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Raman Spectra of Supported Molybdena Catalysts[1]

I. Oxide Catalysts

FRED R. BROWN, LEO E. MAKOVSKY, AND KEE H. RHEE

U.S. Energy Research and Development Administration, Pittsburgh Energy Research Center,
4800 Forbes Avenue, Pittsburgh, Pennsylvania 15213

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Raman spectroscopy has been used to study a variety of supported molybdena catalysts. In contrast to the infrared spectra of such catalysts, the Raman spectra are free of any significant contributions from the support materials, thus permitting observation of fundamental vibrations associated with the incorporated molybdenum components. Depending upon the amount of molybdenum incorporated into the support, the resulting Raman spectra are interpreted as indicating the presence of either bulk MoO_3 or interaction products of the molybdena species and the support or a combination of bulk MoO_3 and interaction species. In contrast to the spectra of the support materials alone, the Raman spectra of supported molybdenum oxide catalysts are generally free of any intense fluorescent background.

INTRODUCTION

Supported molybdena catalysts, in particular promoted molybdenum oxide on alumina or silica–alumina supports, are important for their use in the hydrodesulfurization of petroleum feedstocks and coal. While numerous structural investigations of these types of catalysts, employing various instrumental techniques, have been reported, only two Raman spectroscopic studies have appeared (*1*, *2*). One of these Raman studies (*1*) found no discrete scattering which could be assigned to interaction species, and it was concluded that the interaction species assumed to be present were Raman-inactive. The other Raman study (*2*) was a preliminary communication of the work of two of the present authors. A related Raman study of MoO_3 supported on Vycor glass has been reported (*3*). This study found bands near 987 cm^{-1} which were assigned to MoO_3 in two different environments.

Numerous possibilities exist for the nature of the molybdenum present in the oxide form of such catalysts. Clusters of bulk MoO_3, a surface monolayer of MoO_3 possessing bulk MoO_3 properties, interaction species between the molybdenum oxide and the support, and discrete compound formation from the molybdenum oxide and either any promoters added (e.g., Co or Ni) or the Al of the support are all reasonable possibilities. Because Raman spectroscopy yields data for the vibrational energy spacings of molecules or ions present in a sample and because these data are directly related to the structure of such species, a thorough Raman investigation of molybdena catalysts was deemed appropriate.

This paper describes the results obtained on a number of commercially available catalysts analyzed as received from their respective manufacturers. Because the cata-

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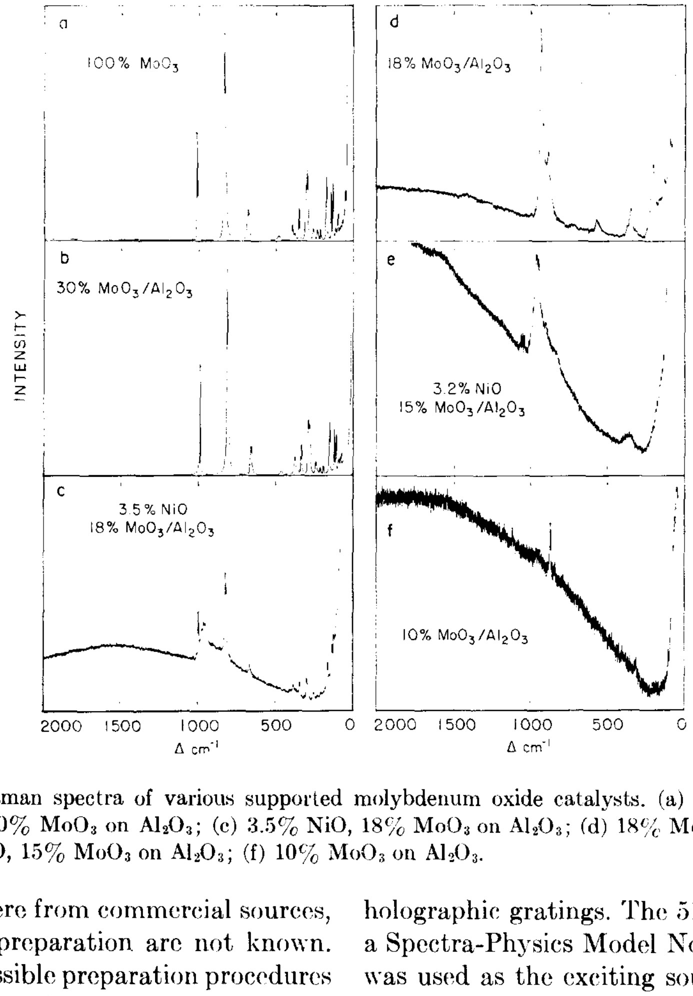

