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Raman Spectra of Supported Molybdena Catalysts

II. Sulfided, Used, and Regenerated Catalysts[1, 2]

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Raman spectroscopy has been used to investigate the structural changes that two supported molybdenum oxide catalysts undergo upon specific chemical treatments. Molecular MoS_2 structures are indicated after sulfidation by a mixture of H_2/H_2S. Catalyst samples used in a coal hydrodesulfurization process yield spectra dominated by intense scattering from carbon deposited in the pores of the catalyst. Spectra of used catalyst samples, subjected to controlled air-firing to 600°C, show that all of the spectral features of the unused catalyst are not recovered after this "regeneration" procedure.

INTRODUCTION

As was shown in the first paper of this series (*1*), Raman spectroscopy can be a powerful technique for investigating the structural characteristics of supported molybdenum oxide catalysts. As a continuation of this work, two molybdenum oxide-supported catalysts, one with an added promoter and one without, have been subjected to various chemical treatments to test the usefulness of Raman spectroscopy for monitoring structural changes in these types of catalysts.

EXPERIMENTAL METHODS

Sulfided catalysts. Sulfiding of the oxide form of the catalysts was accomplished at 450°C with a 4:1 mixture of H_2/H_2S. Total sulfiding time was 4 hr. Two different sulfiding procedures were used. One procedure employed an open system whereby the gaseous mixture was continuously delivered over the catalyst pellets. The second procedure used a closed recirculating system in which the H_2/H_2S mixture was periodically replenished. The degree of sulfidation was controlled so that a substoichiometric quantity of sulfur was incorporated. Spectral results for samples treated by either method were the same.

Used catalysts. Used catalyst samples were carefully removed from coal liquefaction reactors of the SYNTHOIL process under development at the Pittsburgh Energy Research Center of the United States Department of Energy (*2*). These samples were used in the 0.5-ton/day continuous unit for several hundred hours. After removal, the catalyst pellets were soxhlet extracted with benzene and then were air-dried at 80°C.

Air-fired catalysts. Used and sulfided catalyst samples were subjected to air-firing to 600°C either *in situ* in a specially designed Raman cell (*3*) or externally in an open furnace. The firing was controlled

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[2] Part I is Ref. (*1*).

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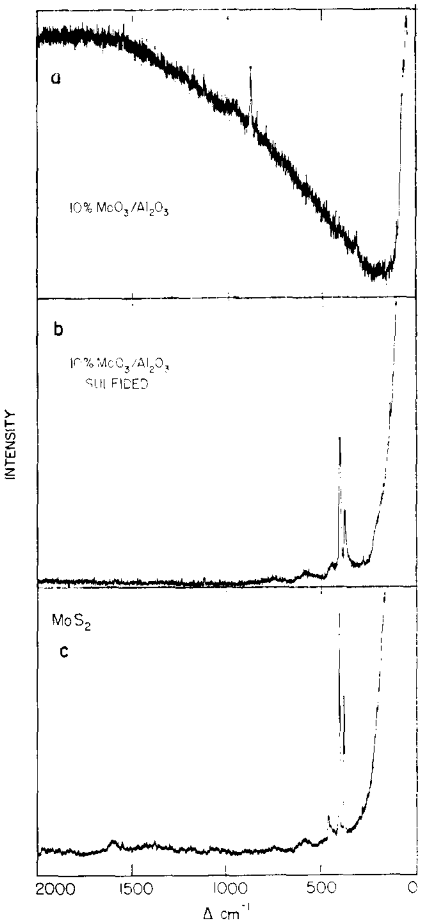

FIG. 1. Raman spectra of: (a) 10% MoO_3 on Al_2O_3 catalyst; (b) sulfided 10% MoO_3 on Al_2O_3 catalyst; (c) molecular MoS_2.

in that the firing gas was initially pure nitrogen to which ever increasing concentrations of air were added, until only air was admitted to the systems. In addition, the temperature of the samples was carefully monitored so that temperature excursions would be avoided. Upon reaching the final temperature, the samples were held there for approximately 6 hr.

Instrumental. The Raman spectra were recorded on a Spex Ramalog[3] spectrometer equipped with halographic gratings. The 5145-Å line from a Spectra-Physics Model No. 165 Ar^+ laser was used as the exciting source. Spectral slitwidth was typically 4 cm^{-1}.

