JOURNAL OF CATALYSIS 85, 488–498 (1984)

Sulfiding of Cobalt Molybdate Catalysts: Characterization by Raman Spectroscopy

G. L. SCHRADER*,[1] AND C. P. CHENG†,[2]

*Department of Chemical Engineering and Ames Laboratory—USDOE, Iowa State University, Ames, Iowa 50011, and †Stauffer Chemical Company, Eastern Research Center, Dobbs Ferry, New York 10522

Received February 21, 1983; revised August 22, 1983

In situ laser Raman spectroscopic studies of the sulfiding of cobalt molybdate hydrodesulfurization catalysts were performed. Sulfiding in 10% H_2S/H_2 at 400°C resulted in the formation of stable MoS_2 structures after 2 h. However, the Raman spectra indicated that small crystallites or surface layers of perhaps distorted MoS_2 were present. Stepwise sulfiding of samples to 150, 250, and 350°C permitted intermediate stages of sulfiding to be examined. Differences were observed for the relative rates of reduction versus sulfur incorporation for $CoMoO_4$, Co_3O_4, MoO_3, and aggregated or polymeric molybdate phases. Cobalt tended to increase the extent of reduction of the catalyst. A previously described model is extended to include the role of cobalt.

1. INTRODUCTION

Cobalt molybdate catalysts have been characterized by an extensive array of techniques (*1, 2*). Spectroscopy has been crucial in determining the structure and chemistry of the oxidic and sulfided state of the catalyst. The oxidic catalyst precursor appears to be relatively complex: several phases of molybdenum and cobalt have been observed, particularly with Raman spectroscopy (*3–11*). Isolated and "raft-like," aggregated or polymeric molybdate species are present (*9, 10, 12–15*). At high loadings, MoO_3 can be detected by Raman spectroscopy and X-ray diffraction. The formation of aluminum molybdate has been detected by several workers (*1, 16, 17*), although different molybdenum incorporation techniques and higher calcining temperatures than those normally used for hydrodesulfurization catalysts seem to be required. Various environments for cobalt have been identified. A Co_3O_4 phase has been detected in several studies (*1, 9*). However, Co may also be incorporated in the alumina lattice. Co–Mo bilayer phases have been suggested; as the loadings of cobalt and molybdenum increase, formation of a cobalt molybdate phase is apparent (*8, 9*).

A fewer number of phases has been suggested for the sulfided form of cobalt molybdate catalysts, and a variety of models has been suggested for the active components. The dominate molybdenum phase is believed to be a microcrystalline form of MoS_2 (*2*). A layered arrangement is indicated from several studies, although the number of layers may be quite low and the occurrence of some disordering or rotation of the layers is likely (*13, 18*). The location of cobalt is less clear. Intercalation at edges of the MoS_2 crystallites has been widely discussed. Another model presumes Co_9S_8 microcrystals which contact MoS_2 species. The existence of a distinct "CoMoS" phase has been reported by Topsøe *et al.* (*19, 20*) using Mössbauer spectroscopy. Partial substitution of molybdenum by cobalt in MoS_2 is proposed for alumina-supported samples.

The conversion of the complex oxide components of the catalyst to the sulfided state has not been extensively studied. Recently, we reported Raman spectra for the *in situ* sulfiding of Mo/γ-Al_2O_3 catalysts (*13*). Through this work, it was possible to

---

[1] To whom correspondence should be addressed.

[2] Current address.

0021-9517/84 $3.00

observe the conversion of oxidic phases to molybdenum oxysulfide species and ultimately to MoS_2 surface layers and crystallites. A model was proposed based on the existence of isolated molybdate, aggregated molybdate, and MoO_3 phases. The existence of reduced phases (involving sulfur vacancies) was confirmed by exposing sulfided samples to oxygen. Relative reactivities of the oxidic and sulfided phases could also be determined.

Here we report the results for similar studies involving Co–Mo/γ-Al_2O_3 catalysts. Of particular interest is the effect which cobalt has on the reactivity of specific phases to sulfiding and/or reduction, as well as the sensitivity of these phases to oxygen. Previous results have indicated that significant structural and chemical changes can occur in the presence of oxygen (*21–23*). *In situ* studies are therefore required, and Raman spectroscopy has been demonstrated to be a very effective method for performing these experiments.

2. EXPERIMENTAL METHODS

The cobalt molybdate hydrodesulfurization catalysts were prepared according to previously described methods (*9*). A γ-Al_2O_3 support from BDH Chemicals was used for all studies (101 m^2/g); ammonium heptamolybdate and cobalt nitrate were obtained from Fischer Scientific Company. Dry impregnation (pore volume filling) techniques with aqueous solutions were used in all preparations. Molybdenum was impregnated first, followed by drying at 110°C for 4 h. Cobalt was then added before final drying (110°C for 4 h) and calcining (500°C for 6 h). Molybdenum loadings were 5, 7.5, 10, and 15 wt%, expressed as MoO_3. Cobalt loadings were maintained at 3 wt%, expressed as CoO.

