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In Situ Laser Raman Spectroscopy of the Sulfiding of $Mo/\gamma\text{-}Al_2O_3$ Catalysts

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Raman spectra of sulfided $Mo/\gamma\text{-}Al_2O_3$ catalysts were obtained using *in situ* techniques for two sulfiding methods. For samples sulfided by 10% H_2S/H_2 at 400°C, MoS_2 structures were observed. A stepwise sulfiding using 10% H_2S/H_2, with spectra recorded at 150, 250, and 350°C, resulted in observation of molybdenum oxysulfide, reduced molybdate, and surface "MoS_2" phases. Reexposure of these samples to air led to radical modification of the oxysulfide structures as well as transformation of some sulfide phases. A model incorporating terminal and bridging Mo–S bonding and anion vacancies is proposed. This model is based on the conversion of isolated and aggregated molybdate and MoO_3 species to oxysulfide and reduced molybdenum phases. Conversion of reduced molybdenum phases to sulfides is observed to be slow.

1. INTRODUCTION

Cobalt molybdate hydrodesulfurization catalysts are typically prepared by the impregnation of an alumina support with aqueous solutions of molybdenum and cobalt salts. Calcination of these materials results in the formation of a complex metal oxide catalyst precursor, which has been extensively characterized by spectroscopic techniques. During activation and use for hydrodesulfurization, the catalyst becomes sulfided. Fewer studies of the sulfided form of the catalyst have been performed: Crucial questions concerning the extent of sulfidation and the structure of the "sulfides" remain. Various proposed models for the sulfided catalyst presume the existence of oxysulfide species, but little direct experimental evidence for such compounds has been reported previously.

The sulfided state of cobalt molybdate catalysts is highly reactive, and careful experimental models and *in situ* spectroscopic techniques are necessary. Kolboe and Amberg (*1*) demonstrated that freshly prepared samples of MoS_2 reacted with oxygen at room temperature, resulting in a temporary increase in hydrodesulfurization activity. De Beer *et al.* (*2*) also reported a similar effect for freshly sulfided $Mo/\gamma\text{-}Al_2O_3$ and $Co\text{–}Mo/\gamma\text{-}Al_2O_3$ catalysts, as did Gissy *et al.* (*3*). Sulfided catalysts which have been exposed to air are likely to differ from the actual state of the functioning catalyst. Laser Raman techniques are well suited for performing *in situ*, studies of hydrodesulfurization catalysts. There is no inherent limitation on the temperatures or pressures at which spectra may be obtained, and samples may be in the form of pellets or powders. Reactive gases may also be present in the sample cell.

The Raman technique has provided considerable information about the nature of the oxide form of hydrodesulfurization cat-

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alysts (*4–12*). Characterization of the fully sulfided form of the catalyst has also been performed (*5, 7, 13*). Chang and Chan (*14*) reported Raman spectra of molybdenum sulfide compounds which may be important in hydrodesulfurization catalysis. The Raman technique is highly sensitive to the composition and structure of oxidic and sulfided cobalt molybdate hydrodesulfurization catalysts.

In order to develop a better understanding of the ultimate sulfided form of the catalyst, Raman studies of the oxide-to-sulfide conversion were performed after various sulfiding procedures. These studies were performed *in situ* in order to avoid sample decomposition by exposure to air.

2. EXPERIMENTAL METHODS

Raman 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 approximately 200 mW (measured at the source) for the 488.0-nm line. A spectral resolution of 5 cm^{-1} was used for all studies. Photon-counting detection was used exclusively. A Nicolet 1180 data system permitted spectral accumulation and routine data processing.

A rotating controlled-atmosphere cell was used to obtain *in situ* spectra (*15*). Another cell using rotary vacuum couplings has also been used for similar studies. Catalysts were prepared according to previously described methods (*10*). The dry impregnation technique involves impregnation of a γ-Al_2O_3 support (BHD Chemicals, 101 m^2/g) with solutions of ammonium heptamolybdate [$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$] (Fischer Scientific Co.). Drying was performed at 110°C for 4 h; calcining occurred at 500°C for 6 h. Molybdenum loadings included 5, 7.5, 10, and 15 wt% expressed as MoO_3.

Sulfiding of the dried and calcined catalysts was performed within the controlled-atmosphere cell. Samples were pressed into 13-mm-diameter disks and inserted into the rotating pellet holder. The apparatus was then purged with helium at room temperature. Two different procedures were employed from the sulfiding process. The first procedure has been used by other researchers (*16, 17*). Samples were heated under helium (60 ml/min) to 400°C for 1 h. The gas stream was then switched to a mixture of 10% H_2S/H_2 (60 ml/min) for the desired duration (5 min to 2 h). The flow was changed to helium, and the Raman spectra were recorded. For some samples, 150 scans were accumulated. The second procedure involved heating samples slowly at a controlled rate and then recording spectra at intermediate temperatures. Following the initial helium purge, the gas flow was switched 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. When the desired temperature was attained (150, 250, 350°C), the flow of H_2S/H_2 mixture was stopped. A helium flow was again introduced, followed by cooling the sample to room temperature and recording of the Raman spectrum. Up to 150 scans were required for some samples because of the black color of the compounds and their poor scattering properties.

Sulfur analyses of the samples were performed by dissolving samples with aqua regia followed with a sulfate determination using barium chloride. Analyses were confirmed by Galbraith Laboratories. Analyses had a reproducibility of ±0.1 wt% sulfur (absolute). Molybdenum analyses were determined by air-firing.

In order to determine the relative stabilities of samples and to observe any structural and compositional transformations, samples were examined after exposure to air for at least an hour at room temperature. Spectra were recorded using a spinning sample holder.

3. EXPERIMENTAL RESULTS

The studies of sulfided catalysts were based on preparation techniques for the dried and calcined catalysts discussed pre-

TABLE 1

Vibrational Spectra of Model Compounds (cm^{-1})

	0–200	201–400	401–600	601–800	801–1000
MoO$_3$[a]	84w 100w 117m 130m 159m 198vw	219vw 246w 285m 293m 338w 356vw 369v	472vw	668w 711vw 775vw	821s 849w 996m
MoO$_2$[a,b]	135s	206s 348m 363m	440w 462w 498w	708s	822m 880w 890w 940w
(NH$_4$)$_6$Mo$_7$O$_{24}$ · 4H$_2$O[a]	115m 135m 199m	224m 252m 308w 339w 363m 375m	543m 570w	625w 633w	863sh 888m 893m 908sh 920s 938s
MoS$_2$[a]		224w 287w 384s	410s 468w		
MoS$_3$[c]	215	317	431 528		
(MoS$_2$)$^{-2}$[d] (T$_d$)	184		458 472		
(OMoS$_3$)$^{-2}$[e] (C$_{3v}$)	183 263		461 470		862 862
(O$_2{}^{92}$MoS$_2$)$^{-2}$[f] (C$_{2v}$)		200 246 267	473 506		801 819
(O$_3$MoS)$^{-2}$[g] (C$_{3v}$)	239	314 331	475		833 822
Na$_2$Mo$_2$O$_2$S$_2$(EDTA)[h] (μ − S)			480		944 950
Na$_2$Mo$_2$O$_3$S(EDTA)[h] (μ − S)			461 483	756	941 957
((S$_2$)$_2$Mo(S$_2$)$_2$Mo(S$_2$)$_2$)$^{-2}$[i] (μ − S and ν − S)		340 360	530		
(Mo$_2$O$_2$S$_2$(C$_2$O$_2$S$_2$-1,2)$_2$)[j] (μ − S)			530		930

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[a] This work.