RESULTS AND DISCUSSION

Sulfided Catalysts

It is generally accepted that supported molybdenum oxide catalysts are at least partially sulfided when used to hydrodesulfurize either petroleum feedstocks or coal. More specifically, it has been proposed that molecular MoS_2 is the active form of such sulfided catalysts (*4–6*). Reproduced in Figs. 1a and b are the Raman spectra of a 10% molybdenum as MoO_3 on Al_2O_3 catalyst in the oxide and sulfide forms, respectively. Figure 1c shows the Raman spectrum of an analytical sample of molecular MoS_2. The measured frequencies of the bands of these and other samples are listed in Table 1. The reported frequencies are believed to be accurate to ± 2 cm^{-1}, unless the band is listed either as a shoulder (sh) or as very broad (vb).

The sharp band at 877 cm^{-1} in Fig. 1a has previously been assigned to the tetrahedral molybdate ion (*1*). After sulfidation, the Raman spectrum (Fig. 1b) shows no evidence of the tetrahedral molybdate ion; indeed, *no* discrete Raman scattering occurs in the molybdenum–oxygen stretching fundamental region (800–1000 cm^{-1}). The only prominent features in the spectrum of the sulfided catalyst are the two sharp intense bands at 407 and 379 cm^{-1}. Comparison of this spectrum with that for an analytical sample of MoS_2 (Fig. 1c) strongly indicates that molecular MoS_2 is present in the sulfided catalyst.

Figure 2a shows the Raman spectrum of another supported molybdenum oxide catalyst. This catalyst consists of 3% cobalt as CoO and 15% Mo as MoO_3 on silica–alumina. Figure 2b shows the spectrum after sulfiding. As with the 10% molybdenum on alumina catalyst, the most prominent features are the two bands near

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[3] Use of brand names facilitates understanding and does not necessarily imply endorsement by the U. S. Department of Energy.

TABLE 1

Raman Frequencies of Supported Molybdenum Oxide Catalysts

10% MoO_3/Al_2O_3 Oxide (1a)[a]		10% MoO_3/Al_2O_3 Sulfide (1b)		3% CoO–15% MoO_3/SiO_2–Al_2O_3 Oxide (2a)		3% CoO–15% MoO_3/SiO_2–Al_2O_3 Sulfide (2b)		3% CoO–15% MoO_3/SiO_2–Al_2O_3 Used (2c)		MoS_2 Molecular (1c)	
cm^{-1}	I[b]	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I
								1605	100		
								1350	60		
								1288 sh[c]	40		
				1003	17						
~966 vb[d]	~15			948	67						
881	100			877	100						
850 vb	~15			845	17						
797 vb	~20			791	20						
		407	100			405	100	405	<1	409	100
~394	13			~388	25						
		379	45			372	55			384	62
~327 vb	~30			~321	44						
~205 vb	~10										
144 vb	30										
~112 vb	30										

[a] Refers to corresponding figure number.
[b] Relative intensity, uncorrected for instrumental response.
[c] Shoulder.
[d] Very broad.

400 cm^{-1}. The lower frequency band at 372 cm^{-1} is broader than that seen previously for the 10% molybdenum on alumina catalyst. This is probably caused by scattering from the silica present in the support material, for silica is known to possess a broad band in this region (*7*). The presence of an MoS_2 structure in this catalyst has been confirmed by X-ray diffraction measurements (*8*).

Molecular MoS_2 has been shown to have a layered structure, somewhat analogous to graphite (*9*). Each layer in MoS_2 consists of S–Mo–S groupings. Adjacent layers in MoS_2 are held together by van der Waals attractive forces between contiguous layers. A low-frequency optical lattice mode of species E_{2g}^2, assigned to the displacement of alternate layers opposite to one another, has been observed in the second-order Raman spectrum of hexagonal MoS_2 at 33.7 (*10*) or 32 cm^{-1} (*11*). In the analytical sample of MoS_2 used in this work, the mode was observed at 33 cm^{-1}. Observation of this mode in the spectra of the sulfided catalysts would be definitive confirmation of the first-order Raman spectra which indicate the presence of the MoS_2 layer structure, i.e., that the molybdenum–sulfur structures are three dimensional. Thus the monolayer of the surface species model, which has frequently been used to interpret data for the oxide forms of the catalysts, would be inadequate to explain the structure of the sulfided forms. All efforts to observe this band in the sulfided catalysts were negative. One particular problem associated with attempts to observe this band was the breadth of the Rayleigh wing of the exciting line, which was significantly more intense in the sulfided catalysts relative to the analytical sample of MoS_2.

Finally, no evidence for the existence of sulfided support (*12*, *13*) or cobalt sulfides, such as Co_9S_8 (*4–6*), is found in the spectra of the sulfided catalysts.