FIG. 1. Raman spectra of various supported molybdenum oxide catalysts. (a) Bulk (100%) MoO_3; (b) 30% MoO_3 on Al_2O_3; (c) 3.5% NiO, 18% MoO_3 on Al_2O_3; (d) 18% MoO_3 on Al_2O_3; (e) 3.2% NiO, 15% MoO_3 on Al_2O_3; (f) 10% MoO_3 on Al_2O_3.

lyst samples were from commercial sources, the details of preparation are not known. The various possible preparation procedures which could have been used to synthesize these samples undoubtedly are partially determinative of the resulting Raman spectra. The purpose of this paper is to indicate that, for any individual sample, definitive structural information for supported molybdena catalysts can be obtained from these data.

EXPERIMENTAL METHODS

Instrumental

The Raman spectra were recorded on a Spex Ramalog[2] spectrometer equipped with holographic gratings. The 5145-Å line from a Spectra-Physics Model No. 165 Ar^+ laser was used as the exciting source. The spectral slit width was typically 4 cm^{-1} and powers of approximately 45 mW, measured at the sample, were used. Absorption of the energy from the intense, finely focused laser beam and concurrent sample decomposition can be acute for samples such as those studied here. Rotation of the sample to provide noncontinuous irradiation of any given spot on the sample was the method utilized to avoid this decomposition. A simple device that rotates the catalyst pellets or extrudates along their cylindrical axes was used on those samples that were analyzed in air. The recording of spectra for samples where strict environmental control was thought necessary was accomplished in a specially designed cell which permits sample rotation and simul-

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[2] Use of brand names facilitates understanding and does not necessarily imply endorsement by the U.S. Energy Research and Development Administration.

taneous environmental control. The details of the cell appear elsewhere (*4*).

RESULTS

Figures 1b–f and 2a show the Raman spectra (to 2000 cm^{-1}) of six supported molybdenum oxide catalysts of various molybdenum and promoter concentrations. The spectra are given in descending order of molybdenum (as MoO_3) concentration. Since the suppliers of the samples generally report the concentration of active components in limited ranges, the concentrations listed are only approximate. Table 1 contains the measured Raman frequencies for these samples. The reported frequencies are believed to be accurate to ±2 cm^{-1}, unless the band is listed as either a shoulder (sh) or very broad (vb).

Initially, it should be noted that the intense fluorescence background problems that occur if attempts are made to record the Raman spectra of support materials, such as silica, alumina, or silica–alumina (*5–7*), are not so severe with these catalyst samples. The origin of this fluorescent background is not entirely understood, but the presence of molybdenum–oxygen-containing structures may be suppressing it in these samples.