[b] See Ref. (*20*): this reference reports no band at 708 cm^{-1}, but rather a strong band at 741 cm^{-1}.

[c] See Refs. (*14, 21*).

[d] See Ref. (*22*).

[e] See Ref. (*23*).

[f] See Ref. (*24*).

[g] See Ref. (*25*).

[h] See Ref. (*26*): partial spectra reported only; other samples of sulfur bridging compound provided in this article.

[i] See Ref. (*27*): partial spectrum reported only.

[j] See Ref. (*28*): partial spectrum reported only.

viously (*10*). The Raman spectra of the oxidic samples indicated that at low loadings of molybdenum, an aggregated or polymeric molybdate phase existed. The degree of aggregation was dependent on the loading of molybdenum: "isolated" molybdate species may exist at very low loadings while large "rafts" of molybdate structures exist at higher loadings. Formation of multilayers of molybdenum oxide species has also been indicated by Raman studies of pyridine adsorption (*18, 19*). This may occur prior to complete coverage of the alumina surface. At higher coverages of molybdenum (Mo(7.5) for this particular surface area alumina), formation of molybdenum trioxide is apparent.

The Raman spectra of the sulfiding of Mo/γ-Al_2O_3 samples are reported here for both methods of sulfiding. The vibrational spectra of model compounds used in data interpretation are given in Table 1.

(*a*) *Mo/γ-Al_2O_3 Catalysts Sulfided at 400°C*

A typical procedure for sulfiding Mo/γ-Al_2O_3 catalysts consists of heating the sample up to 400°C under helium for 1 h, followed by passing a mixture of 10% H_2S/H_2 over the sample for 2 h. The spectra of all catalysts prepared in this manner showed bands at 225(m), 291(w), 385(m), and 407(s) cm^{-1}. These bands are very similar to those reported for MoS_2, although broadening is apparent as well as some slight shifting of band positions. No Raman bands attributable to any other species could be detected in these spectra. Spectra were also recorded after very brief exposure to the H_2S/H_2 mixture. The *in situ* spectra of Mo(5)/γ-Al_2O_3 and Mo(15)/γ-Al_2O_2 sulfided for 5 and 15 min are shown in Fig. 1. Weak bands at 385 and 407 cm^{-1} are observed after 5 min; after 15 min of sulfiding, spectra similar to those for 2-h samples are observed.

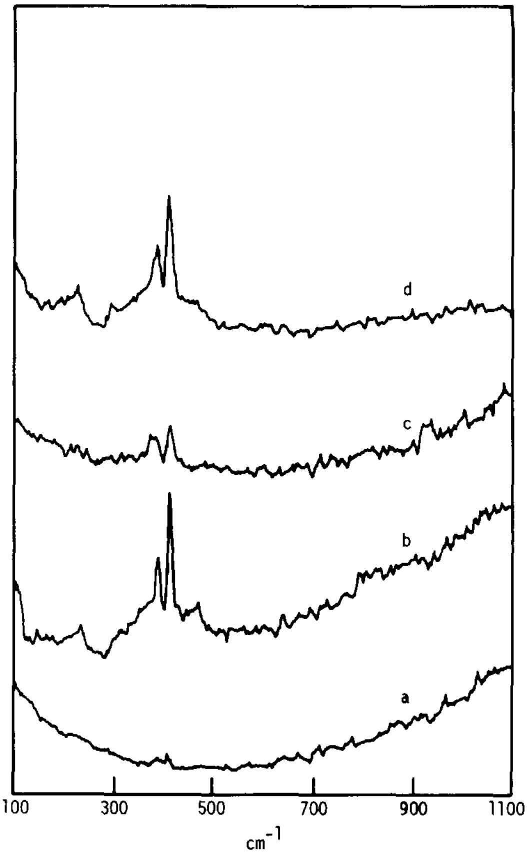


FIG. 1. Raman spectra of Mo/γ-Al_2O_3 sulfided at 440°C. (a) Mo(5) sulfided for 5 min; (b) Mo(5) sulfided for 15 min; (c) Mo(15) sulfided for 5 min; (d) Mo(15) sulfided for 15 min.

Mo/γ-Al_2O_3 samples sulfided for 2 h at 400°C were relatively stable to air as indicated by very little change in their Raman spectra upon exposure to the atmosphere. Such treatment apparently involves extensive formation of MoS_2 which has some resistance to oxygen. In general, the crystallinity of the MoS_2 (indicated by the sharpness of the Raman bands) increased for prolonged sulfiding, particularly for samples with high molybdenum loadings.

However, exposing samples sulfided for less than 2 h to air resulted in drastic alteration of the Raman spectra (Fig. 2). Complete destruction of MoS_2 is apparent for samples which had been sulfided for 5 min. For low loadings, broad bands appear in the regions 200–400 cm^{-1} and 800–1000 cm^{-1}. These bands are typical of reduced molybdenum oxide species (*29*). Similar bands appear in the Mo(15) spectrum, in addition

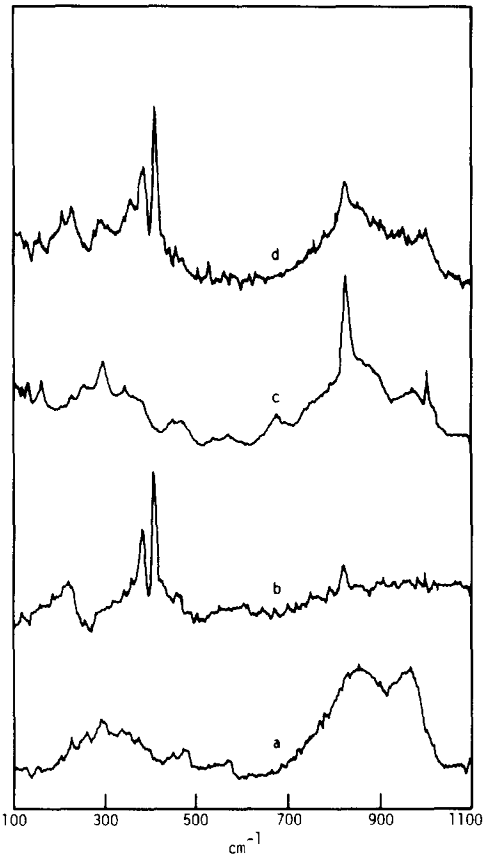


FIG. 2. Raman spectra of Mo/γ-Al_2O_3 sulfided at 400°C after exposure to air. (a) Mo(5) sulfided for 5 min; (b) Mo(5) sulfided for 15 min; (c) Mo(15) sulfided for 5 min; (d) Mo(15) sulfided for 15 min.

to MoO_3 bands which were the dominant bands in the initial oxide spectrum. For Mo(5) samples which have been sulfided for 15 min, exposure to air also results in a band appearing near the most intense peak of MoO_3. The spectrum of MoO_3 is much more apparent for the Mo(15) sample.

