined MoO_3/TiO_2 mixture agree with spectra obtained from catalysts prepared by equilibrium adsorption and incipient wetness impregnation; the nature of the surface molybdate species is relatively independent of the preparation method. © 1987 Academic Press, Inc.

INTRODUCTION

This research was undertaken to investigate the interaction of molybdenum oxide with various metal oxide supports. In particular, the work was focused on the phenomenon of spreading which is thought to occur in some oxide systems. The following binary oxide mixtures were studied: MoO_3/SnO_2, MoO_3/TiO_2 (anatase), MoO_3/Al_2O_3, MoO_3/SiO_2, and MoO_3/MgO.

Most researchers working with such catalyst systems are concerned with using methods which will achieve good dispersion of the molybdenum in the catalyst precursor. They use techniques such as incipient wetness impregnation (*1–6*), liquid phase equilibrium adsorption (*5, 7–10*), or gas phase adsorption (*10–12*) to facilitate formation of the molybdenum oxide "monolayer." The nature of the adsorbed species (e.g., tetrahedral versus octahedral coordination, isolated MoO_4^{2-} species versus isopolyanions such as the paramolybdate anion $Mo_7O_{24}^{6-}$) depends on the preparation procedures used (loading method, pH, drying and calcination conditions, etc.). However, the spontaneous dispersion of many oxides or salts as a monolayer onto supports of large surface area has been described by Xie *et al.* (*13*), and the available data make it reasonable to question whether the ultimate surface molybdenum oxide formed is affected by the path used to obtain it.

This study involved starting with a poor dispersion of molybdenum and a support, i.e., a mechanical mixture, and investigating the nature of the interaction between the molybdenum oxide and the support upon calcination. This was done to provide information about the surface mobility of molybdenum and the strength of oxide–oxide interactions. Raman and Fourier transform infrared (FTIR) spectroscopies were used in conjunction with X-ray diffraction for this investigation.

The Raman spectra of various molybdenum–oxygen isopolyanions (such as $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$) all exhibit five characteristic frequency ranges of vibrational modes at 210, 310–370, 500–650, 700–850, and 900–1000 cm^{-1}. These are usually assigned, respectively, to Mo—O—Mo deformations, Mo=O bending vibrations,

---

[1] Chemistry Department, Nanjing University, Nanjing, Peoples' Republic of China.

0021-9517/87 $3.00
Copyright © 1987 by Academic Press, Inc.
All rights of reproduction in any form reserved.

symmetric Mo—O—Mo stretches, antisymmetric Mo—O—Mo stretches, and symmetric and antisymmetric terminal Mo═O stretches (*3*).

The spectra of supported molybdena species resemble those of the Mo—O polyanions with respect to the observed frequency ranges. However, the differences in spectra obtained from samples with different loadings, preparation conditions, and calcination conditions are subtle enough as to preclude ready identification. Most of the peaks of particular interest in the Raman spectra of supported molybdenum catalysts occur between 900 and 1000 cm^{-1}. While many investigators have proposed assignments for these bands, the literature dealing with the MoO_3/Al_2O_3 system illustrates the difficulty with which spectroscopic data are interpreted.

Stencel *et al.* (*6*) reported that the position of the most intense Raman band varied from 938 to 970 cm^{-1} as the MoO_3 concentration was increased; this band was simply assigned to a symmetric stretch of a Mo═O surface species. Brown *et al.* (*14*) postulated that the band observed in various positions between 930 and 970 cm^{-1} was due to an octahedral molybdenum–oxygen surface structure. Sombret *et al.* (*15*) found that the frequency of the band associated with the surface molybdate species increased from 930 to 966 cm^{-1} as the MoO_3 content increased from 4 to 24 wt%. The 930-cm^{-1} peak was attributed to isolated tetrahedral species whereas the 966-cm^{-1} peak was assigned to distorted polymeric octahedral species.

Jannibello *et al.* (*16*) observed a Raman band at 940 cm^{-1} on calcined samples which had been prepared by impregnation; this band was surmised to be the symmetric Mo═O stretching vibration of tetrahedral MoO_4^{2-} with an increased double bond character. Contradicting this assignment, Medema *et al.* (*17*) and Knözinger and Jeziorowski (*18*) suggested that the peak near 950 cm^{-1} can be attributed to a two-dimensional polymeric molybdenum–oxygen surface species built from MoO_6 octahedra.

Wang and Hall (*9*) asserted that the ratio of intensities at 950 and 970 cm^{-1} could be used as a measure of the ratio of tetrahedrally to octahedrally coordinated molybdenum surface species. This result is predicated on the assumption that the 950-cm^{-1} band corresponds to the Mo═O vibration of a tetrahedral molybdate group bonded to the support. They also offered an alternative interpretation in which the 950-cm^{-1} peak was assigned to small clusters containing less than about seven molybdenum atoms whereas the 970-cm^{-1} band was ascribed to larger polymolybdate clusters.