Samples were sulfided within a controlled atmosphere Raman cell (*24*). Using this cell it was possible to spin samples to minimize heating effects by the laser. Catalysts were pressed into 13-mm disks for these studies. Samples were placed in the rotating cell, and the cell was then purged with helium. Two different procedures were employed in sulfiding. The first method has been used by other researchers (*25, 26*). Samples were heated under a flow of helium (60 ml/min) to 400°C. After 1 h at this temperature, the gas stream was changed to a mixture of 10% H_2S/H_2 (60 ml/min) for specific time periods (5 min to 2 h). The flow was then changed to helium, and the Raman spectrum was recorded with the sample at room temperature. For some samples, up to 150 scans were accumulated. The second sulfiding procedure involved heating the catalysts at a controlled rate and recording spectra after attaining several intermediate temperatures (*13*). Following the initial helium purge at room temperature, the gas flow was changed to the 10% H_2S/H_2 mixture (60 ml/min); simultaneously, the temperature of the cell was raised at a rate of 5°C/min. At temperatures of 150, 250, and 350°C, the flow of the sulfiding gas was stopped. A helium flow was again introduced, followed by cooling the sample to room temperature and recording of the Raman spectrum. Again, up to 150 scans were typically required because of the highly colored nature of the compounds and their poor scattering properties.

Sulfur analyses were performed by dissolving samples with aqua regia followed by a sulfate determination using barium chloride. Analyses were confirmed by Galbraith Laboratories. Analyses had a reproducibility of 0.1 wt% (absolute).

As in our previous studies (*13*), samples were exposed to air after sulfiding in order to determine the relative stability of structures by observing changes in the Raman spectrum. Exposure to air for 1 h at room temperature was typical. Spectra were recorded using a spinning sample holder.

All spectra were recorded using a Spex Ramalog 5 spectrometer equipped with holographic gratings and a "third monochromator." A Spectra-Physics 164 argon ion laser was used at an intensity of 200 mW (measured at the source) for the 488.0-nm line. Spectral resolution of 5 cm^{-1} was used for all studies. Spectral accumulation and routine data processing was performed with a Nicolet 1180 data system.

3. EXPERIMENTAL RESULTS

Raman spectra are reported for both the 400°C and the stepwise sulfiding processes. Previous results (*13*) have demonstrated that intermediate structures and compositions for these catalysts may be highly reactive at temperatures near 400°C. In general, stepwise heating resulted in the development of more complex Raman spectra.

The experimental results are closely related to studies of the Mo/γ-Al_2O_3 catalyst. A model of this system has been proposed involving molybdenum species with various degrees of aggregation. "Isolated" molybdate species may exist at very low loadings; polymeric molybdates exist at higher loadings, probably forming raft-like structures (*9, 10, 12*). Multi-layer formation of molybdates has also been proposed (*12*). At high coverages of molybdenum, MoO_3 can be detected by Raman spectroscopy. This model has been recently extended to include transformations occurring under sulfiding conditions: formation of reduced and partially sulfided phases has been proposed (*13*). MoS_2 surface phases and crystallites are formed at higher temperature sulfiding conditions.

Our previous studies (*9*) of Co–Mo/γ-Al_2O_3 catalysts dealt primarily with constant cobalt loadings of 3% (CoO). This study also used these samples—which had molybdenum loadings of 5, 7.5, 10, and 15% (MoO_3). In the oxidic form, these samples were comprised of phases and surface species which have been observed in general for cobalt molybdate hydrodesulfurization catalysts: Co_3O_4, MoO_3, $CoMoO_4$, and isolated and aggregated (polymeric) molybdates.

3*a*. *Co–Mo/γ-Al_2O_3 Catalysts Sulfided at 400°C*

Co–Mo/γ-Al_2O_3 catalysts were heated to 400°C under helium for 1 h. The sample was then exposed to a gas mixture of 10% H_2S/H_2 for 2 h. Samples were black in color, and spectral accumulation was necessary. The spectra of these samples had significant bands only at 386 and 407 cm^{-1}; no new bands were apparent for samples with different loadings of molybdenum. The position of the bands are similar to the most intense Raman bands of MoS_2. Some shifting of the bands is apparent, however. In addition, the bands are somewhat broader than for the corresponding spectra of sulfided Mo/γ-Al_2O_3 samples. This may be only partially attributed to the weak Raman scattering from these catalysts because of their intensely dark color, since the Mo/γ-Al_2O_3 catalysts were also black.

The spectra of the samples remained essentially unchanged after the samples were exposed to air. Calcination in oxygen for 2 h at 400°C produced a relatively strong, broad spectral band in the region 800–1000 cm^{-1}. No oxide phases such as MoO_3 or $CoMoO_4$ could be identified.

When Co–Mo/γ-Al_2O_3 catalysts were sulfided at 400°C for shorter periods of time, results similar to the Mo/γ-Al_2O_3 systems were observed. The spectrum of Co(3)Mo(10)/γ-Al_2O_3 (Fig. 1a) which had been sulfided at 400°C for 5 min indicated the presence of MoS_2 with very weak bands at 385 and 407 cm^{-1}; an extremely weak band at 940 cm^{-1} due to $CoMoO_4$ could be observed after accumulation of 200 scans (not shown). After sulfiding for 15 min (Fig. 1b), a spectrum very similar to that of a sample sulfided for 2 h at 400°C (Fig. 1c) was obtained. Samples sulfided for 5 and 15 min were sensitive to exposure to air: bands due to MoS_2 disappeared rapidly, although no additional bands appeared.