Used and Regenerated Catalysts

The Raman spectrum of the CoO–MoO_3 on SiO_2–Al_2O_3 catalyst after use in a coal liquefaction reactor is reproduced in Fig. 2c.

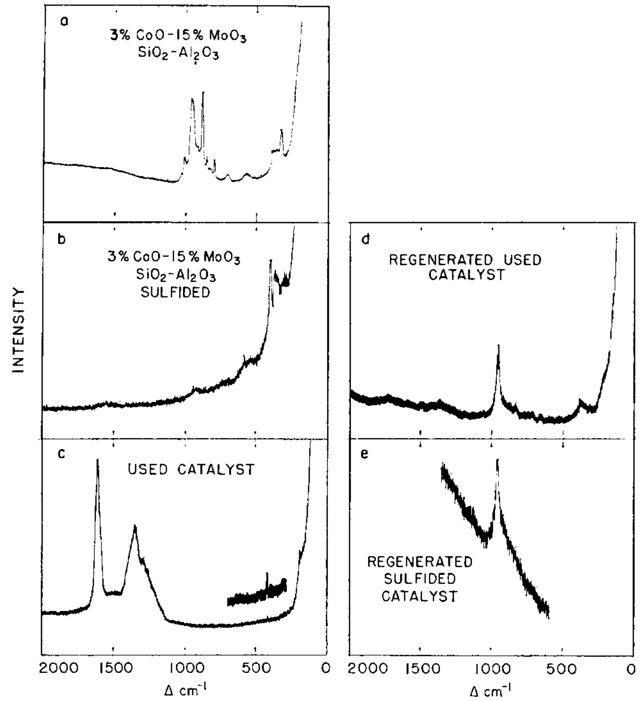

FIG. 2. Raman spectra of 3% CoO–15% MoO_3 on SiO_2–Al_2O_3 catalyst after various chemical treatments: (a) oxide form; (b) sulfide form; (c) after use in a coal liquefaction reactor; (d) air-fired (regenerated) used catalyst; (e) air-fired (regenerated) sulfided catalyst.

The intense bands between 1200 and 1700 cm^{-1} are assigned to the carbon network which is known to form in the pores of the catalyst during its use in a hydrodesulfurization process. The spectrum is remarkably similar to that for 94% carbon anthracite coal (*14*), from which it is deduced that the material is high in carbon content and highly ordered. No evidence for any molybdenum–oxygen structures (at 800–1000 cm^{-1}) is observed. Only upon increasing the sensitivity of the measurements could the presence of any molybdenum–sulfur species (near 400 cm^{-1}) be detected. This decrease in intensity of the molybdenum–sulfur structures is attributed to the structures being masked by the carbon network, as opposed to their being depleted during the coal conversion process.

Regeneration procedures for this catalyst involve controlled air-firing at temperatures up to 600°C. This procedure was followed for both the used *and* presulfided catalyst samples. The resulting Raman spectra are shown in Figs. 2d and e, respectively. The spectra are essentially the same, but both differ from the starting catalyst (Fig. 2a) in that the sharp bands previously assigned to tetrahedral MoO_4^{-2} (*1*) are no longer observed. This loss of the MoO_4^{-2} cannot be ascribed to some unique functioning of the coal liquefaction reactor, because they are also removed from the air-fired presulfided samples. The effect which the loss of the MoO_4^{-2} species would have upon catalyst activity was tested spectrally by resulfiding both samples with the aforementioned H_2/H_2S treatment, followed by the rerecording of their spectra. In each case, a spectrum identical to that obtained for a once presulfided catalyst (Fig. 2b) was observed. Therefore, to the extent that Fig. 2b represents the "true" form of the active sulfided catalyst, loss of the MoO_4^{-2} structures upon use and subsequent air-fired regeneration does not affect the activity of the catalyst. A more adequate test of the relative activity of the catalysts just described would be either a microreactor study with model compounds or actual use of the samples under process design conditions. The former experiments are planned.

CONCLUSIONS

Raman spectroscopy can be applied to supported molybdenum oxide catalysts to deduce structural changes that occur upon chemical treatment of the oxide forms of the catalysts. Sulfiding of the catalysts results in first-order Raman spectra essentially identical to that of molecular MoS_2. Catalysts samples used in a hydrodesulfurization of coal process yield spectra dominated by a carbon network that masks the catalyst proper. Spectra of samples "regenerated" by air-firing show the absence of features previously assigned to the tetrahedral molybdate ion. Analogous air-firing procedures applied to catalyst samples that were presulfided with a H_2/H_2S mixture also show that the tetrahedral molybdate structures had been specifically removed, thus indicating that the loss of these structures is not attributable to the coal liquefaction process per se.

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