The chemical and physical transformations for these different molybdenum loadings as indicated by the spectra are quite distinct. Sulfiding of Mo(5) samples appears to be slower because of the presence of polymeric molybdate species. The surface polymolybdate phase in these samples is resistant to sulfiding but apparently not as resistant to reduction. Results for Mo(15) indicate that MoO_3 is relatively easily sulfided at this temperature. As MoS_2 is formed on these samples, structural rearrangement occurs: Larger crystallites of MoS_2 result at higher loadings of molybdenum. MoS_2 formed at brief time periods (apparently from MoO_3) for these higher loadings can be relatively rapidly reoxidized to MoO_3; however, MoS_2 produced at longer sulfiding periods is more stable. Exposure of sulfided Mo(5) samples to air results in the uptake of oxygen by reduced molybdate species; for longer sulfiding periods, reoxidation tends to result in the formation of MoO_3.

Calcination of these samples at 400°C in oxygen was also performed. Irreversible changes in the Raman spectra were observed. In general, the degree of polymerization of the surface species increased as indicated by the high-wavenumber band shifts for Mo(15) from 920 and 970 cm^{-1} to 940 and 980 cm^{-1} (assigned to the polymo-

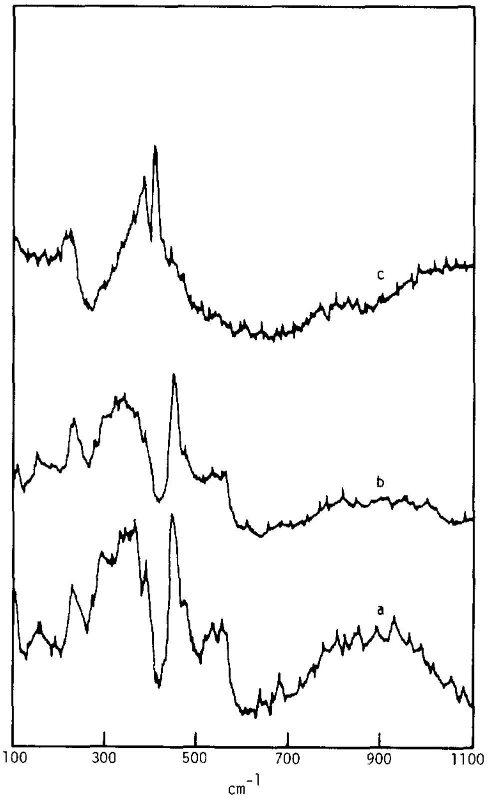


FIG. 3. Raman spectra of sulfided Mo(5)/γ-Al_2O_3. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

lybdate phase (*10*)). Relatively larger amounts of MoO_3 were formed.

(*b*) *Mo/γ-Al_2O_3 Catalysts Sulfided at Intermediate Temperatures*

In order to better understand the mechanism of oxide-to-sulfide conversion, a stepwise sulfiding operation was performed. Intermediate molybdenum compounds and structures may be thermodynamically unstable at 400°C, and rapid conversion to MoS_2 may predominate.

The *in situ* Raman spectra of Mo(5), Mo(7.5), Mo(10), Mo(15) (MoO_3) on γ-Al_2O_3 at temperatures of 150, 250, and 350°C are shown in Figs. 3–6. The band positions are summarized in Table 2, and the compositions of these samples are provided in Table 3. Samples sulfided at 100°C had very poor Raman spectra: The white, oxidic catalysts quickly blackened after exposure to H_2S/H_2. All spectra represent accumulations of up to 150 scans. The spectra are complex, particularly at the lower temperatures. However, molybdenum oxides, reduced molybdenum oxides, molybdenum oxysulfide, and molybdenum sulfide species are revealed by these spectra.

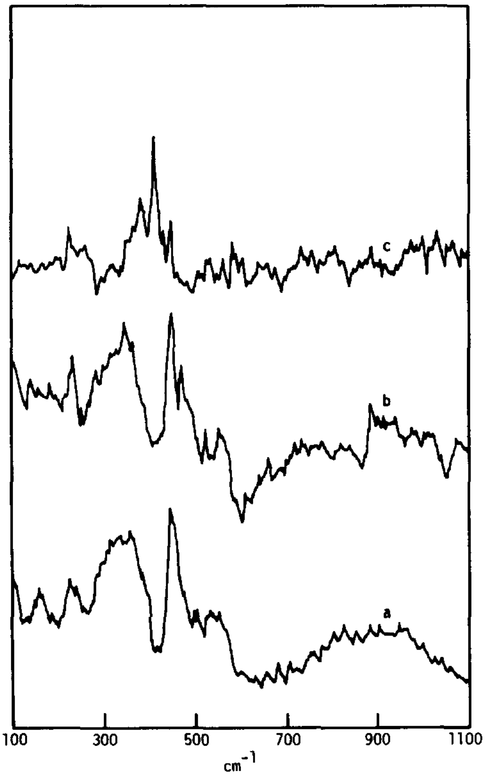


FIG. 4. Raman spectra of sulfided Mo(7.5)/γ-Al_2O_3. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

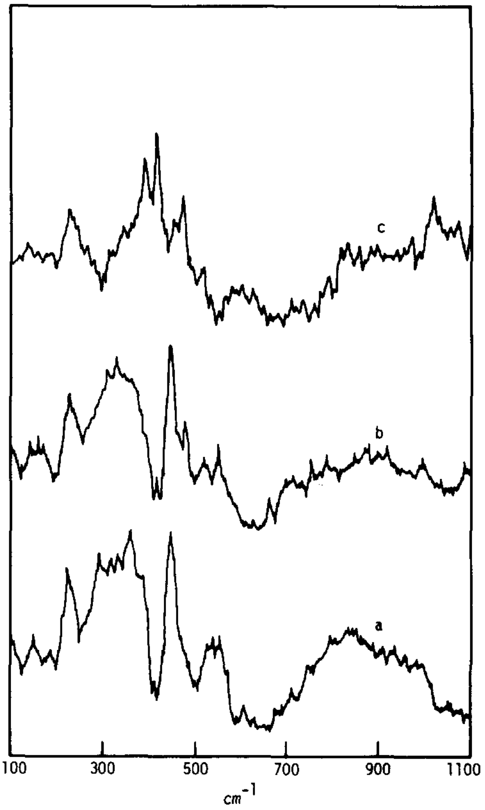


FIG. 5. Raman spectra of sulfided Mo(10)/γ-Al_2O_3. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