3*b*. *Co–Mo/γ-Al_2O_3 Catalysts Sulfided at Intermediate Temperatures*

A stepwise sulfiding process was performed to provide a better understanding of the oxide-to-sulfide conversion. Previous results using this sulfiding technique for

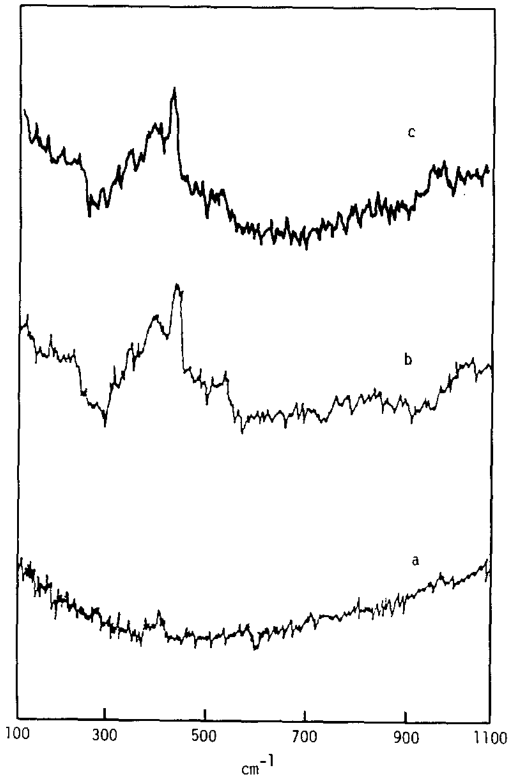

FIG. 1. Raman spectra of sulfided Co(3)Mo(10)/γ-Al_2O_3. At (a) 400°C for 5 min, (b) 400°C for 15 min, (c) 400°C for 2 h.

Mo/γ-Al_2O_3 samples (*13*) indicated that partially sulfided and reduced species could be detected. These species are likely to be very reactive and rapidly converted to MoS_2 under the 400°C sulfiding procedure. Stepwise-sulfided samples were also more sensitive to exposure to air.

The *in situ* Raman spectra of Co(3) Mo(5), Co(3)Mo(7.5), Co(3)Mo(10), and Co(3)Mo(10) on γ-Al_2O_3 sulfided at 150, 250, and 350°C are shown in Figs. 2–5. Band positions are summarized in Table 1, and compositions are given in Table 2 (sulfur only).

The spectra obtained for samples containing cobalt were generally simpler than those for Mo/γ-Al_2O_3 (*13*). The most striking difference in the spectra was the much reduced intensity of molybdenum oxysulfide species; some spectral bands assigned to these species were completely absent for cobalt-containing samples. However, the metal–oxygen vibrational bands for phases such as Co_3O_4 and $CoMoO_4$ were more persistent than molybdenum–oxygen bands present for Mo/γ-Al_2O_3.

For Co(3)Mo(5)/γ-Al_2O_3 samples, the major bands in the Raman spectrum of the oxidic form are due to Co_3O_4, aggregated molybdate species, and cobalt molybdate. After sulfiding to 150°C (Fig. 2a), broad bands were observed at 325 and 480 cm^{-1}. A band at 690 cm^{-1} due to Co_3O_4 and a band at 940 cm^{-1} due to $CoMoO_4$ were present at about the same intensity as the unsulfided samples. With increasing sulfiding temperature, these bands were much reduced in intensity. The spectrum of 250°C samples were remarkably free of spectral bands. No bands due to MoS_2 could be observed; similarly Co_9S_8 was not detected, although Ra-

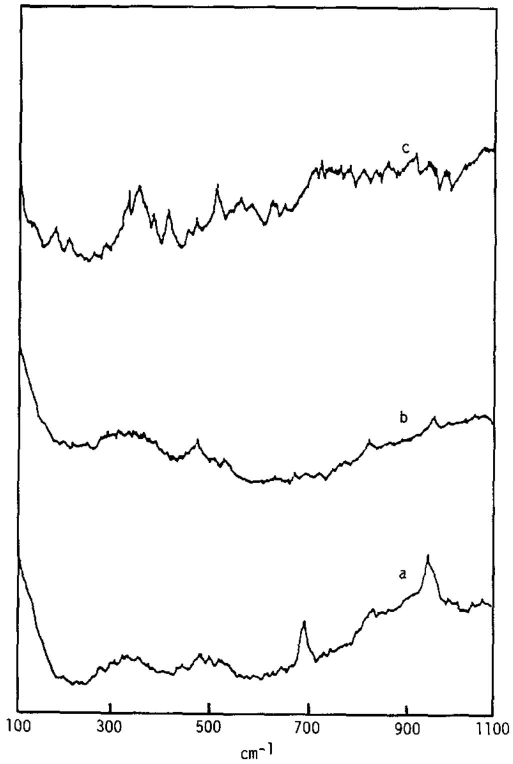

FIG. 2. Raman spectra of sulfided Co(3)Mo(5)/γ-Al_2O_3. At (a) 150°C, (b) 250°C, (c) 350°C.

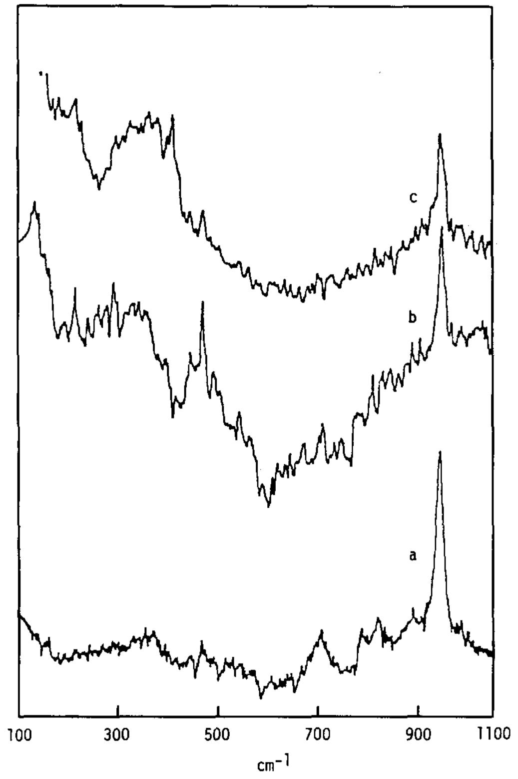

FIG. 3. Raman spectra of sulfided Co(3)Mo(7.5)/γ-Al_2O_3. At (a) 150°C, (b) 250°C, (c) 350°C.

man scattering from this compound is very weak. After sulfiding to 350°C (Fig. 2c), a broad band near 350 cm^{-1} and a band at 407 cm^{-1} are the only spectral features. Compared to Mo(5)/γ-Al_2O_3 samples, formation of MoS_2 for the cobalt samples apparently occurred to a much lesser extent.