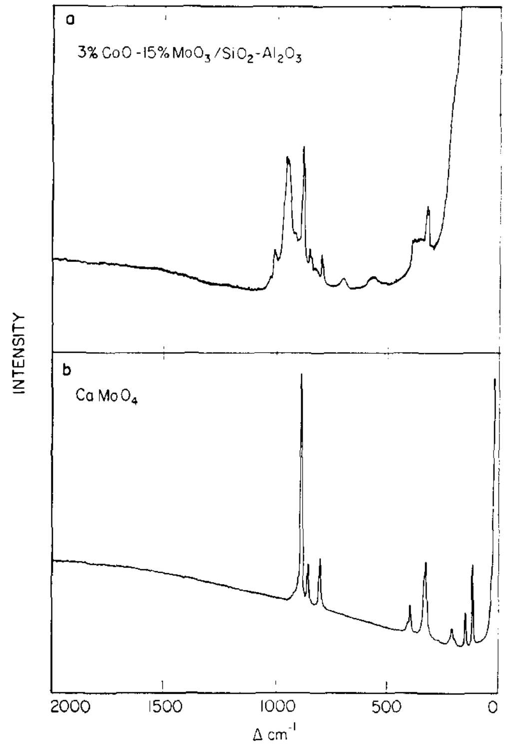

FIG. 2. Raman spectra of: (a) 3% CoO, 15% MoO_3 on SiO_2–Al_2O_3; (b) 100% $CaMoO_4$.

Figure 1b shows the Raman spectrum of a catalyst consisting of 30% molybdenum as MoO_3 on Al_2O_3. The spectrum shows no evidence for the presence of any species other than bulk MoO_3. The spectrum of bulk MoO_3 is shown in Fig. 1a. Except for the very slight intensity reversal that occurs for the doublet at 284 and 291 cm^{-1}, the catalyst spectrum is an exact duplicate of that for bulk MoO_3.

Figure 1c shows the Raman spectrum of a catalyst consisting of 3.5% nickel as NiO and 18% molybdenum as MoO_3 on Al_2O_3. This spectrum also shows the presence of bulk MoO_3, again with the intensity reversal of the 284- and 291-cm^{-1} doublet. The overall decrease in intensity of the bands assigned to bulk MoO_3 as compared to the two preceding spectra is attributable to the decrease in total concentration of bulk MoO_3 present. The broad band centered at ~950 cm^{-1}, not present in the prior two spectra, occurs in the spectral region for molybdenum–oxygen-stretching fundamentals. A description of the nature of the band at ~950 cm^{-1} will be presented later. Results identical to those shown in Fig. 1c were also obtained for a catalyst procured from the same manufacturer, differing only slightly in component concentrations; i.e., 3.2% nickel as NiO and 15% molybdenum as MoO_3 on Al_2O_3. The spectrum of this catalyst is not reproduced here.

The spectrum shown in Fig. 1d is for a catalyst containing 18% molybdenum as MoO_3 on Al_2O_3. No evidence for bulk MoO_3 occurs in the spectrum. Rather, a number of reasonably sharp, intense peaks at the frequencies given in Table 1 are present.

As shown in Fig. 1e, only one prominent

feature occurs in the spectrum of a catalyst containing 3.2% nickel as NiO and 15% molybdenum as MoO_3 on Al_2O_3. This intense, broad band centered at approximately 955 cm^{-1} is similar to the 950-cm^{-1} band present in the spectrum shown in Fig. 1c. No evidence for bulk MoO_3 occurs in the spectrum, notwithstanding the concentration of active components is very similar to that of the sample reported in Fig. 1c.

Figure 1f shows the spectrum of a catalyst containing 10% molybdenum as MoO_3 on Al_2O_3. Though the spectrum is of poorer quality, primarily because of the high background, as compared to most of the others, discrete bands have been measured and are given in Table 1. Except for the band at ~950 cm^{-1}, which has a greatly reduced intensity, the measured bands do not appear in any of the previously described spectra.

The spectrum of the catalyst to which primary effort has been directed is shown in Fig. 2a. This catalyst, containing 3% cobalt as CoO and 15% molybdenum as MoO_3 on SiO_2–Al_2O_3, is the catalyst being used in the coal liquefaction SYNTHOIL process being developed at the Pittsburgh Energy Research Center of the U.S. Energy Research and Development Administration (*8*). This spectrum appears as a combination of the spectra reproduced in Fig. 1c and f; the broad band at ~950 cm^{-1} and the sharp bands at 877, 845, 791, and 321 cm^{-1} all appear.