A broad band in the region of the spectrum 700–1000 cm^{-1} is observed in samples sulfided at 150°C. This band is not due to fluorescence; rather, it is indicative of a partially reduced molybdenum oxide species. Similar results are obtained if dehydrated ammonium heptamolybdate is reduced in hydrogen (*29*). Broad, weak bands are also apparent in the region 100–400 cm^{-1} of these types of samples. In general, the bands in the region 800–1000 cm^{-1} are rather weaker than might be expected. Re-

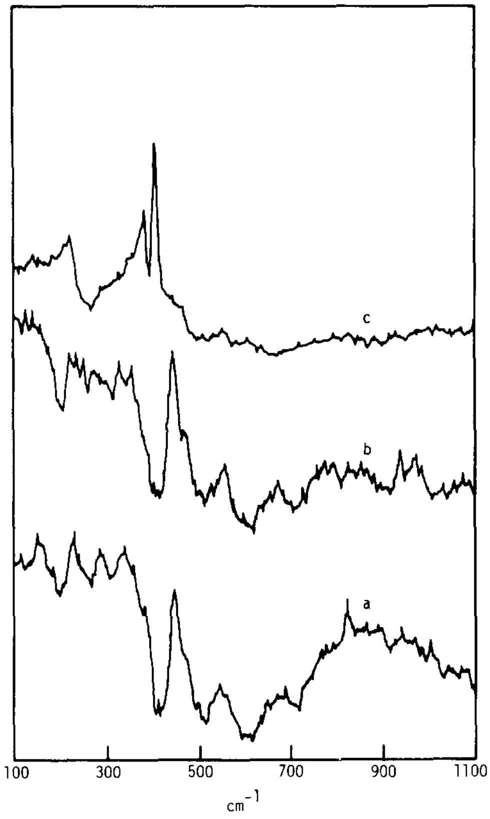


FIG. 6. Raman spectra of sulfided Mo(15)/γ-Al_2O_3. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

duction of the polymeric surface molybdate species probably results in the development of some oxygen vacancies. This is consistent with the low reactivity toward sulfiding. At higher (Mo(15)) molybdenum loadings, a residual MoO_3 band is observed at 815 cm^{-1} (Fig. 6). The oxidic form of these catalysts contained large amounts of MoO_3—a very strong Raman scatterer.

A complex, yet very reproducible, band structure is observed in the region 200–600 cm^{-1}. Oxysulfide species typically have strong bands in this region. The general band positions in this region are remarkably similar for all loadings of molybdenum. The bands may be grouped into regions of 500–550 cm^{-1}, 440–480 cm^{-1}, 300–400 cm^{-1}, and 220–230 cm^{-1}.

The bands appearing at 440–480 cm^{-1} (and particularly at 440–445 cm^{-1}) are the dominant bands appearing in these spectra. The most intense band (442–445 cm^{-1}) undergoes a slight shift to higher frequencies as higher sulfiding temperatures are employed. The position of the higher-wavenumber band (about 465 cm^{-1}) is relatively unperturbed as temperatures are increased; however, there generally appears to be an increase in intensity at higher temperatures. These bands are assigned to metal–sulfur vibrations for oxysulfide species. Model compounds (see Table 1) have bands in similar positions, and the bands are attributed to bridging Mo–S–Mo species for reduced molybdenum compounds or Mo^{6+} oxysulfide species. The general upward shift of the lower band is indicative of increased sulfur coordination. Spectra of oxysulfide compounds should also have bands in the region 800–1000 cm^{-1}: near 830–880 cm^{-1} for $O_xMoS_{4-x}^{2-}$ species and near 730–760 cm^{-1} and 930–960 cm^{-1} for bridged species. As previously discussed, broad bands are present in the region of the spectrum 800–1000 cm^{-1}, but these bands are more characteristic of reduced molybdenum oxide species. The 440 to 480-cm^{-1} bands are therefore due to molybdenum–sulfur vibrations for more highly reduced samples. Oxygen "vacancies" are likely to exist for such samples. If molybdenum–oxygen bands are present, they are likely to be associated with the alumina surface (Mo–O–Al). These bands, however, are very weak in the Raman spectrum (*10*). As sulfiding temperatures increase, sulfur is introduced into the coordination vacancies, and increased Mo–S–Mo bridge bonding results. This interpretation is consistent with the conception of a surface molybdate phase whose chemistry is strongly affected by the presence of alumina. However, disruption of the initial polymeric oxide surface structure is likely to result at higher sulfiding temperatures.

Bands in the region 500–550 cm^{-1} are present in all spectra. The bands are broad, and their position varies somewhat depending on the temperature and loading of the sample. These bands are all in the region of S–S vibrations as indicated by spectra for $Mo_2O_2S_2(S_2)_2^{2-}$ and $Mo_2(S_2)_6^{2-}$. Analogous Raman bands have been reported for solid-state compounds such as MoS_3 where S–S bonding occurs (*14*, *21*). S–S bonding could exist at the edges of surface polymolybdate

TABLE 2

Band Positions for Stepwise Sulfiding (cm^{-1})

Sample	0–200	201–400	401–600	601–800	801–1000
Mo(5)					
150°C	154w	225m 289m 330 } m 360 } br 385m	442s 469w 525w 550w		800–1000m,br
250°C	150w	225m 290 } m 335 } br 381w	446s 464w 526w 557w		800–1000m,br
350°C		217m 358w 398m	405s 438w		
Mo(7.5)					
150°C	152w	225m 290 } 317 } m 334 } br 356 } 379 }	443s 463sh 521w 556w		800–1000m,br
250°C	152w	226m 305 } 327 } m 362 }	445s 462s 475m 520w 548w		800–1000m,br
350°C		320 } m 350 } 384w	407w 442s 465sh		
Mo(10)					
150°C	154w	220w 335 } m 357 } 380w	441s 462sh 526w 549w		800–1000m,br
250°C		225m 341 } m 362 }	444s 465m 518w 544w		800–1000w,br
350°C		219m 380m	405s 433m 520w 568w		

TABLE 2—*Continued*

Sample	0–200	201–400	401–600	601–800	801–1000
Mo(15)					
150°C	150m	228m 285m 329m 360sh 381w	441s 461sh 535w		800–1000m,br
250°	141 161 } w	221m 327 358 } m 381sh	444s 463m 550w		800–1000w,br
350°C		222m 384m	407s 448w 467w		

species which have been partially sulfided. The position of these bands is related to the oxidation state of the molybdenum and to the presence of oxygen vacancies. Bands shifted to high wavenumbers (540–550 cm^{-1}) are probably due to more reduced species. As the temperature of the sulfiding increases, the lower-wavenumber band is reduced in intensity as sulfided polymolybdate species are converted to molybdenum sulfide structures.