From their Raman and FTIR spectroscopic results on the MoO_3/TiO_2 system, Ng and Gulari (*5*) concluded that bands at 955 cm^{-1} or lower could be attributed to the terminal Mo═O stretch of tetrahedral species, whereas bands higher than 955 cm^{-1} arose from the terminal Mo═O stretch of polymeric octahedral species. Regarding the tetrahedral species, they explained the shift in frequency observed for the supported catalyst relative to that found in aqueous solution by invoking the idea of a strong interaction with the titania surface; this hypothesis is similar to that proposed by Jannibello *et al.* (*16*) for the case of the alumina support.

The aforementioned literature constitutes a useful framework within which the spectra obtained in the present study can be evaluated and interpreted.

EXPERIMENTAL

Laser Raman spectroscopy, Fourier transform infrared spectroscopy, and X-ray diffraction were utilized in this study.

The Raman spectrometer was a Spex Ramalog 5 (Model 14018) equipped with a third monochromator to resolve weak bands near the exciting line. The monochromatic light source was a Spectra Physics Model 164 argon ion laser powered by a Spectra Physics Model 265 exciter. The spectrometer was interfaced with a DEC

PDP-11/03-LC minicomputer system to facilitate data acquisition and manipulation. All spectra were recorded using the 488.0-nm line of the argon laser for excitation. A rotating lens assembly was used to minimize sample degradation due to localized heating of the catalyst sample by the laser beam. A quartz flow cell with a Nichrome wire heater was used for the high temperature oxygen treatments. The design permits the collection of Raman spectra from samples contained in the cell under various atmospheres.

Infrared spectra were recorded using a Nicolet 7199 Fourier transform infrared spectrometer operated with a spectral resolution of 1 cm^{-1}. All spectra were collected at beam temperature (ca. 310 K). Samples were pressed into self-supporting wafers and placed into a heatable IR cell equipped with CaF_2 windows.

A Picker X-ray diffractometer was used in the X-ray diffraction experiments. CuK_α radiation was passed through a Ni filter and two 1° slits.

The pure oxides used in this study were prepared as follows:

The MoO_3 phase was prepared by thermal decomposition of $(NH_4)_6MoO_7 \cdot 4H_2O$ at 720 K in air for 6 h.

The anatase form of TiO_2 was obtained from the hydroxide by calcination at 770 K in air for 6 h. The titanium hydroxide was prepared by adding an aqueous solution of $TiCl_4$ to an aqueous solution of $(NH_4)_2SO_4$ and H_2SO_4. This mixture was boiled for 1 h; NH_4OH was added to maintain a pH of 1.0. The precipitate was filtered and washed with distilled water until no chloride ions were detected in the filtrate. This titanium hydroxide was then dried in an oven.

The method used to prepare SnO_2 was similar to that described for TiO_2. The hydroxide was obtained by adding NH_4OH to an aqueous solution of $SnCl_4 \cdot 5H_2O$. The precipitate was then filtered, washed, and dried in the same manner as the titanium hydroxide precipitate.

The MgO was obtained by decomposition of $Mg(OH)_2$ under vacuum while heating to 1270 K, followed by oxidation in O_2 at 970 K for 3 days. The $Mg(OH)_2$ was formed by precipitation of an aqueous solution of $Mg(NO_3)_2$ (Aldrich 99.999%) with NH_4OH (*7*).

The silica and alumina supports were obtained from commercial sources. The SiO_2 used in this study was Cab-O-Sil. The γ-Al_2O_3 used was Davison SMR 7-5913.

Each sample was prepared by mechanically mixing the two pure oxides of interest. In each case, the amount of MoO_3 used was calculated to be less than that required for monolayer coverage, based on BET surface area measurements of the complementary oxide (Table 1).

A series of Raman spectra was obtained for each binary oxide system. First, the Raman spectra of the untreated mechanical mixture was obtained in air. The mixture was then subjected to calcination in air at 720 K for 24 h. The Raman spectrum of this calcined sample was also recorded in air. The sample was then treated under flowing oxygen at 720 K for approximately 8 h. At the end of the treatment, the sample was isolated in the flow cell and cooled to room temperature. At this point, the Raman spectrum was recorded with the sample in oxygen.