DISCUSSION

Efforts to make a consistent interpretation of all of these spectra, together with those for catalysts studied but not reported here, are difficult primarily because of the lack of information concerning the methods of preparation of these commercially obtained catalyst samples. The properties of the support, method of active component incorporation, and conditions of calcination are three variables that could reasonably be expected to affect the structure and resulting Raman spectra of the catalysts. Other factors which could also be important in determining the obtained Raman data are the presence and concentration of any promoters added to the catalyst, the presence of impurities, and the relative stability to thermal decomposition of the components under laser excitation in the spectrometer. Notwithstanding these difficulties, some generalized discussion and conclusions as to the structural features of these catalysts can be made.

If the molybdenum oxide precursor to the catalyst is assumed to interact chemically with the surface of the support upon calcination (*9–12*), addition of this precursor into the catalyst in an amount in excess of that required to cover the support surface completely with a monolayer of molybdenum oxide–support interaction species might be expected to leave bulk MoO_3 remaining in the pore structure of the catalyst. This rationale is used to interpret the spectra in Figs. 1b and c; i.e., bulk MoO_3 appears in these spectra because those sites on the support surface chemically reactive to the molybdenum oxide species are limited, and, once they are filled with interaction species, the catalyst precursor (e.g., ammonium paramolybdate) decomposes upon calcination to bulk MoO_3.

The dehydrogenation activity of molybdena–alumina catalysts has been found to increase linearly with molybdenum oxide content until a certain percentage loading of the molybdenum oxide occurs, at which point the activity remains constant (*13*). This transition point in activity could be related to the maximum amount of molybdenum that can chemically interact with the support. The amount of MoO_3 necessary to cover the surface of the support completely with interaction species can be estimated by knowing the surface area of the support and assuming a 15-$Å^2$ area for a surface-interacted MoO_3 group. If the amount of molybdenum incorporated

TABLE 1

Raman Frequencies of Supported Molybdenum Oxide Catalysts and Model Compounds

MoO_3 1a^a Fisher Scientific		30% MoO_3/Al_2O_3 1b Climax Molybdenum Co.		3.5% NiO– 18% MoO_3/Al_2O_3 1c American Cyanamid		18% MoO_3/Al_2O_3 1d Unknown		3.2% NiO– 15% MoO_3/Al_2O_3 1e American Cyanamid		10% MoO_3/Al_2O_3 1f Harshaw Chemical Co.		3.0% CoO–15% $MoO_3/SiO_2–Al_2O_3$ 2a Harshaw Chemical Co.		$CaMoO_4$ 2b Alpha Products	
cm^{-1}	I^b	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I
		1028	1												
		1007	5									1003	22		
998	48	997	54	996	51										
				958	39			960	100	$\sim$966 vb^c	$\sim$15	948	76		
								949	93						
						942	100								
						928 sh^d	50								
						898	37	904	22						
						882 sh	22			881	100	877	100	879	100
										$\sim$850 vb	$\sim$15	845	22	847	18
								832	20						
821	100	820	100	821	100										
										797 vb	$\sim$20	791	18	794	22
								$\sim$760	$\sim$10						
668	14	667	14	667	12										
						$\sim$576	7								
474	2	472	1												
														402 sh	5
										$\sim$394	13	$\sim$388	21	392	14

381	7	380	8	379	7	381 sh	6						
367	3	369 sh	3	365	3								
						358	14						
341	15	338	14	338	14								
								~327 vb	~30	~321	34	323	35
294	26	292	27	291	24								
286	32	285	25	285	17								
												268	~2
248	5	245	6	245	11								
220	4	219	3	219	5	218	33						
								~205 vb	~10			203	7
												191	3
200	5	199	3	198	4								
161	30	158	25	159	32								
								~144 vb	30			143	15
						138	12						
132	24	129	20	130	24								
118	27	117	17	118	24								
								~112 vb	30			112	35
				109	8	106	11						
101	4	99	4	99	4								
85	9	84	6										

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[a] Refers to spectrum number in Figs. 1 and 2 and in the text.