The region of the spectrum 200–400 cm^{-1} is complex: Bands for Mo–O–Mo and Mo–S–Mo bridging bonds are observed in this region. A band at 380 cm^{-1} is particularly informative. In all spectra, this band is observed to decrease in intensity as the sulfiding temperature increases; the band is only apparent as a shoulder in the 250°C spectra. Bridging Mo–O–Mo bonds for oxysulfide species typically have bands in this region. As these oxygens in the partially sulfided polymolybdate surface species are replaced by sulfur, the intensity of the 380-cm^{-1} band decreases. Bands present in the lower range of this region are also attributable to molybdenum–oxygen bonds (for reduced molybdates and oxysulfide compounds) and molybdenum–sulfur bonds (for oxysulfide compounds). Spectra of reduced molybdates (*29*) have bands below 200 cm^{-1}; metal–oxygen vibrations in oxysulfides generally appear above 300 cm^{-1}.

TABLE 3

Composition of Stepwise-Sulfided Samples

Sample	Sulfur content (wt% sulfur)		
	150°C	250°C	350°C
Mo(5)	0.99	1.3	1.3
Mo(7.5)	1.4	1.6	1.6
Mo(10)	1.6	2.0	2.3
Mo(15)	1.6	1.8	2.3
	S/Mo ratio		
Mo(5)	0.89	1.2	1.2
Mo(7.5)	0.84	0.98	1.0
Mo(10)	0.72	0.92	1.0
Mo(15)	0.49	0.54	0.70

One characteristic band appears at about 150 cm^{-1}. This band is attributable to a molybdenum–oxygen vibration, whose intensity parallels that of the 380-cm^{-1} band. Assignment is made to bridging oxygens in partially sulfided polymolybdate species.

The Raman spectra of samples sulfided at temperatures up to 350°C are remarkably simpler. The most intense bands in these spectra are close to the 410- and 384-cm^{-1} bands of MoS_2. However, some slight shifts and band broadening are observed. The broadness of the bands for the Mo(5) and

Mo(7.5) spectra is very distinctive. These spectral qualities are reproducible, and do not simply reflect a poor signal intensity. Up to 300 scans of these samples resulted in little alteration of bandwidth. Recent Raman results which we have obtained for disordered MoS_2 samples indicate that such spectra are typical of disordered structures. This disorder may be due to a displacement or rotation of MoS_2 layers (*30*). The Raman spectra of the 350°C samples also have a rather broad background in the 225-cm^{-1} region. This feature is attributed to a residual reduced oxysulfide species—maintained, perhaps, because of interaction with the support.

The sulfur analyses of these samples indicate clearly a S/Mo ratio of less than 2. Both the stoichiometry and the Raman spectra would imply that conversion to MoS_2 is incomplete: Only a very few layers of MoS_2-like structures exist on the surface. The minimum number required by the Raman spectrum is probably two. Samples with the lowest loading of molybdenum clearly showed bands for MoS_2. This may be due to a greater reactivity of isolated molybdate species to sulfiding compared to a greater reactivity of polymolybdate species to reduction.

(*c*) *Reoxidation of Mo/γ-Al_2O_3 Catalysts Sulfided at Intermediate Temperatures*

The Raman spectra of Mo(5), Mo(7.5), Mo(10), and Mo(15) (MoO_3) which have been sulfided at various temperatures and then exposed to air at room temperature for at least 1 h are shown in Figs. 7–10. The band positions are summarized in Table 4. Many of the bands in these spectra are quite broad even after accumulation of up to 150 scans. In general, fewer bands are apparent in the spectra of the reoxidized samples, compared to the partially sulfided samples. The majority of bands which are absent were attributed to oxysulfide species.

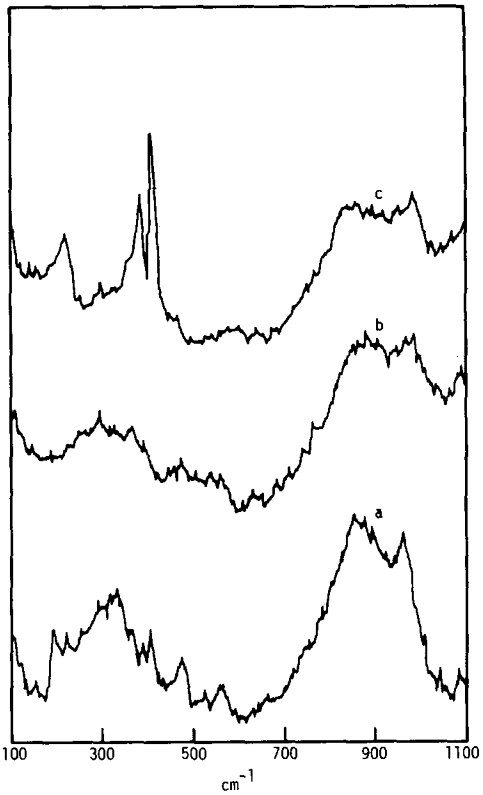


FIG. 7. Raman spectra of sulfided Mo(5)/γ-Al_2O_3 after exposure to air. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

The spectra of 150°C and 250°C samples have two characteristic regions of bands: 200 to 400 cm^{-1} and 800 to 1000 cm^{-1}. These broad bands are also present in the spectra of the partially sulfided samples, being more evident in the 150°C spectra. The bands in these regions have been assigned to reduced molybdenum oxide species. The similarity of the bands to those in the spectra of partially sulfided samples (although the bands appear to have lower intensity in the sulfided spectra due to the presence of other more intense bands) indicates that a portion of the reduced oxides reoxidizes slowly. However, it is clear from the spectra that some sharper bands result from the reoxidation process, particularly at the 820- and 1000-cm^{-1} regions. These regions are characteristic for MoO_3. For higher loadings of molybdenum, MoO_3 was very apparent in the spectra of the oxidic precursor, and these bands clearly emerge

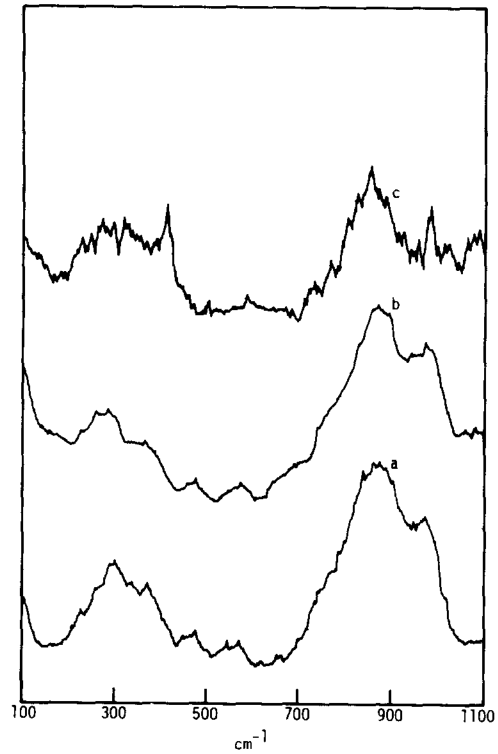


FIG. 8. Raman spectra of sulfided Mo(7.5)/γ-Al_2O_3 after exposure to air. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

as the samples are reoxidized. Moreover, even samples with lower loadings of molybdenum have bands similar to MoO_3. The oxide–sulfide–oxide transformation therefore involves some conversion of polymolybdate species to MoO_3.