Similar catalyst pretreatment protocols were employed in FTIR experiments on the MoO_3/Al_2O_3 system. To observe pyridine adsorption on a mechanical mixture of the two oxides, the mixture was treated in flowing oxygen at 420 K for 8 h. The sample cell was then evacuated at 420 K to a pressure of 10^{-4} Torr for 1 h. A background IR spec-

TABLE 1

	Surface area (m^2/g)	Wt% MoO_3
SnO_2	31	1.9
TiO_2 (anatase)	21	1.25
SiO_2 (Cab-O-Sil)	300	12.5
Al_2O_3	170	10.0
MgO	61	5.0

trum was collected at this point. The sample was exposed to 4 Torr pyridine at 420 K for 1 h, evacuated to 10^{-4} Torr, and cooled to room temperature. At this point the FTIR spectrum of adsorbed pyridine was recorded. The background spectrum was subtracted to facilitate analysis of the adsorbed species.

Pyridine adsorption was also observed on calcined samples. The mechanical mixture of MoO_3 and Al_2O_3 was first calcined in air at 720 K for 24 h and then treated in flowing oxygen at 720 K for 8 h. The sample cell was evacuated to 10^{-4} Torr for 1 h at 720 K and then cooled to collect a background spectrum of the catalyst. The sample was exposed to 4 Torr pyridine for 1 h at either 370 or 420 K. The cell was then evacuated for 1 h and cooled to room temperature. The FTIR spectrum of adsorbed pyridine was then recorded.

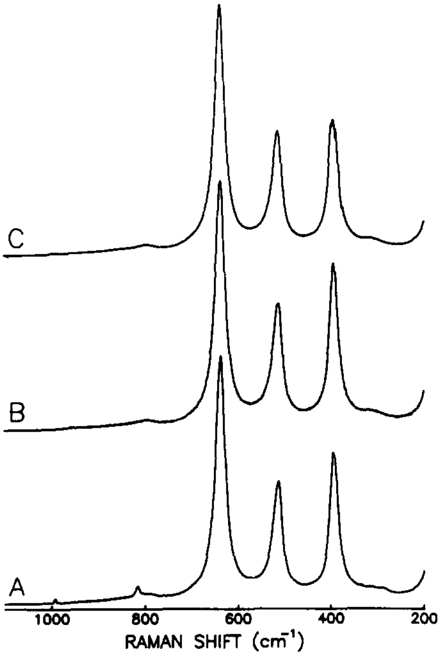

FIG. 1. Raman spectra of a mechanical mixture containing 1.25 wt% MoO_3 in TiO_2 (anatase). (A) Untreated mechanical mixture; spectrum recorded in air. (B) Mechanical mixture calcined at 720 K in air for 24 h; spectrum recorded in air. (C) Mechanical mixture calcined at 720 K in air for 24 h and calcined at 720 K in flowing oxygen for 8 h; spectrum recorded in oxygen.

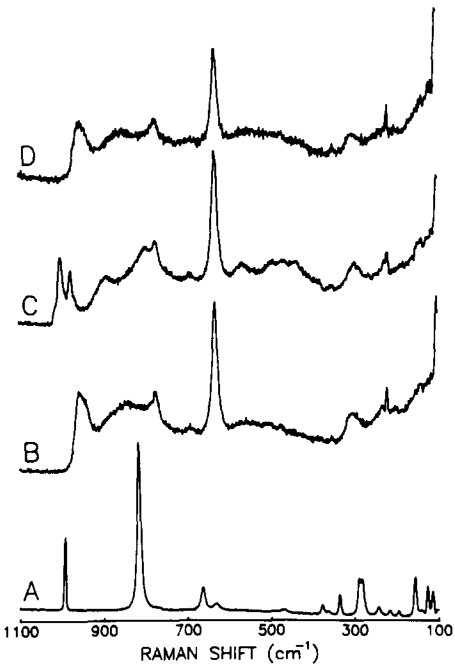

FIG. 2. Raman spectra of a mechanical mixture containing 1.9 wt% MoO_3 in SnO_2. (A) Untreated mechanical mixture; spectrum recorded in air. (B) Mechanical mixture calcined at 720 K in air for 24 h; spectrum recorded in air. (C) Mechanical mixture calcined at 720 K in air for 24 h and calcined at 720 K in flowing oxygen for 8 h; spectrum recorded in oxygen. (D) Mechanical mixture calcined at 720 K in air for 24 h and calcined at 720 K in flowing oxygen for 8 h; top of flow cell was then removed, exposing the sample to air; spectrum recorded in air.

RESULTS

Raman Spectroscopy

The five series of Raman spectra obtained from the different samples are shown in Figs. 1–5. The Raman peaks observed in the present work in the region 800–1100 cm^{-1} are summarized in Table 2.