Raman spectra of samples prepared with loadings of Co(3)Mo(7.5)/γ-Al_2O_3 (*9*) had stronger cobalt molybdate bands in the oxidic form. A Co_3O_4 phase was also present, as well as an aggregated molybdate species. Formation of some MoO_3 was apparent. Sulfiding up to 150°C (Fig. 3a) results in the disappearance of most spectral features due to the aggregated phase. The Co_3O_4 band (near 700 cm^{-1}) is also reduced in intensity. However, the intensity of the 940 cm^{-1} cobalt molybdate band is strong in this spectrum, as it is for the higher temperatures. Formation of MoS_2 structures at 350°C (Fig. 3c) is indicated by a broad band in the 405 cm^{-1} region. For samples at this same molybdenum loading but not containing cobalt, much stronger MoS_2 bands are present. No metal–oxygen vibrations for Co_3O_4 or aggregated molybdate phases are indicated by the Raman spectrum of the 350°C sample; only the intense cobalt molybdate band is present.

At higher loadings of molybdenum, more complex spectra were obtained. After sulfiding at 150°C, bands assigned to $CoMoO_4$, Co_3O_4, and MoO_3 were present in the spectrum of Co(3)Mo(10)/γ-Al_2O_3 (Fig. 4a). As for previous samples, destruction of aggregated molybdenum phases appears to be extensive. However, a more complex structure is present in the regions 250–360 and 440–550 cm^{-1}. Bands in this region are typical of metal oxysulfide species; the positions are similar to those for molybdenum oxysulfide species as reported previously (*13*). However, the presence of cobalt has

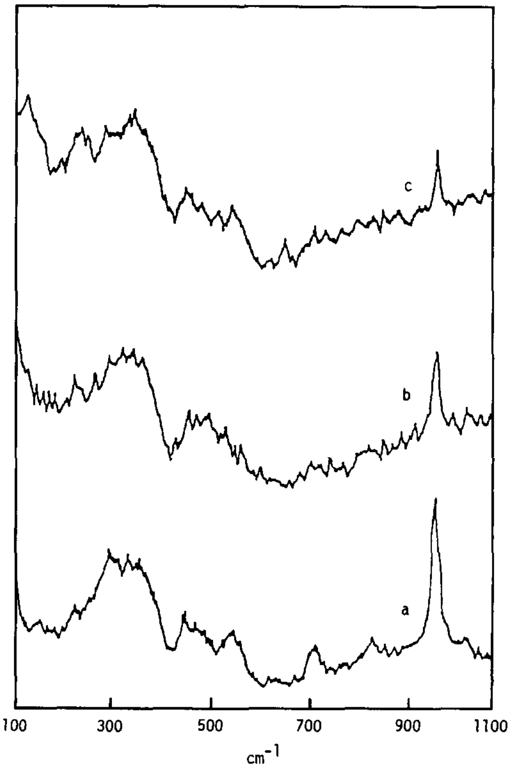

FIG. 4. Raman spectra of sulfided Co(3)Mo(10)/γ-Al_2O_3. At (a) 150°C, (b) 250°C, (c) 350°C.

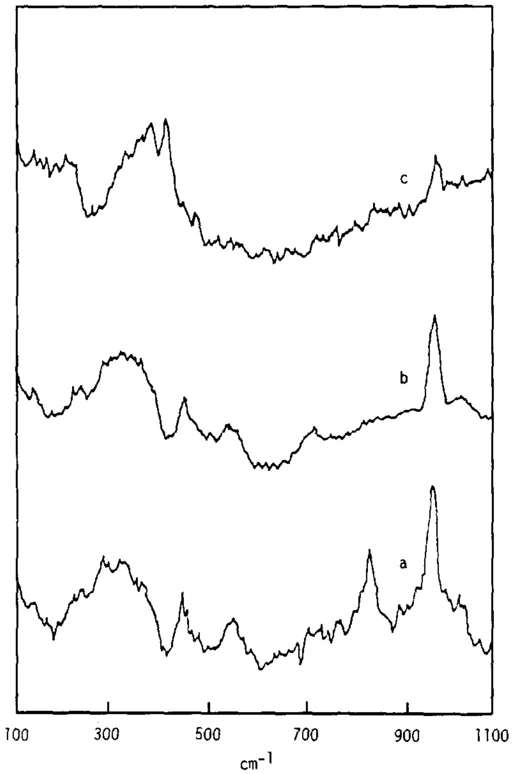

FIG. 5. Raman spectra of sulfided Co(3)Mo(15)/γ-Al_2O_3. At (a) 150°C, (b) 250°C, (c) 350°C.

resulted in important changes in the spectral features. Only a weak band in the region 440–480 cm^{-1}, which was assigned to a molybdenum–sulfur vibration (*13*), could be observed. No band is present in the 150-cm^{-1} region which was assigned to a molybdenum–oxygen vibration for Mo/γ-Al_2O_3 samples (*13*). In general, these samples appear to be more strongly reduced because of the presence of cobalt; this reduction appears to occur also at the expense of sulfiding, particularly at low temperatures. The bands due to oxysulfide species tend to weaken and broaden as sulfiding occurs at higher temperatures. At 250°C, Co_3O_4 and MoO_3 phases have been largely converted (Fig. 4b). $CoMoO_4$ is relatively unreactive at temperatures as high as 350°C. The spectrum of this catalyst at this temperature (Fig. 4c) is rather simple: the broad shoulder structures in the 400-cm^{-1} region indicate formation of some MoS_2 structures.