[b] I, relative intensities, uncorrected for instrumental response.

[c] vb = Very broad.

[d] sh = Shoulder.

into the catalyst exceeds this calculated amount, then some bulk MoO_3 might reasonably be expected to result. If one assumes a surface area of approximately 200 m^2/g for the supports used in the manufacture of the catalysts studied here, then "saturation" of the surface should occur at the addition of approximately 20% MoO_3. The spectra in Figs. 1b and c are consistent with this analysis in that bulk MoO_3 is observed; it is noted though that the spectrum in Fig. 1d is not.

The *absence* of bands assignable to interaction species in Fig. 1b for the 30% MoO_3 on Al_2O_3 catalyst is probably due to (a) differences in the polarizability tensors for bulk MoO_3 as compared to those for any interaction species and (b) the presence of bulk MoO_3 physically covering any interaction species.

The presence of bulk MoO_3 in these two high concentration catalyst samples was shown to be confined to the outermost sections of the pellets by the recording of Raman spectra of pellets from which the outermost layers had been carefully removed. The spectrum of the inner layers of the 30% MoO_3 on Al_2O_3 catalyst shows a significant intensity reversal and slight increase in frequency of the two strongest MoO_3 bands (at 998 and 821 cm^{-1}). Equally important, the MoO_3 bands between 100 and 250 cm^{-1} are completely absent from the spectrum. The band intensity changes and the shifts in frequency are interpreted as showing the result of chemical interaction between the molybdenum-containing species and the Al_2O_3 support. Furthermore, the absence of the low-frequency bands, which are modes associated with the three-dimensional framework of bulk MoO_3, undoubtedly indicates that the molybdenum is dispersed as a monolayer or, at most, a few monolayers over the surface of the Al_2O_3 support. The Raman spectrum of an internal layer of the 3.5% NiO–18% MoO_3 on Al_2O_3 catalyst also shows no evidence for bulk MoO_3; only the broad band at $\sim$950 cm^{-1} is obvious.

One of the theories for the structure of these catalysts is that the molybdenum oxide exists as a monolayer of MoO_3 which retains the properties of bulk MoO_3 (*14–16*). The results presented here for those catalysts containing 15% or less MoO_3 are inconsistent with this theory. No evidence for species possessing the properties of bulk MoO_3 is found for these catalysts.

The spectrum of the catalyst shown in Fig. 1d is very similar to the spectrum for an analytical sample of $Al_2(MoO_4)_3$. The only spectral differences between the catalyst and the aluminum molybdate are: (a) slight ($<$10 cm^{-1}) frequency shifts of some of the bands and (b) the absence of bands and shoulders in the spectrum of the catalyst, which are assigned to crystal splittings in the pure compound. As previously discussed, these spectral changes are interpreted as indicating the chemical interaction of the molybdenum and the support such that the crystalline three-dimensional character of the pure compound is destroyed.

The sharp bands at 877, 845, 791, and 321 cm^{-1} present in the spectra shown in Figs. 1f and 2a are assigned to the tetrahedral molybdate ion, MoO_4^{-2}. Raman spectra of analytical samples of various molybdates, such as $NiMoO_4$, $CoMoO_4$ (two forms), and $CaMoO_4$, and values from the infrared spectra of these and other molybdates confirm this assignment. Figure 2b reproduces the Raman spectrum of an analytical sample of $CaMoO_4$.