The spectra for the MoO_3/TiO_2 (anatase) system are displayed in Fig. 1. The peaks at 393, 512, and 636 cm^{-1} are associated with anatase. The characteristic MoO_3 peaks at 816 and 992 cm^{-1} are clearly present in spectrum 1A for the mechanical mixture of MoO_3 and TiO_2. When the mechanical mixture was calcined, these two peaks disappeared as shown by spectrum 1B. A small broad feature is also present at 961 cm^{-1} in

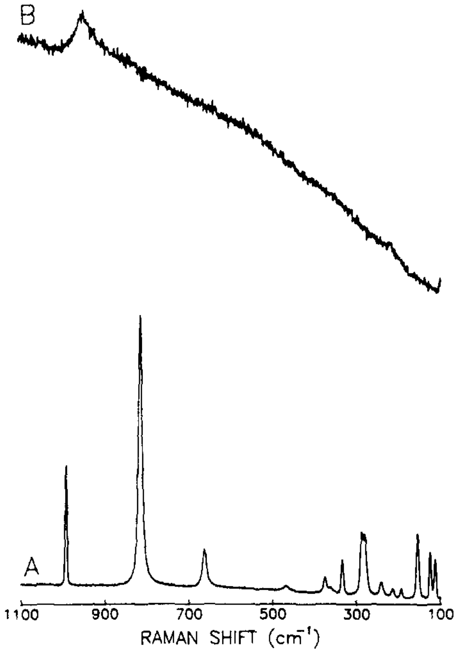

FIG. 3. Raman spectra of mechanical mixture containing 10 wt% MoO_3 in Al_2O_3. (A) Untreated mechanical mixture; spectrum recorded in air. (B) Mechanical mixture calcined at 720 K in air for 24 h; spectrum recorded in air.

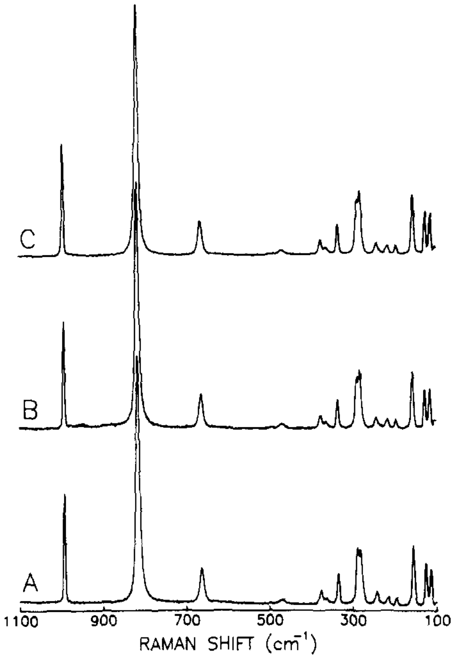

FIG. 4. Raman spectra of mechanical mixture containing 12.5 wt% MoO_3 in silica. (A) Untreated mechanical mixture; spectrum recorded in air. (B) Mechanical mixture calcined at 720 K in air for 24 h; spectrum recorded in air. (C) Mechanical mixture calcined at 720 K in air for 24 h and calcined at 720 K in flowing oxygen for 8 h; spectrum recorded in oxygen.

TABLE 2

Summary of Mo–O Peaks Found in the Region 800–1100 cm^{-1}

	Calcined	Treated in O_2
TiO_2	961	—
	—	996
SnO_2	—	799
	840	—
	—	890
	950	—
	—	976
	—	1001
Al_2O_3	947	—
SiO_2	663	
	816	
	992	
MgO	855	
	907	
	955	
	967	
	1094	

spectrum 1B. This peak sharpens and shifts to 996 cm^{-1} when the calcined catalyst is further heated in oxygen and the spectrum collected with the sample under an oxygen atmosphere. This band is associated with a surface molybdate species (*4, 5*). These results are consistent with the idea of the bulk molybdenum oxide spreading on the surface of the titanium oxide.

Figure 2 contains a series of spectra for the MoO_3/SnO_2 system. The spectrum corresponding to the mechanical mixture (2A) resembles the spectrum of pure MoO_3; the small peak at 632 cm^{-1} is the only spectral feature attributed to SnO_2. Calcination had a dramatic effect on the sample, as seen in spectrum 2B. Most of the peaks associated with MoO_3 disappeared, most notably those at 816 and 992 cm^{-1}. It should be noted that spectrum 2B is shown with a greater sensi-