Raman bands attributed to oxysulfide species are strongly reduced in intensity by exposure to air. The 440- to 445-cm^{-1} band which was very dominant in the sulfided spectra is strongly reduced in intensity and broadened. Oxygen attack at Mo–S–Mo bonds therefore appears to be vigorous, perhaps enhanced by the presence of reduced molybdate species (oxygen "vacancies"). Bands in the 550-cm^{-1} region, however, are less perturbed by the addition of oxygen. These bands were attributed to S–S bonds for reduced molybdates, generated from polymolybdates.

This general trend toward destruction of the oxysulfide species is further indicated by the behavior of bands in the region 300–400 cm^{-1}. These bands (assigned to Mo–S–Mo vibrations for oxysulfides) are greatly reduced in intensity. However, bands below 200 cm^{-1} which were assigned to Mo–O–Mo vibrations for reduced molybdates (150 cm^{-1}, for example) are not severely altered in intensity for the 150°C samples.

The Raman spectra of samples sulfided at 350°C clearly show the presence of MoS_2 at all molybdenum loadings. In all spectra, the MoS_2 bands for the reoxidized samples are not significantly changed from those of sulfided samples. The samples also consistently have a broad band in the 225-cm^{-1} region of the spectrum. This band is now more clearly assigned to a metal sulfide–support interaction involving a metal–oxygen bond.

However, a new spectral feature is ob-

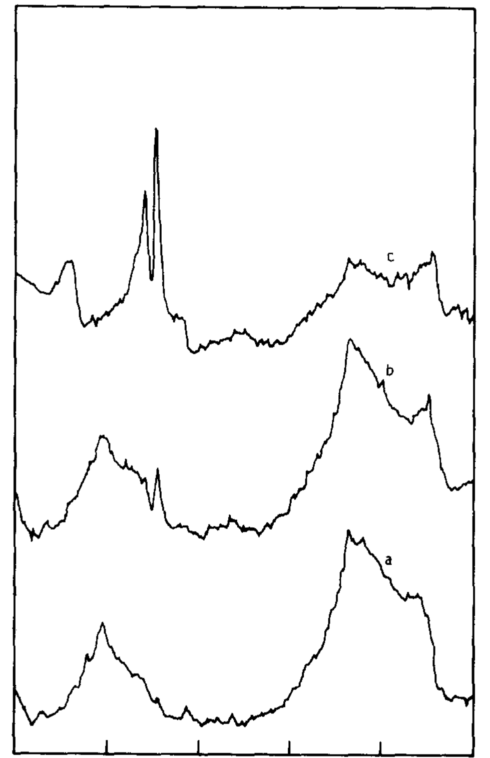


FIG. 9. Raman spectra of sulfided Mo(10)/γ-Al_2O_3 after exposure to air. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

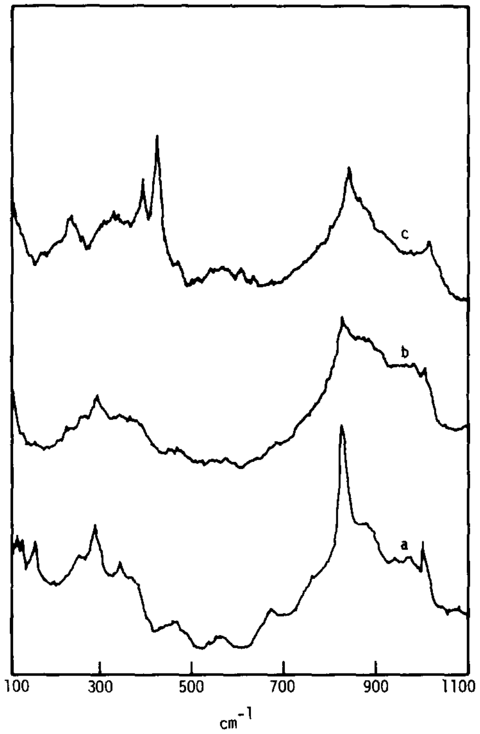


FIG. 10. Raman spectra of sulfided Mo(15)/γ-Al_2O_3 after exposure to air. (a) Sulfided up to 150°C; (b) sulfided up to 250°C; (c) sulfided up to 350°C.

served in the region 800–1000 cm^{-1} of the 350°C spectra. These broad spectral features are present in the spectra of the samples sulfided at lower temperatures. Such bands are assigned to reduced molybdenum species which interact with oxygen to give strong Raman signals. The spectra indicate that reduced species are likely present in the 350°C samples also, although the intensity of these bands decreases as the sulfiding temperature increases. However, the Raman scattering intensity of molybdenum–oxygen bands is strong, and therefore these species can be detected upon reexposure of samples to air. Some transformation of the MoS_2 phases is also likely, and the generally stronger bands near 820 and 1000 cm^{-1} for higher loadings of molybdenum are indications of some conversion of this phase to MoO_3.

TABLE 4

Band Positions for Reoxidized Samples (cm^{-1})

Sample	0–200	201–400	401–600	601–800	801–1000
Mo(5)					
150°C	189w	221w 335m 362sh	405w 477w 555w		856s,br 959s
250°C		318w,br 362w,br			882s,br 976s,br
350°C		219m 294w 382m	405s 454w		847m,br 977m,br
Mo(7.5)					
150°C		295m,br 363w,br	441w 471w 535w 565w		849s,br 965s,br
250°C		252⎫ m 290⎭ br 365m	467w 572w		860s,br 971s,br
350°C		224w 296⎫ m 380⎭ br	407w 466w		848s,br 973s,br
Mo(10)					
150°C		250w 282m,br 365sh	405w 468w		819w 854s,br 971m,br
250°C		284m 382w	405w		820m 840br 975br 996m
350°C		221⎫ m 286⎭ br 384m	406s 458w		820m 840br 975br 996m
Mo(15)					
150°C	189m	250w 287m 338w 364sh	461w 552w	668w	820s 867m,br 963m,br 995m
250°C		223w 251w 284m 340⎫ m 369⎭ br	464w 560w		820s 882m,br 970m,br 996m
350°C		220w 290w 384m	407s		821s 840s,br 995s

4. DISCUSSION OF RESULTS

Various models have been proposed for the sulfided state of cobalt molybdate hydrodesulfurization catalysts, including the monolayer model (*31*), the pseudointercalation model (*32–34*), and the synergy by contact model (*35*). However, the monolayer model—which more directly describes the genesis of supported cobalt molybdate catalysts (*36*)—is more clearly related to these studies of the oxide-to-sulfide transformation.