The oxidic form of Co(3)Mo(15)/γ-Al_2O_3 catalysts had relatively large amounts of MoO_3 present, with smaller amounts of $CoMoO_4$ and particularly Co_3O_4 (9). A weak background spectrum of aggregated molybdate species is apparent also. Sulfiding at 150°C results in a relatively complex spectrum (Fig. 5a): $CoMoO_4$ (940 cm^{-1}), MoO_3 (819, very weak 998 cm^{-1}), and molybdenum oxysulfide species are present. Reflecting the trend with the Co(3)Mo(10) sample, the bands for the oxysulfide are more distinct; the intensity of the molybdenum–sulfur vibration near 445 cm^{-1} is appreciably greater in the 150°C spectrum, compared to samples with lower molybdenum loading. Broadening occurs as higher sulfiding temperatures are used. The MoO_3 phase has been converted at 350°C (Fig. 5c). As in samples with lower molybdenum loading, $CoMoO_4$ can be detected at sulfiding temperatures as high as 350°C. Formation of MoS_2 structures at this temperature is apparent by a band at 405 cm^{-1}. Destruc-

TABLE 1

Band Positions for Stepwise Sulfiding

Sample	Region (cm^{-1})				
	0–200	201–400	401–600	601–800	801–1000
Co(3)Mo(5)					
150°C		325w,br	480w,br	690s	820w 940s 950sh
250°C		330w,br	467w 525vw		820w 940w
350°C		350m	407w		
Co(3)Mo(7.5)					
150°C		354w,br	468w,br	700m	820w 940s
250°C	135m	335w,br	466m		940s
350°C		360m,br	405m 465w		940m
Co(3)Mo(10)					
150°C		290m,br 345m,br	445w 530w	700m	821w 940s 950sh
250°C		325m,br	460w,br		940s
350°C		222w,br	407br		940m
Co(3)Mo(15)					
150°C		325w,br	445m 530m,br		819m 940s 998vw
250°C		325m,br	445m	700w	940s
350°C		370m,br	405m	700w	940m

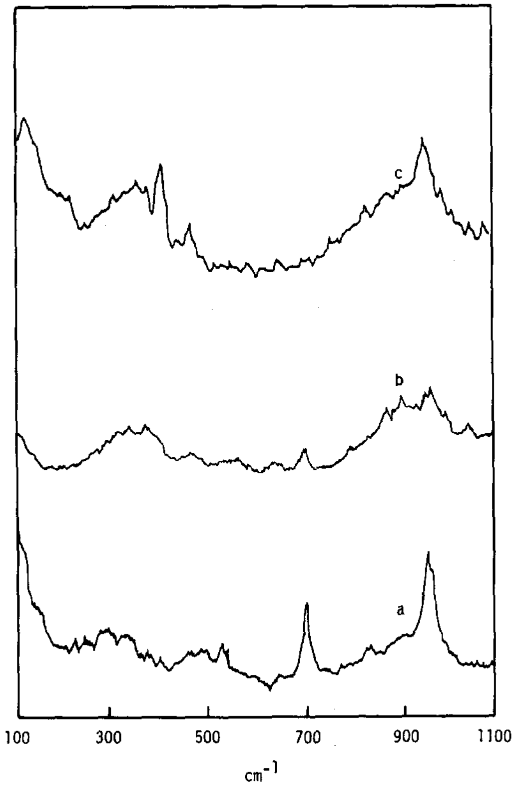

FIG. 6. Raman spectra of sulfided Co(3)Mo(5)/γ-Al_2O_3 (after exposure to air). At (a) 150°, (b) 250°C, (c) 350°C.

tion of the molybdenum oxysulfide phase occurs as higher sulfiding temperatures are used, as was reported for Mo/γ-Al_2O_3 samples.

3c. *Reoxidation of Co–Mo/γ-Al_2O_3 Catalysts Sulfided at Intermediate Temperatures*

After sulfiding up to 150, 250, and 350°C, the Co–Mo/γ-Al_2O_3 samples were exposed to air at room temperature. The Raman spectra of these samples are shown in Figs. 6–9. Band positions are summarized in Table 3. As for the sulfided samples, accumulation of up to 150 scans was necessary because of the highly colored nature of the catalysts.

TABLE 2

Sulfur Analyses for Sulfided Co–Mo/γ-Al_2O_3 Catalysts

Sample	Sulfur content (wt% sulfur)		
	150°C	250°C	350°C
Co(3)Mo(5)	1.7	1.9	2.4
Co(3)Mo(7.5)	1.7	2.0	1.8
Co(3)Mo(10)	1.6	2.0	2.1
Co(3)Mo(15)	1.7	1.8	2.4
		S/Mo	
Co(3)Mo(5)	1.5	1.7	2.1
Co(3)Mo(7.5)	1.0	1.1	1.0
Co(3)Mo(10)	0.73	0.90	0.95
Co(3)Mo(15)	0.50	0.55	0.72

In general the Raman spectra of these samples are relatively simple. The oxysulfide and MoS_2 regions of the spectra have only low intensity bands. The most prominent broad band centered near 360 cm^{-1} was previously assigned to molybde-