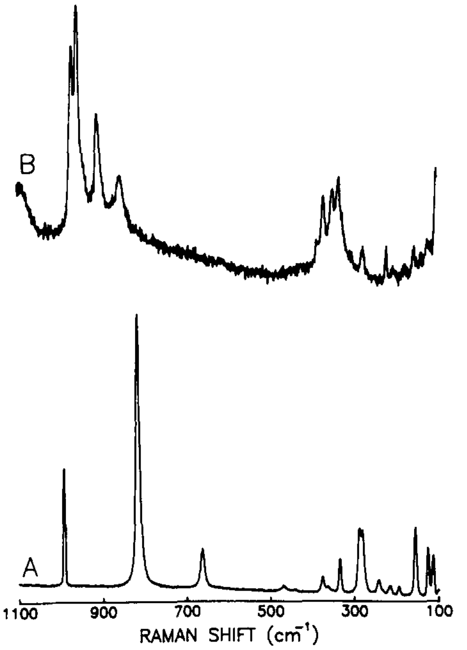

FIG. 5. Raman spectra of mechanical mixture containing 5 wt% MoO_3 in MgO. (A) Untreated mechanical mixture; spectrum recorded in air. (B) Mechanical mixture calcined at 720 K in air for 24 h; spectrum recorded in air.

tivity than spectrum 2A; the Sn—O—Sn stretching mode at 632 cm^{-1} was actually of the same intensity in both spectra. The absence of the MoO_3 peaks facilitates observation of a peak in spectrum 2B at 775 cm^{-1} which is due to the SnO_2 phase. Also noteworthy is the appearance of new peaks at 840 and 950 cm^{-1}.

Treatment in flowing oxygen effects further changes, as seen in spectrum 2C. The peaks at 840 and 950 cm^{-1} disappear. New peaks at 799, 890, 976, and 1001 cm^{-1} are observed. Interestingly, these changes are easily reversed. Spectrum 2D was obtained after oxygen treatment but the Raman cell was opened to the atmosphere before the spectrum was collected; it is identical to spectrum 2B.

The Raman spectra for the MoO_3/Al_2O_3 system are plotted in Fig. 3. The spectrum obtained for the mechanical mixture (3A) is dominated by the spectral features associated with the pure MoO_3 phase. The only indication of the presence of Al_2O_3 is the increased background fluorescence. Calcination resulted in a drastic decrease in the intensity of the Raman spectrum. Spectrum 3B consists of the fluorescence band characteristic of Al_2O_3, with a broad peak appearing at 947 cm^{-1}; all bulk phase MoO_3 peaks disappeared upon calcination.

The spectra of the MoO_3/SiO_2 system are presented in Fig. 4. The mechanical mixture has a spectrum (4A) which is virtually indistinguishable from that of pure MoO_3. Calcination had little effect on the spectrum of the MoO_3/SiO_2 sample as seen in spectrum 4B.

One of the only detectable differences in spectrum 4B relative to spectrum 4A is a change in the relative peak intensities of the doublet at 280–287 cm^{-1}. The lower frequency peak is the more intense one in the spectrum of pure MoO_3 whereas the higher frequency peak dominates in the spectra of the untreated mechanical mixtures of MoO_3 with SnO_2, Al_2O_3, SiO_2, or MgO. However, in the spectrum of the calcined MoO_3/SiO_2 catalyst, the peak at 281 cm^{-1} is again the more intense of the two peaks. Brown *et al.* (*14*) observed a similar reversal in the relative peak intensities of the doublet at 284–291 cm^{-1} in the spectrum of a commercial MoO_3/Al_2O_3 catalyst compared to that of pure MoO_3. The other distinctive feature of spectrum 4B is the appearance of a weak broadband at 950 cm^{-1}.

Finally, the spectra of the MoO_3/MgO system are shown in Fig. 5. Spectrum 5A was obtained from the mechanical mixture of 5 wt% MoO_3 in MgO. All of the peaks (with the possible exception of a small peak at 441 cm^{-1}) are associated with the bulk MoO_3 phase. Calcination produced changes in the sample as seen in spectrum 5B. The characteristic "fingerprint" of bulk phase MoO_3 is the set of three peaks in the metal–oxygen stretching region, 663, 816, and 992 cm^{-1}. These peaks are *absent* in the spectrum of the calcined material. New peaks are evident at 855, 907, 955, 967, and 1094 cm^{-1}; these are associated with the formation of surface molybdenum oxide species.

FTIR Spectroscopy

Alumina does not generally contain Brønsted acid sites, but it does have Lewis acidity. For example, Suarez *et al.* (*8*) demonstrated this with experiments on pyridine adsorption on alumina. Their FTIR data showed the presence of two types of Lewis acid sites, but no Brønsted acid sites. Addition of molybdena to the alumina resulted in the formation of Brønsted acid sites. This Brønsted acidity has been associated with an alumina hydroxyl in close proximity to a molybdenum cation (*19*).