Determination of the coordination of the molybdenum present in these types of catalysts has prompted as much discussion as the question how, if at all, the molybdenum oxide interacts with the surface of the support. Conclusions that the molybdenum is primarily tetrahedral (*9*), primarily octahedral (*15*), or a mixture depending upon the molybdenum oxide concentration (*10, 17*) have been reached. Though no overall conclusions as to the coordination of molybdenum can be reached from the work presented here, two catalyst samples do definitely show the presence of tetrahedral molybdenum (samples shown in Figs. 1f and 2a), and another definitely shows the presence of octahedral molybdenum (sample shown in Fig. 1d). Quantization of the amounts of specifically coordinated molybdenum was not attempted. Even qualitative estimates would probably not be meaningful, for it was found that different individual pellets from the sample shown in Fig. 2a showed varying peak heights between the bands assigned to tetrahedral MoO_4^{-2} and the band centered at ~950 cm^{-1}. Why the relative intensities of these bands should vary among pellets from the same lot is not understood. Lastly, it should be noted that the only samples which definitively show tetrahedral MoO_4^{-2} were from the same commercial source. All other catalyst samples reported here were from various other sources.

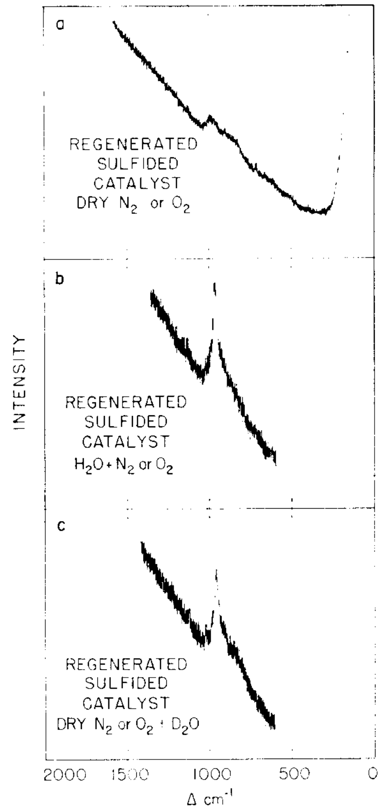

FIG. 3. Raman spectra of sulfided 3% CoO, 15% MoO_3 on SiO_2–Al_2O_3 subsequent to calcination: (a) Dry N_2 or O_2 as backfilling medium; (b) $H_2O + N_2$ or O_2 as backfilling medium; and (c) $D_2O + N_2$ or O_2 as backfilling medium.

The last remaining prominent band to be assigned is the broad band centered at ~950 cm^{-1} that appears in many of the spectra. Figure 3 shows the spectral results of experiments in which the gaseous environment surrounding the catalyst samples was strictly controlled. Figure 3a is the spectrum that results from calcination of a sulfided sample of the 3% CoO and 15% MoO_3 on a SiO_2–Al_2O_3 catalyst and then exposure of the sample to either dry N_2 or dry O_2. This type of procedure is a typical method of "regeneration"; i.e., one might expect that after such treatment, the spectrum in Fig. 2a should again be obtained. (The method of sulfidation and the resulting Raman spectra of samples so treated will be discussed in Part II of this series.) It is noted that all of the bands are essentially gone. Upon recalcination followed by exposure to N_2 or O_2 saturated with water vapor, the spectrum in Fig. 3b results. The ~950-cm^{-1} band is now most prominent. Conjecturing that hydroxyl formation occurred on the catalyst or support materials or that simple hydration occurred, the experiments were duplicated with 99.9% D_2O substituted for the water vapor. To insure that the catalyst sample was indeed exposed to D_2O, the vacuum line and Raman cell were exposed to the room temperature vapor pressure of D_2O ten times, in the sequence: expose for 2 min, pump for 2 min, reexpose for 2 min, etc. An infrared gas cell was simultaneously so treated with D_2O. After the ten exposures of D_2O, the infrared gas phase spectrum showed no evidence of H_2O or HDO; only D_2O was observed. The Raman spectrum of the catalyst so treated with D_2O is shown in Fig. 3c and is exactly the same as that for the catalyst treated with H_2O shown in Fig. 3b. These experimental sample treatments were performed in various orders, and analogous results were always obtained; i.e., a greatly reduced band when no H_2O or D_2O was present and an intense band at exactly the same frequency if H_2O or D_2O was present.