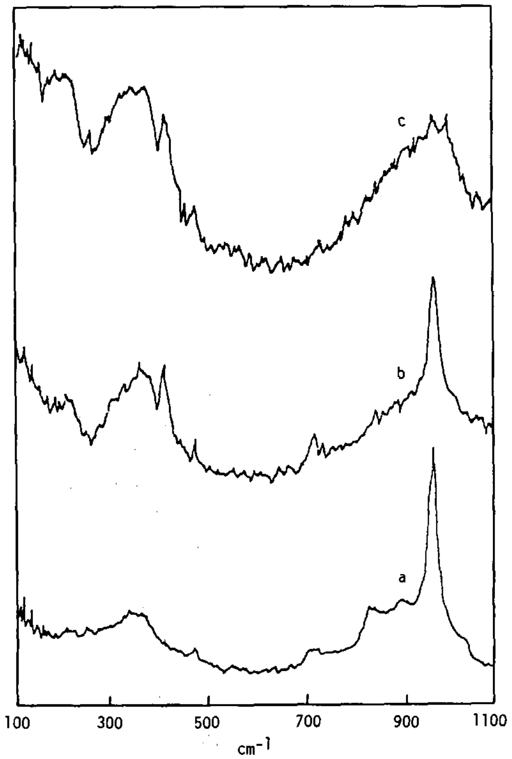

FIG. 7. Raman spectra of sulfided Co(3)Mo(7.5)/γ-Al_2O_3 (after exposure to air). At (a) 150°C, (b) 250°C, (c) 350°C.

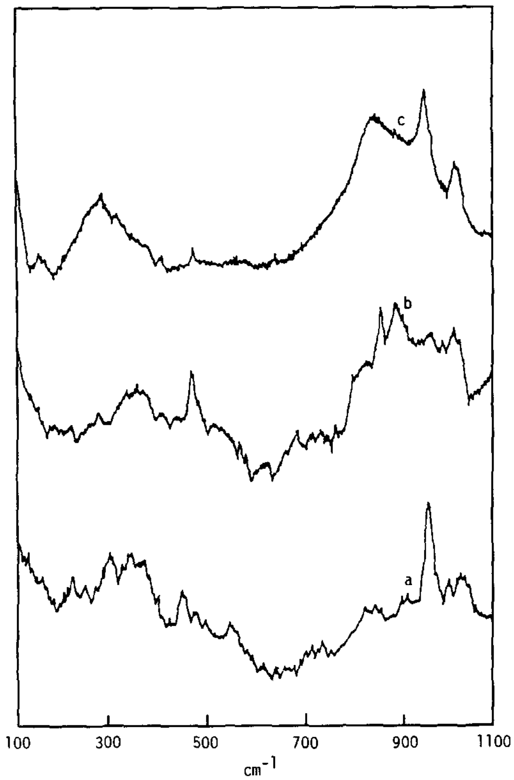

FIG. 8. Raman spectra of sulfided Co(3)Mo(10)/γ-Al_2O_3 (after exposure to air). At (a) 150°C, (b) 250°C, (c) 350°C.

num–oxygen–molybdenum bridging vibrations (*13*). For higher molybdenum loadings, molybdenum–sulfur vibrations for oxysulfide species tend to be more distinguishable near 470 cm^{-1}.

The metal–oxygen vibration region in the region 700–1000 cm^{-1} has considerably more structural information. The $CoMoO_4$ band near 940 cm^{-1} is very prominent, as it was in most sulfided spectra. There is an increase in the relative intensity of this band upon exposure to air. Bands due to MoO_3 are also apparent. While these bands were observed in the 150°C sulfided spectra, their intensity is significantly improved when samples sulfided at 250 and 350°C are exposed to oxygen. Broad Raman bands in the region 800–1000 cm^{-1} are also observed (see Fig. 8c), although the intensity of $CoMoO_4$ and MoO_3 bands obscure this region for some spectra. These spectral features are attributed to reduced molybdate phases (*13*). A Co_3O_4 band near 700 cm^{-1} can also be observed in some spectra.

4. DISCUSSION OF RESULTS

The Raman spectra of the sulfided cobalt molybdate catalysts provided information about the reduction and sulfiding of the various oxide phases. A model for the structure of sulfided Mo/γ-Al_2O_3 catalysts has been presented previously (*13*). Modifications of this model are proposed to include the effect of the presence of cobalt.

The most unreactive phase present on these catalysts was $CoMoO_4$ (a, β, or purple). At low temperatures, this phase is very persistent; this is a quite remarkable phenomenon for even the samples with the lowest loading of molybdenum. At 350°C, extensive transformation of $CoMoO_4$ occurs as indicated by the strong decrease in

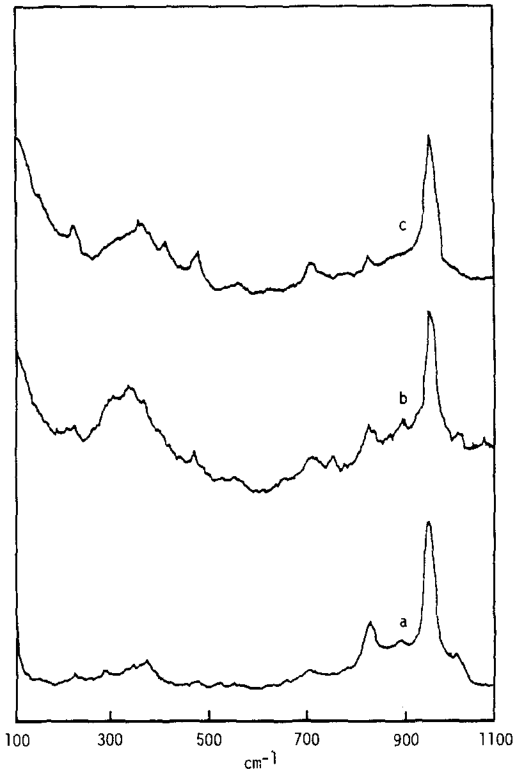

FIG. 9. Raman spectra of sulfided Co(3)Mo(15)/γ-Al_2O_3 (after exposure to air). At (a) 150°C, (b) 250°C, (c) 350°C.