The FTIR spectra obtained from experiments wherein pyridine was adsorbed on a mechanical mixture of MoO_3 and Al_2O_3 all showed the absence of peaks at 1540 and 1638 cm^{-1}. This result demonstrates that the mechanical mixture does not possess Brønsted acidity (*20, 21*). However, following calcination at 720 K for 8 h, the oxidized catalyst was found to have Brønsted acid sites. Thus, upon calcination there apparently is a spreading of MoO_3 which results in a greater degree of interaction between the molybdena and alumina.

X-ray Diffraction

The diffraction pattern obtained from the mechanical mixture of MoO_3 and Al_2O_3 contains lines at $d = 0.381$, $d = 0.346$, and $d = 0.327$ nm which are attributed to the (110), (040), and (021) planes, respectively, of the orthorhombic MoO_3 phase. These characteristic MoO_3 peaks are not present in the X-ray data taken after calcination in air at 720 K for 24 h. This result supports the hypothesis that the molybdenum oxide phase is spreading on the surface of the alumina when the sample is heated.

The diffraction pattern obtained from the mechanical mixture of MoO_3 and SiO_2 shows the same three MoO_3 peaks in the region investigated. Calcination of the sample caused these peaks to decrease in intensity, but they did not disappear. The presence of a bulk MoO_3 phase even after calcination was also indicated by the Raman data. However, the Raman data do not seem to corroborate the conclusion drawn from the X-ray diffraction data that the amount of bulk phase MoO_3 appeared to decrease upon calcination. This discrepancy may be addressed by the observation that Raman spectroscopy may be quite sensitive to the bulk phase relative to a surface layer. Chan *et al.* (*22*) have studied this phenomenon in the WO_3/Al_2O_3 system and have estimated the relative Raman cross sections of the different tungsten oxide phases. Their results showed that the Raman intensity of the bulk WO_3 phase is 160 times that of the surface tungsten oxide phase per unit WO_3 content. Thomas *et al.* (*23*) report that the Raman cross section of WO_3 is five to six times higher than that of the surface tungsten oxide species in SiO_2. Consequently, only small amounts of crystalline WO_3 in the catalyst are needed to produce strong Raman peaks. Similarly, the amount of MoO_3 present after calcination of the MoO_3/SiO_2 catalyst may be sufficient to give rise to a strong MoO_3 Raman signal, yet diminished enough to cause a decrease in the intensity of the X-ray diffraction peaks.

DISCUSSION AND CONCLUSIONS

The formation of a surface molybdenum oxide has been well documented in the literature for supported molybdenum catalysts. The coordination and aggregation of the adsorbed species are believed to be sensitive to the catalyst preparation protocol followed. However, there is some evidence that the nature of the final calcined material is relatively independent of the method used to load the support.

We have diverged from the established preparation procedures by making mechanical mixtures of molybdenum trioxide with various oxide supports. We have found that a surface molybdate species can be formed by thermally induced spreading. The interaction between MoO_3 and supports such as

TiO_2, SnO_2, Al_2O_3, and MgO is favorable for this phenomenon to occur. This is in agreement with the recent study by Hayden *et al.* (*24*) who employed controlled atmosphere electron microscopy to observe the spreading of molybdena on alumina. The present data from the SiO_2 system are not conclusive.

Our Raman results for the MoO_3/TiO_2 system agree with those of Ng and Gulari (*5*) and Liu *et al.* (*4*). Comparison of the Raman spectra of calcined MoO_3/TiO_2 catalysts with a partial monolayer loading of molybdenum obtained by equilibrium adsorption, dry impregnation, or calcination of a mechanical mixture shows that the peak associated with a surface molybdenum oxide has approximately the same frequency (961 cm^{-1}) in all three cases. This evidence supports the idea that the nature of the molybdenum in the surface molybdate species on titania is similar regardless of how the surface phase is formed.

Both our Raman results and our X-ray diffraction data indicate the disappearance of bulk phase MoO_3 upon calcination of the MoO_3/Al_2O_3 mixture. In addition, the FTIR experiments provide evidence that the MoO_3 has spread on the alumina, forming Brønsted acid sites which are not present in the case of the mechanical mixture. According to the model of Hall (*19*), the Brønsted sites are alumina hydroxyl groups in close proximity to molybdenum cations. Following calcination, there is apparently a more intimate interaction between the molybdenum and the alumina, a result which is consistent with the formation of a surface molybdenum oxide.

There are some discrepancies between our Raman results for the MoO_3/Al_2O_3 system and those reported in the literature. The peak at or near 950 cm^{-1} has been identified by several research groups (*2, 3, 6, 7, 9, 10*). However, most of the investigators also found peaks at 860 and 970 cm^{-1} which are associated with surface molybdate species. The low signal to noise ratio of the calcined MoO_3/Al_2O_3 spectrum prevents the confident assertion that the surface molybdate species present are fundamentally different when different preparation methods are employed. The fluorescence of this sample precluded improvements in the spectra via the use of slower scanning speeds or averaging of multiple scans. Thus, the possibility remains that the difference can be attributed to a weaker interaction between MoO_3 and Al_2O_3 (relative to the MoO_3/TiO_2 system discussed above) such that the loading method becomes important for determining the final state of the molybdenum on the surface.

