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Direct Observation by Controlled Atmosphere Electron Microscopy of the Changes in Morphology of Molybdenum Oxide and Sulfide Supported on Alumina and Graphite

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The changes in morphology of monolayer quantities of molybdenum oxide and sulfide phases supported on nonporous alumina and graphite thin films were studied by controlled atmosphere electron microscopy in oxygen and in H_2S/H_2 gas mixtures. When molybdenum oxide was supported on alumina and heated in oxygen at temperatures up to 825 K, a strong oxide–support interaction was observed, resulting in a highly dispersed molybdenum phase. When supported on graphite, the support interaction was weaker and bulk molybdenum oxide formed that became mobile on the surface at temperatures higher than 930 K. On mixed supports containing both alumina and graphite regions, the mobile molybdenum oxide particles on graphite at 930 K were observed to disappear when they contacted alumina edges due to rapid spreading of the molybdenum oxide over the alumina surface. This behavior can be explained by the relatively low surface energies for MoO_3 and graphite compared to the high surface energy for Al_2O_3. The molybdenum oxide–support interaction on alumina was broken by sulfiding in 5% H_2S/H_2 at ca. 750 K, with the formation of crystallites of MoS_2 located preferentially at grain boundaries on alumina. Larger particles were obtained at higher sulfidation temperatures. Reoxidation at temperatures higher than 645 K redispersed the crystallites due to spreading of molybdenum oxide over alumina. On the graphite support, a MoS_2 "rag phase" was formed from the MoO_3 crystallites upon treatment in 5% H_2S/H_2 at 475 K, and molybdenum species did not spread over the graphite surface during reoxidation at temperatures up to 1100 K. Finally, sulfidation and reoxidation of a cobalt-promoted molybdenum/alumina specimen showed behavior similar to that observed for the unpromoted samples. © 1987 Academic Press, Inc.

INTRODUCTION

Both alumina- and carbon-supported molybdenum disulfide catalysts are known to be active for reactions such as hydrodesulfurization and hydrogenation. The alumina-supported system has been studied extensively (*1–3*), whereas interest in the carbon-supported system has arisen more recently (*4–8*). The same types of active sites for hydrodesulfurization (HDS) may be present on both systems, because like the alumina-supported catalyst, the carbon-supported catalyst is promoted by cobalt and a Co–Mo–S phase with the same Mössbauer emission spectroscopy (MES) parameters is known to exist (*4, 5, 9*). The difference between the supports is in their interaction with molybdenum oxide and sulfide species, with the carbon believed to have the weaker interaction. For example, the Debye temperature of promoted MoS_2/Al_2O_3 as measured by MES was greater than that of promoted MoS_2/C, indicating that MoS_2 was held more strongly on the former support (*10, 11*).

Previous results for the alumina-supported system have indicated that in the oxide form, molybdenum oxide species may be present in thin clusters or islands of a few monolayers in thickness (*12, 13*).

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These species are sufficiently highly dispersed that they cannot be readily detected by transmission electron microscopy (*14*). Conversion of the oxide form to the sulfided form by treatment with 6% H_2S/H_2 mixtures at temperatures in excess of ca. 670–770 K has been shown to result in the formation of MoS_2 (*14*); reoxidation of these catalysts at 770 K caused the disappearance of these particles from the bright-field electron micrographs, suggesting that the sulfide form had been reversibly converted to the oxide form of the catalyst. In addition, the interaction between the MoS_2 crystallites and alumina in the sulfide form of the catalyst was observed to be weaker at higher sulfiding temperatures (*14*), and this was linked to a Type I to Type II transition observed in cobalt-promoted MoS_2/alumina catalysts (*15, 16*).

For the carbon-supported system, the oxide form of the catalyst has not been extensively studied. For the sulfide form, HDS activities of cobalt-promoted MoS_2/C are approximately equal to the high-activity Type II form of cobalt-promoted MoS_2/Al_2O_3, the former of which is believed to have a weaker sulfide–support interaction (*15*). Nevertheless, even though carbon is generally thought to be an inert support, there are indications that the interaction between it and the major component sulfide is sufficiently strong to have an effect on catalyst activity. For example, the chemical environment of carbon-supported cobalt sulfides has been observed to be unlike that of any known bulk cobalt sulfide compound as observed by MES measurements (*10, 11*), indicating that transition metal sulfides may be bonded in different ways than on metal oxide supports, perhaps by carboxylic acid, phenolic, or lactonic groups to the carbon surface (*6*).

In this paper, the results of an *in situ* electron microscopy study that characterize the structure of both alumina- and graphite-supported molybdenum oxide and sulfide catalysts are presented. These studies using a controlled atmosphere electron microscope enabled the transformations in particle morphology to be observed dynamically and allowed the temperatures at which these phenomena occurred to be determined. In addition, the influence of a cobalt promoter on Mo/Al_2O_3 was probed, and the effect of the carbon support was studied by use of a mixed alumina/graphite support system. The mixed support offered two important features: (a) simultaneous observation of the behavior of catalyst particles on two support media under identical conditions, and (b) insight into events occurring at the interface between the two supports and the Mo species.