TABLE 3

Band Positions after Exposure to Air

Sample	Region (cm^{-1})				
	0–200	201–400	401–600	601–800	801–1000
Co(3)Mo(5)					
150°C		300w,br	523w	690s	940s 951sh
250°C		300w,br		690w	940w
350°C		365m,br	407m		940m
Co(3)Mo(7.5)					
150°C		340,w,br	466w	700w	817m 883m 940s
250°C		219w,br 350m,br	406m 463w	700w	819vw 941s
350°C		214w,br 360m,br	405m 463w		885m,br 937m,br
Co(3)Mo(10)					
150°C		365w,br	445w	700vw	820w,br 884vw 940s 995w,br
250°C		360w,br	466w	698w	820m 881m,br 940w 995w
350°C		285m,br			819m,br 885m,br 941s 995m
Co(3)Mo(15)					
150°C			470w	690w	819s 940s 950sh 995w
250°C		350m,br	464w	700w	819m 869w,br 940s 950sh 996w
350°C		380w,br	404w 466w	700w	820m 940s 996w

intensity of the Raman band near 940 cm^{-1}. Cobalt present in this phase would not appear to be involved in the formation of intercalated or "edge-decorated" MoS_2, since for Co(3)Mo(10) and Co(3)Mo(15) samples, formation of MoS_2-like structures (surface layers) occurs before the $CoMoO_4$ Raman bands disappear. The experimental results indicate that reduction of $CoMoO_4$ is much more significant than sulfiding: reexposure to oxygen results in an almost complete recovery in the intensity of the Raman band. X-ray diffraction studies by Chung (*27*) support this conclusion: diffraction peaks due to $CoMoO_4$ disappeared after the catalyst was sulfided to 400°C for 2 h, but reappeared when the sample was reoxidized in air at 500°C.

Co_3O_4 is resistant to sulfiding at 150°C, although significant reduction occurs. A strong increase in the Raman band at 680–700 cm^{-1} due to this species occurs as 150°C samples are reexposed to oxygen. This tendency is also observed for the 250°C samples, although the trend is not easily observed for samples with higher molybdenum loadings. However, samples sulfided at 350°C show little indications of Co_3O_4, and this phase does not reappear after exposure to air. It may be possible that conversion to Co_9S_8 has occurred. X-ray diffraction studies by deBeer *et al.* (*28*) and Gajardo *et al.* (*29, 30*) have indicated the presence of Co_9S_8. However, Raman scattering from this phase is very weak, and other studies by Brown *et al.* (*6*) and Medema *et al.* (*7*) have also been unable to detect this phase.

Oxide samples with molybdenum loadings of 10 and 15% had Raman bands due to MoO_3. This phase is relatively unreactive at 150°C. At 250°C, reduction of this phase occurs; reexposure of samples to oxygen results in a reappearance of the Raman bands. At higher temperatures, conversion to MoS_2 structures is considerable. These species are quite stable to exposure to air.

In comparing the results for Mo/γ-Al_2O_3 and Co–Mo/γ-Al_2O_3 samples, the greatest differences in reduction and/or sulfiding exist for the aggregated or polymeric molybdenum phase. Previously reported results (*13*) indicated that the aggregated phase for Mo/γ-Al_2O_3 is converted largely to a complex oxysulfide. Bridging oxygen and sulfur atoms as well as vacancies are included in this model. Reduction of the sample also results in some molybdenum–molybdenum bonding. Exposure of these samples to oxygen results in a loss of sulfur bonding but only a slow reincorporation of oxygen. The Raman results indicated that the reduced phases were remarkably stable at room temperature. The presence of cobalt has a significant effect on the nature of the oxysulfide phase. (See Ref. (*13*) for a comparison with Mo/γ-Al_2O_3 samples. In general, the spectra of Co–Mo/γ-Al_2O_3 samples reported in this paper are most clearly understood by the absence of bands which were present for Mo/γ-Al_2O_3 samples.) In general, the intensity of both bridging sulfur (440–445 cm^{-1}) and oxygen (150, 380 cm^{-1}) bands is decreased. Bands due to sulfur–sulfur vibrations appear to be less affected, particularly bands in the 540-cm^{-1} region which are due to more reduced oxysulfide phases. The major effect of cobalt, therefore, is to increase the reduction of the oxysulfide phase. In fact, the spectra of the sulfided Co–Mo/γ-Al_2O_3 catalysts are more similar to the spectra of the reduced (rather than sulfided) Mo/γ-Al_2O_3 catalysts (*13*). The spectra of cobalt molybdate catalysts which are reexposed to air also indicate an increased state of reduction for the oxysulfide phase. The Raman spectrum in the region 800–1000 cm^{-1} for 250°C samples after exposure to air is particularly informative. A complex band structure is observed, as opposed to the rather broad feature (halfwidth of 100 cm^{-1}) present (*13*) in the spectrum of Mo/γ-Al_2O_3 samples (or as observed at 350°C for Co–Mo/γ-Al_2O_3 samples). The appearance of this region of the spectrum is generally similar to that of reduced molybdenum oxides including MoO_2 and shear structure compounds such as Mo_4O_{11} and $Mo_{17}O_{47}$ (*31*). These phases are ultimately converted to sulfided phases at higher temperatures, although reexposure to air indicates that some reduced phases are present for the higher temperature samples. Nevertheless, there has been a considerable change in the structure of the reduced phases. These phases are probably strongly influenced by the development of MoS_2-like phases, e.g., there has been an increased rate of sulfiding compared to reduction at 350°C.