The loading method appears to be critical for the MoO_3/SiO_2 system. The Raman spectra of the calcined and oxygen-treated catalysts prepared by mechanical mixing provide minimal evidence for the formation of surface molybdate species or for the disappearance of the bulk MoO_3 starting material; a weak peak at 950 cm^{-1} is the only indication of an interaction species. The X-ray diffraction patterns before and after calcination do suggest a partial disappearance of MoO_3 upon heating.

More positive proof of the existence of surface molybdate species on silica is seen in the Raman results of Cheng and Schrader (*2*). Spectra recorded after calcination of their dry impregnated silica catalysts contained peaks at 856, 880, 950, and 980 cm^{-1} in addition to MoO_3 peaks which were present at all compositions (5 to 20 wt% MoO_3). The residual MoO_3 phase in their catalysts suggests that the interaction between the two oxides is not very strong. It is not surprising, therefore, that mechanical mixing followed by calcination is insufficient to induce spreading of the molybdenum as a monolayer on the silica surface.

In concert with the disappearance of all of the MoO_3 peaks, the new peaks observed in the Raman spectrum of calcined MoO_3/MgO are commonly associated with the formation of a surface molybdenum oxide layer. The peak at 950 cm^{-1} was observed in the spectra of both MoO_3/SnO_2 and

MoO_3/Al_2O_3 following calcination (Figs. 2 and 3); this peak is variously assigned to either a monomeric tetrahedral molybdate species or an octahedral isopolymolybdate species. The peaks at 855 and 970 cm^{-1} have also been reported for the MoO_3/SiO_2 (*2*) and the MoO_3/Al_2O_3 (*2, 7, 9, 10*) systems. It should be noted that for the MoO_3/MgO system the Raman peaks for the calcined sample are significantly narrower than are those of calcined samples of the other oxide combinations.

The Raman results for the MoO_3/SnO_2 system are particularly interesting. As with the MoO_3/MgO system, the MoO_3 peaks disappear upon calcination and new peaks appear at frequencies characteristic of surface molybdate species. In addition, the MoO_3/SnO_2 system exhibits behavior similar to that noted by Stencel *et al.* (*6*) and Chan *et al.* (*7*) for other catalyst systems; that is, the Mo=O stretching vibration frequency is sensitive to the extent of hydration of the catalyst. Stencel *et al.* found that the Mo=O stretching band is at about 1000 cm^{-1} in calcined samples of MoO_3/Al_2O_3 whereas in samples exposed to water vapor the frequency is near 950 cm^{-1}. Chan *et al.* found that the Raman bands of the supported surface oxide species sharpen and shift in frequency at elevated temperatures due to the desorption of water from the surface. This phenomenon was observed for the V_2O_5/Al_2O_3, WO_3/Al_2O_3, MoO_3/Al_2O_3, and WO_3/TiO_2 systems. They asserted that this information provides a means of distinguishing between surface oxide and bulk oxide phases since only the Raman bands of the surface oxide species are sensitive to changes in extent of hydration. Thus, the readily reversible shift in frequency of the Raman bands of the calcined mechanical mixtures of MoO_3 and SnO_2 upon sequential exposure to oxygen and ambient atmospheres provides reasonable proof that the MoO_3 has spread to form a surface oxide.

This hydration/dehydration effect has also been reported for MoO_3/TiO_2 and MoO_3/SiO_2. This effect is not obvious from our data on the MoO_3/SiO_2 system; the only feature possibly attributable to a hydration-sensitive surface oxide is the weak broadband at 950 cm^{-1} in the Raman spectrum of the calcined mechanical mixture. However, such a frequency shift does occur in the Raman spectrum of the MoO_3/TiO_2 system of the present work as noted in the Results section. This shift provides further evidence that thermally induced spreading takes place in the mechanical mixture of MoO_3 and TiO_2 to the extent that a surface oxide layer is formed.

Using either the dry impregnation or the equilibrium adsorption methods of loading to prepare MoO_3/TiO_2 catalysts, Ng and Gulari (*5*) observed that no MoO_3 formation occurred until monolayer coverage was exceeded. They concluded that molybdenum anions bind very tightly and uniformly to the titania until monolayer coverage is reached; only when it is exceeded can a MoO_3 phase be formed. We found spreading to occur upon calcination of a mechanical mixture. Yet the Raman spectrum of our calcined material contained a surface molybdate peak identical to that found in their work. This result implies that a fairly active migration and redistribution of the molybdenum must be operative in order for the environment (coordination, aggregation, distortion, etc.) of the molybdenum to be the same no matter which preparation technique is used. This requires a considerable degree of surface mobility in balance with an apparently strong support interaction.