In the monolayer model, the molybdate species form a monolayer which is in registry with the γ-Al_2O_3 surface. Both tetrahedrally and octahedrally coordinated molybdenum cations are included and a "capping" oxygen layer is presumed. Schuit and Gates (*31*) propose that the catalyst operates in a reduced and partially sulfided state. Removal of O^{2-} ions or replacement of O^{2-} ion with S^{2-} ions occurs in the capping layer only, and because of the size of the S^{2-} ion, only half as many S^{2-} ions as O^{2-} ions are placed in the capping layer. The resulting stoichiometry is $0 < S/Mo < 1$ since Mo–O bonds to the support would have to remain intact for the monolayer to be preserved. Sulfur vacancies are included in the model for the functioning catalyst and are proposed to be the sites for catalytic activity. Schuit and co-workers (*36*) have indicated, however, that extensive modification of the oxidic monolayer may occur during sulfiding, resulting in an entirely different structure.

An extensive model of molybdena-on-alumina catalysts has been proposed by Massoth (*37, 38*) based on the stoichiometry of reduction and sulfiding. Massoth's model is based on one-dimensional chains of MoO_2 attached to the alumina surface, which is a modification of an earlier two-dimensional model—and which also differs from the monolayer model. Massoth examined the effects of variations in the sulfiding conditions on the catalyst stoichiometry. The factors affecting the sulfur content included temperature, H_2S partial pressure, and reaction time, with the latter two factors being much less important. In addition, the effect of sample prereduction was examined.

Massoth's model permits considerably more oxygen to be replaced by sulfur, compared to the monolayer model: A one-to-one replacement of oxygen atoms in the MoO_2 structure for sulfur is proposed. However, exchange of oxygen in the underlying layers is not proposed until temperatures exceed 400°C. The overall stoichiometry of the catalysts is believed to be closer to MoO_xS_y, where $x + y = 3$, rather than $MoO_2 + MoS_2$.

In interpreting his experimental results, Massoth points out that sulfiding of Mo/γ-Al_2O_3 catalysts is significantly different than sulfiding MoO_3. MoO_3 undergoes rapid reduction to MoO_2 followed by slow sulfiding in an H_2S/H_2 atmosphere. However, the Mo/γ-Al_2O_3 catalysts showed an immediate gain in weight, indicating that the dominant reaction is exchange of "catalyst reactive oxygen" for sulfur. A distribution of oxygen reactivities on the catalyst is presumed, and a large portion of such reactive oxygen is presumed on the fully oxidized catalyst. As treatment with H_2S/H_2 is performed at higher temperatures, some reduction and formation of anion vacancies was suggested. Massoth proposed that H_2S prevented catalyst overreduction.

Massoth's results for prereduced samples indicated that sulfur incorporation could occur without concomitant oxygen loss, but only at moderate to high prereductions. At high prereductions, only strongly bound oxygen was present, and oxygen replacement was more difficult. Sulfur addition to vacancies was then possible, but Massoth's model proposes that the filling of anion vacancies is incomplete. The anion vacancies due to strong reduction persisted to some degree after sulfiding.

The results of this study indicate that a modification of the monolayer model is necessary. The model of the oxysulfide system as revealed by the Raman spectra is related to Massoth's observations.

The Raman spectra of the catalysts which have been sulfided under H_2S/H_2 at 150, 250, 350, and 400°C indicate clearly a strong dependence on temperature. There exist significant differences in the behavior of samples with various molybdenum loading, but in all spectra, the existence of molybdenum oxides, reduced molybdenum oxides (oxygen vacancies), oxysulfide spe-

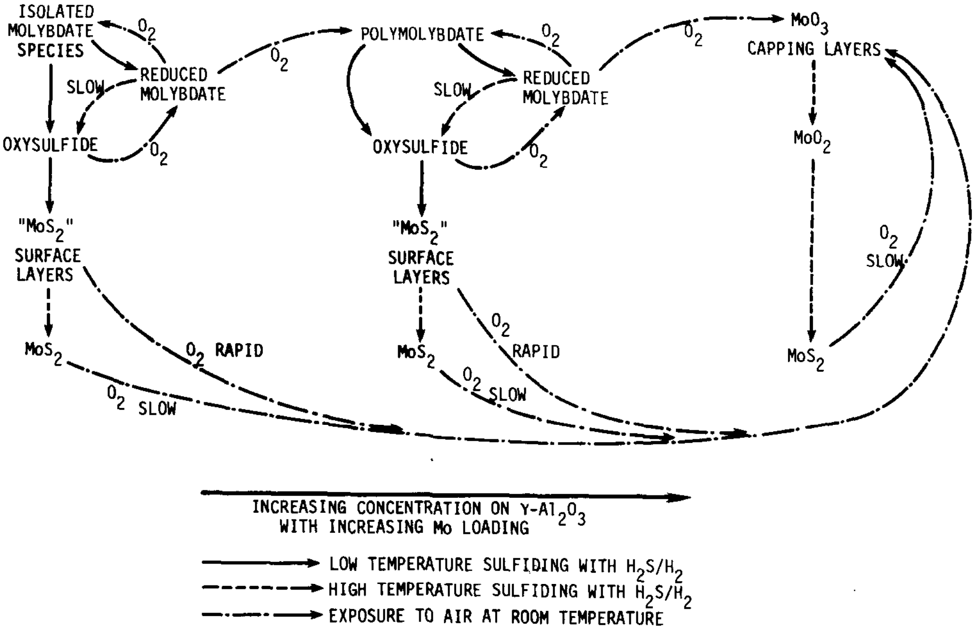


FIG. 11. Transformation of phases during sulfiding and exposure to air.

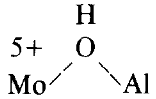
cies, and sulfides can be observed. The previously presented results are summarized in Fig. 11. The effect of exposure to oxygen is also indicated. The oxide precursor structures are based on previous Raman results (*4–12*) which indicate that three oxide species exist: isolated molybdenum species, polymolybdate species (perhaps forming layers), and MoO_3 (at considerably higher loading).

Proposed in this model of the phase transformations are both oxysulfide and reduced molybdate phases. The Raman spectra clearly indicate that these distinct species exist. In agreement with Massoth's model (*37*), sulfiding of reduced molybdate phases (for example, produced from polymolybdates) is more difficult. Conversion of this phase to MoO_3 is slow compared to "MoS_2" surface layers. The oxysulfide species are complex, and include different states of molybdenum reduction. The "MoS_2" surface layers are considered to be highly reactive, disordered "sulfides" which are bound extensively to the alumina by Mo–O–Al bonds. Higher temperatures result in greater formation of MoS_2 bulk-like structures.