In addition to increasing the reduction of the oxysulfide species, the presence of cobalt seems to affect the formation of MoS_2 structures. Only very weak bands due to MoS_2 were observed for the 350°C cobalt molybdate samples; this is in marked contrast to the Mo/γ-Al_2O_3 results, particularly for higher loadings of molybdenum (*13*). Cobalt appears to be able to break up or prevent the formation of crystalline MoS_2. DeBeer (*26*) suggested that cobalt caused the formation of smaller crystallites of MoS_2, allowing easier intercalation of cobalt. Based on the Raman spectra of the oxysulfide species at 150 and 250°C, however, it is also possible that the increased rates of reduction, compared to sulfiding, may inhibit the formation of MoS_2. Under similar stepwise sulfiding conditions, therefore, MoS_2-like structures would be formed for Mo/γAl_2O_3 catalysts whereas for the Co–Mo/γ-Al_2O_3 system, reaction proceeds to the extent of considerable reduction, but only partial sulfiding. This results in the formation of a precursor phase which is converted to more distinct MoS_2-like structures only at 350–400°C.

REFERENCES

1. Massoth, F. E., "Advances in Catalysis and Related Subjects," Vol. 27, p. 265. Academic Press, New York, 1978.
2. Massoth, F. E., and MuraliDhar, G., *in* "Hydrodesulfurization Catalysis," Proceedings, Fourth Int. Conf. Chem. and Uses of Molybd. (H. Barry, Ed.). Climax Molybdenum Co., Golden, Colorado, 1982.
3. Villa, P. L., Trifiro, F., and Pasquon, I., *React. Kinet. Catal. Lett.* **1,** 341 (1974).
4. Brown, F. R., and Makovsky, L. E., *Appl. Spectrosc.* **31,** 44 (1977).
5. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50,** 162 (1977).
6. Brown, F. R., Makovsky, L. E., and Rhee, K. H., *J. Catal.* **50,** 385 (1977).
7. Medema, J., van Stam, C., deBeer, V. H. J., Konigs, A. J. A., and Konigsberger, D. C., *J. Catal.* **53,** 386 (1978).
8. Jeziorowski, H., and Knozinger, H., *J. Phys. Chem.* **83,** 1166 (1979).
9. Cheng, C. P., and Schrader, G. L., *J. Catal.* **60,** 276 (1979).
10. Wang, L., and Hall, K. W., *J. Catal.* **66,** 251 (1980).
11. Zingg, D. S., Makovsky, L. E., Tischer, R. E.,

Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84,** 2898 (1980).

12. Schrader, G. L., and Cheng, C. P., *J. Phys. Chem.,* **87,** 3675 (1983).

13. Schrader, G. L., and Cheng, C. P., *J. Catal.* **80,** 369 (1983).

14. Cirillo, A. C., Dollish, F. R., and Hall, W. K., *J. Catal.* **62,** 379 (1980).

15. Hall, W. K., *in* "The Genesis and Properties of Molybdena-Alumina and Related Catalyst Systems," Proceedings, Fourth Int. Conf. Chem. and Uses of Molybd. (H. Barry, Ed.). Climax Molybdenum Co., Golden, Colorado, 1982.

16. Stork, W. H. J., Coolegem, J. G. F., and Pott, G. T., *J. Catal.* **32,** 497 (1974).

17. Harrell, D. G., and Schrader, G. L., unpublished results.

18. Chien, F. Z., Moss, S. C., Liang, K. S., and Chianelli, R. R., *J. Phys.* (Orsay, Fr.) **42,** C4-273 (1981).

19. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Mørup, S., *J. Catal.* **68,** 433 (1981).

20. Wivel, R., Candia, R., Clausen, B. S., Mørup, S., and Topsøe, H., *J. Catal.* **68,** 453 (1981).

21. Kolboe, S., and Amberg, C. H., *Canad. J. Chem.* **44,** 2623 (1966).

22. DeBeer, V. H. J., van der Aalst, M. J. M., Machiels, C. J., and Schuit, G. C. A., *J. Catal.* **43,** 78 (1976).

23. Gissy, H., Bartsch, and Tanielian, C., *J. Catal.* **65,** 150 (1980).

24. Cheng, C. P., Ludowise, J. D., and Schrader, G. L., *Appl. Spectrosc.* **34,** 146 (1980).

25. Massoth, F. E., *J. Catal.* **30,** 204 (1973).

26. DeBeer, V. H. J., Ph.D. thesis, Eindhoven University of Technology, Eindhoven, Netherlands, 1975.

27. Chung, K. S., Ph.D. thesis, University of Utah, Salt Lake City, Utah, 1979.

28. DeBeer, V. H. J., Bevelander, C., van Sint Fiet, T. H. M., Werter, P. G. A., and Amberg, C. H., *J. Catal.* **43,** 68 (1976).

29. Gajardo, P., Grange, P., and Delmon, B., *J. Phys. Chem.* **83,** 1771 (1979).

30. Gajardo, P., Grange, P., and Delmon, B., *J. Phys. Chem.* **83,** 1779 (1979).

31. McCormick, R. L., and Schrader, G. L., submitted for publication.