As a contrast to the titania catalyst, Ng and Gulari suggest that if the dry impregnation method is used, MoO_3 formation on Al_2O_3 can be detected even at submonolayer loadings. They conclude that if bulk MoO_3 formation is to be avoided, equilibrium adsorption is the method of choice. However, once this bulk phase was formed, Wang and Hall (*10*) found it possible to eliminate it simply by subjecting the catalyst to repeated reduction and oxidation treatments. The disappearance of the

MoO_3 bands indicates that spreading has occurred. This is exactly what we found by intentionally starting with bulk MoO_3. Wang and Hall also obtained the same spectrum by using a preparation method involving adsorption of $Mo(CO)_6$ vapor. They concluded that bound molybdenum clusters are the dominant surface species, and apparently the aggregation and coordination are the same no matter which loading technique is used. Sufficient calcination eliminates the differences.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support provided by W. R. Grace, the Shell Foundation, the Wisconsin Alumni Research Foundation, and the National Science Foundation (Grant Number CPE-8410387).

REFERENCES

1. Cheng, C. P., Ludowise, J. D., and Schrader, G. L., *Appl. Spectrosc.* **34,** 146 (1980).
2. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60,** 276 (1979).
3. Jeziorowski, H., and Knözinger, H., *J. Phys. Chem.* **83,** 1166 (1979).
4. Liu, Y. C., Griffin, G. L., Chan, S. S., and Wachs, I. E., *J. Catal.* **94,** 108 (1985).
5. Ng, K. Y. S., and Gulari, E., *J. Catal.* **92,** 340 (1985).
6. Stencel, J. M., Makovsky, L. E., Sarkus, T. A., DeVries, J., Thomas, R., and Moulijn, J. A., *J. Catal.* **90,** 314 (1984).
7. Chan, S. S., Wachs, I. E., Murrell, L. L., Wang, L., and Hall, W. K., *J. Phys. Chem.* **88,** 5831 (1984).
8. Suarez, W., Dumesic, J. A., and Hill, C. G., Jr., *J. Catal.* **94,** 408 (1985).
9. Wang, L., and Hall, W. K., *J. Catal.* **66,** 251 (1980).
10. Wang, L., and Hall, W. K., *J. Catal.* **83,** 242 (1983).
11. Buiten, J., *J. Catal.* **10,** 188 (1968).
12. Sonnemans, J., and Mars, P., *J. Catal.* **31,** 209 (1973).
13. Xie, Y., Gui, L., Lin, Y., Zhao, B., Yang, N., Zhang, Y., Guo, Q., Duan, L., Huang, H., Cai, X., and Tang, Y., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 5, p. 147. Dechema, Frankfurt-am-Main, 1984.
14. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50,** 162 (1977).
15. Sombret, B., Dhamelincourt, P., Wallert, F., Muller, A. C., Bouquet, M., and Grosmangin, J., *J. Raman Spectrosc.* **9,** 291 (1980).
16. Jannibello, A., Marengo, S., Trifiro, F., and Villa, P. L., paper A presented at the second International Symposium on "Scientific Bases for the Preparation of Heterogeneous Catalysts." Louvain-la-Neuve, Belgium, Sept. 4–7, 1978.
17. Medema, J., van Stam, C., de Beer, V. H. J., Konings, A. J. A., and Koningsberger, D. C., *J. Catal.* **53,** 386 (1978).
18. Knözinger, H., and Jeziorowski, H., *J. Phys. Chem.* **82,** 2002 (1978).
19. Hall, W. K., *in* "Proceedings, 4th International Conference: The Chemistry and Uses of Molybdenum, Golden, Colorado, 1982."
20. Little, L. H., "Infrared Spectra of Adsorbed Species," Academic Press, New York, 1966.
21. Tanabe, K., *in* "Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 2. Springer-Verlag, New York, 1981.
22. Chan, S. S., Wachs, I. E., and Murrell, L. L., *J. Catal.* **90,** 150 (1984).
23. Thomas, R., Mittelmeijer-Hazeleger, M. C., Kerkhof, F. P. J. M., Moulijn, J. A., Medema, J., and de Beer, V. H. J., *in* "Proceedings, 3rd International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, Michigan, 1979."
24. Hayden, T. F., Dumesic, J. A., Sherwood, R. D., and Baker, R. T. K., *J. Catal.* **105,** 299 (1987).