The existence of oxysulfide species and reduced molybdates suggested by Massoth's model and our measurements of S/Mo compositions are consistent. However, the various Mo–O or Mo–S bondings which are indicated by the Raman spectra must be accounted for: Bridge bonding must be included specifically. The monolayer model permits the existence of Mo–S–Mo and Mo–O–Mo bonding. However, since complete coverage of the alumina surface by molybdenum is suggested, the desired sulfur-for-oxygen exchange as suggested by Massoth is not possible for the monolayer model.

A model which is consistent with the Raman spectra obtained in this study has been suggested (*18, 19*). Incomplete monolayer coverage by the molybdate species is proposed: Preferential interaction at hydrogen bonding sites (octahedral) has been demonstrated to occur (*18, 19*). A significant portion of the γ-alumina surface is open (Lewis acid sites). Thus, more extensive exchange of oxygen for sulfur, as suggested in Massoth's model, is possible. In addition, polymeric coordination involving sharing of edges and vertices of molybdenum octahedra is included. Although a strict modification of the monolayer model would require formation of columns (or "chains") of molybdenum octahedra sharing edges, a more general model of "patches or rafts" of polymeric species seems more reasonably based on the Raman spectra of the oxidic precursor (*18, 19, 39*).

The complex Raman spectra of the sulfided samples can be interpreted in terms of the transformation of this oxidic structure. A schematic of the reactions occurring during low- and high-temperature sulfiding and during reexposure to air is shown in Fig. 12. Sulfiding at low temperatures results in extensive sulfiding at the edges or corners of molybdate aggregates. A one-to-one replacement with oxygen is possible—even at some highly reactive bridging oxygen sites near these edges. Replacement of terminal oxygens over large regions of the molybdate rafts occurs. Mo–O–Al bonds are only indirectly perturbed under these conditions. Oxygen vacancies also result under these reducing conditions. The Raman spectra indicate that these vacancies are mainly at bridging positions. Incomplete conversion of terminal oxygens to sulfides results in OH hydroxy groups which have Brønsted acidity. These OH groups may be associated with Al surface atoms to form


$$\overset{5+}{\mathrm{Mo}}\diagup\overset{\mathrm{H}}{\mathrm{O}}\diagdown\mathrm{Al}$$

species. Circillo *et al.* (*39*) proposed such structures based on NMR studies for reduced $Mo/\gamma\text{-}Al_2O_3$ catalysts; a similar model based on initial oxidic clusters or rafts was proposed. Additional work by Hall and LoJacono (*40*) has indicated an enhanced acidity of reduced catalysts. Other workers including Kiviat and Petrakis (*41*), Moné and Moscou (*42, 43*), Martinez and Mitchell (*44*), and Cheng and

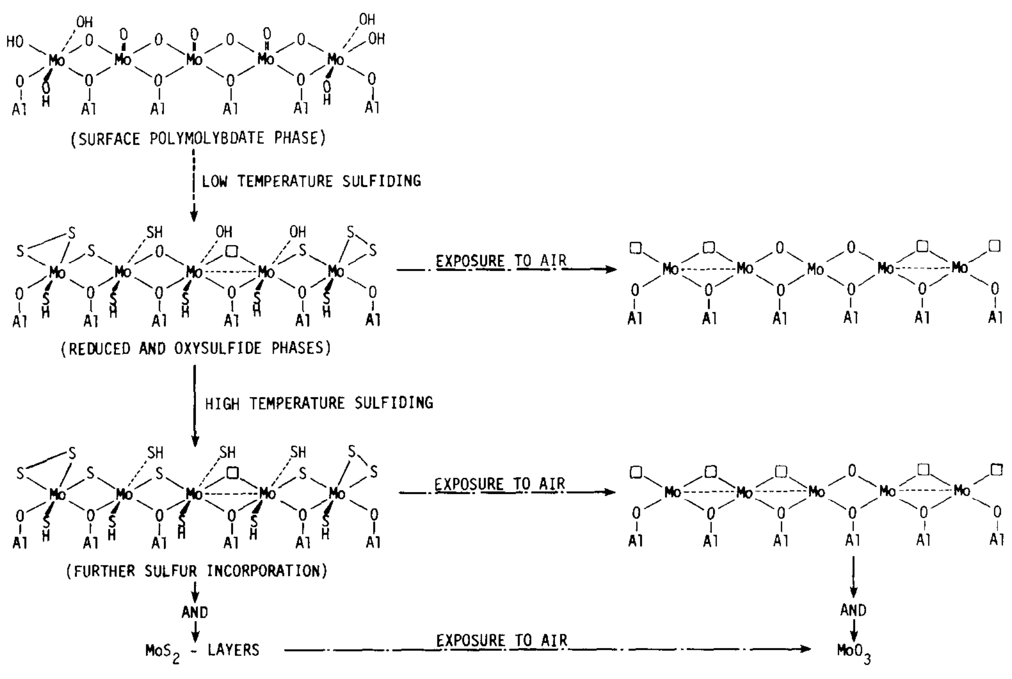


FIG. 12. Model for partially sulfided and reduced $Mo/\gamma\text{-}Al_2O_3$.

Schrader (*18, 19*), have demonstrated an appearance of Brønsted acidity resulting from molybdenum addition to γ-Al_2O_3. The existence of molybdate species in clusters implies that formation of molybdenum metal–metal bonds is likely.

At higher temperatures for sulfiding further replacement of bridging oxygens proceeds; however, reduced sites are less likely to sulfide. The formation of metal–metal bonds may be responsible for this decreased activity. Destruction of Mo–O–Al bonds is more difficult, and it is therefore possible for the incipient MoS_2 layers to be highly influenced (disordered) by the support. Incorporation of S at the support locations results in a "detachment" from the surface and development of bulk-like MoS_2 crystallites.

Exposure of samples to air is also indicated in this schematic. Reaction at Mo–S–Mo bridging sites produces "vacancies" and stronger molybdenum–molybdenum bonding. Terminal SH groups are also destroyed. Oxygen can be reintroduced at vacancies, however, and particularly at sites which were reduced originally. Samples sulfided at higher temperatures actually result in the initial existence of more anion vacancies upon exposure to air. However, conversion to oxides is more readily accomplished now because of the larger number of reactive, reduced sites. The extent of formation of extensively oxidized structures such as MoO_3 would therefore be increased. In this model, oxidation of surface "MoS_2" layers is accomplished rapidly, and these reactive, disordered forms of MoS_2 are more readily converted to MoO_3-like structures through disruption of the MoS_2–support interaction.

Incorporated in this model is also a ranking of the oxide precursors according to the ease of conversion to sulfide structures. MoO_3 phases appear to be the most difficult to sulfide at low temperatures. However, at higher temperatures, conversion to MoS_2 structures is relatively rapid. Polymolybdate phases are more easily transformed, but the product is a mixture of reduced and sulfided phases. The extent of reduction increases with increasing cluster or raft size. Finally, isolated molybdate species, which may strongly interact with the alumina support, are the most difficult to sulfide. However, a greater conversion to MoS_2-like structures results because reduction at bridging Mo–O–Mo positions is not as probable.

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