These experiments show that the band cannot be assigned to a hydrogenic vibration. Even a hydrogenic deformation mode should show a significant lowering in frequency upon substitution of deuterium for the hydrogen. The band could be assigned to a vibration resulting from the formation of complexes analogous to aquo (H_2O) or hydroxo (OH) coordination compounds. The infrared and Raman spectra of such complexes do possess bands in the 800- to 1000-cm^{-1} region, but these bands have been assigned to the rocking mode of aquo complexes and the bending mode of the hydroxo complexes (*18*). Again, these two modes involve significant displacements of the hydrogen atom(s) and, upon deuterium substitution, significantly lower frequencies should occur. The metal–oxygen stretching fundamental in the aquo complexes is typically found in the 400-cm^{-1} region, substantially lower than the ~950-cm^{-1} band of the catalyst samples. Even if it is argued that the 950-cm^{-1} band is the molybdenum–oxygen stretch of such a coordination complex, *some* shift upon deuteration should have occurred (*19*). Thus, not only the relatively high frequency of the band but also the absence of *any* shift upon deuterium substitution argue against assigning the ~950-cm^{-1} band to a metal–oxygen stretch of an aquo or hydroxo complex.

Notwithstanding the behavior of the band relative to the presence or absence of water, it is possible to assign it to a fundamental of the catalyst proper; i.e., to a vibration involving molybdenum and oxygen. A fundamental vibration of a molecule or ion will be Raman-active if the molecule or ion undergoes a change of its polarizability during this vibration (*20*). This polarizability is a measure of the susceptibility to distortion under the influence of an electric field of the nuclei and electrons of the molecule or ion; i.e., a measure of the ability of the electric field to *induce* a dipole moment in the molecule or ion. The intensity of a Raman-active fundamental is proportional to the amplitude of this induced dipole moment. Adsorption of water onto the surface of the catalyst could reasonably be expected to alter the electronic configuration of the constituent molybdenum–oxygen groups of the surface. This change could result either in a non-Raman-active fundamental becoming active or a low-intensity Raman transition becoming more intense. Stated more specifically, the oxygen from the adsorbed water could be "completing" the octahedral coordination of the molybdenum. Thus, the ~950-cm^{-1} band would be assigned to the symmetric stretch of a pseudo MoO_6 octahedral group. The appearance of the ~950-cm^{-1} band in the region of molybdenum–oxygen stretching fundamentals associated with octahedrally coordinated molybdenum upon treatment of the catalyst with H_2O or D_2O and the insensitivity of the band to spectral shift upon D_2O substitution for H_2O are consistent, through the above analysis, with the band being assigned to a fundamental of the catalyst. Further work to ascertain the exact nature of this band is in progress.

CONCLUSIONS

The following conclusions are drawn:

(1) Raman spectra of supported molybdenum oxide catalysts of various concentrations can be obtained. Depending upon the amount of molybdenum incorporated into the catalyst and the method of preparation, evidence for bulk MoO_3, tetrahedral MoO_4^{-2}, $Al_2(MoO_4)_3$, and other interaction products is found in individual samples.

(2) The exact nature of the ~950-cm^{-1} band present in many of the catalyst samples is not entirely known. It is postulated that the band is assignable to a molybde-

num–oxygen structure on the surface of the catalyst, the intensity of which increases due to changes in the electronic structure of the molybdenum–oxygen species induced by water adsorbed onto the surface of the catalyst.

(3) Many of the different structural features observed for the various catalysts studied are most probably attributable to differences in sample preparation procedures. Spectroscopic studies, similar to those reported here for catalyst samples prepared under well-defined experimental conditions are in progress. Included in these additional studies are efforts to obtain information concerning the effects of added promoters, such as Ni or Co. Such effects, if present in the promoted molybdenum catalysts reported here, are not spectrally obvious.

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