EXPERIMENTAL

Model γ-Al_2O_3, Mo/γ-Al_2O_3, Co/γ-Al_2O_3, CoMo/γ-Al_2O_3, and Mo/γ-Al_2O_3/C (graphite) (hereafter referred to as Al, Mo/Al, Co/Al, CoMo/Al, and Mo/Al/C) catalysts were prepared by depositing molybdenum and cobalt onto thin films of γ-Al_2O_3 and graphite ca. 40 nm thick. Nonporous alumina model support films were formed by anodization of 0.025-mm-thick aluminum foils (Alfa), followed by heating in flowing oxygen at 900 K; the aluminum backing was then removed by amalgamation (*17, 18*). Transmission specimens of single crystal graphite were prepared from naturally occurring material obtained from Ticonderoga, New York, by a standard extraction and cleaving procedure (*19*). A mixed-support specimen (Mo/Al/C) was prepared by floating sections of the alumina film onto graphite specimens. All samples were mounted on stainless-steel grids.

Molybdenum was introduced onto the supports by vacuum evaporation of molybdenum trioxide powder from a resistively heated, alumina-coated molybdenum boat at 10^{-4} Pa, or as the metal by passing a high current through a molybdenum filament. In both cases the loading was approximately equivalent to one monolayer. Cobalt was deposited to a similar thickness by evaporation of spectrographically pure cobalt wire from a tungsten filament of 10^{-4} Pa.

The specimens were mounted in a JEOL 200 CX TEM/STEM electron microscope modified for controlled atmosphere studies. With this technique it is possible to observe continuously the changes in appearance of a specimen as it undergoes reaction with a gas and also perform *in situ* chemical analysis of particular features of interest. Dynamic events are recorded on video tape via a closed-circuit television link and under stable conditions we have been able to achieve a point to point resolution on the TV monitor of better than 1.0 nm. In the present study, the behavior of the supported Mo and Co samples was monitored during treatments in oxygen (4.1×10^2 Pa) and 5% H_2S/H_2 (6.8×10^1 Pa). These gases were obtained from Scientific Gas Products, Inc., with stated purities of >99.9% and they were used without further purification.

Particle sizes were obtained directly from selected sets of micrographs, and each average particle size was determined from the measurements of over 100 particles located on at least four different regions of a given specimen.

RESULTS

Molybdenum/Alumina

These specimens were subjected to two cycles in O_2 and in 5% H_2S/H_2. The appearance of a sample treated in O_2 at 825 K is presented in Fig. 1 and it is identical to that of a blank alumina support treated under the same conditions. A survey of the surface shows featureless areas separated by grain boundaries and a complete absence of small, discrete crystallites.

TABLE 1

Particle Size Measurements for Alumina-Supported Molybdenum Specimens (Mo/Al)

Treatment	Temperature (K)	Average particle diameter (nm)
Sulfidation in 5% H_2S/H_2	775	12 ± 4
	815	13 ± 4
	875	17 ± 5
Reoxidation in O_2	460– 480	20 ± 7
	520	19 ± 7
	645– 665	29 ± 11
Resulfidation in 5% H_2S/H_2	830– 835	31 ± 8
	895	30 ± 12
	995–1020	17 ± 9
	800	21 ± 8

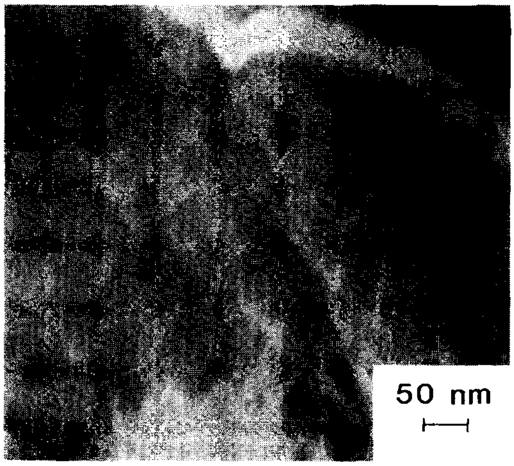


FIG. 1. Micrograph of a molybdenum/alumina specimen during treatment with oxygen at 825 K. This figure is identical to that of a blank alumina specimen when treated under the same conditions.

After cooling to 300 K in O_2, the specimens were reheated to 875 K in 5% H_2S/H_2. Continuous observations of the samples showed no change in the appearance of the surface below 710 K, but on heating to 775 K a number of small crystallites of similar size were observed to nucleate across the featureless background of the alumina support. Raising the temperature to 815 K led to the formation of more particles, and at 875 K the average particle size was significantly increased (see Table 1). The formation and growth of one particular particle is highlighted by the arrows in Figs. 2a–c for conditions where the temperature was progressively increased from 705 to 875 K. Figure 3 is a selection of micrographs taken from different regions of a specimen at 875 K in the H_2S/H_2 gas mixture. In addition to the formation of particles on the alumina plane, many of the edges began to develop a wispy texture, probably due to needle-shaped MoS_2 crystallites bonded to these regions. The directional nature of these needles was such that they grew in parallel fashion along the edges, suggesting that the crystallites were bonded in a preferred ori-

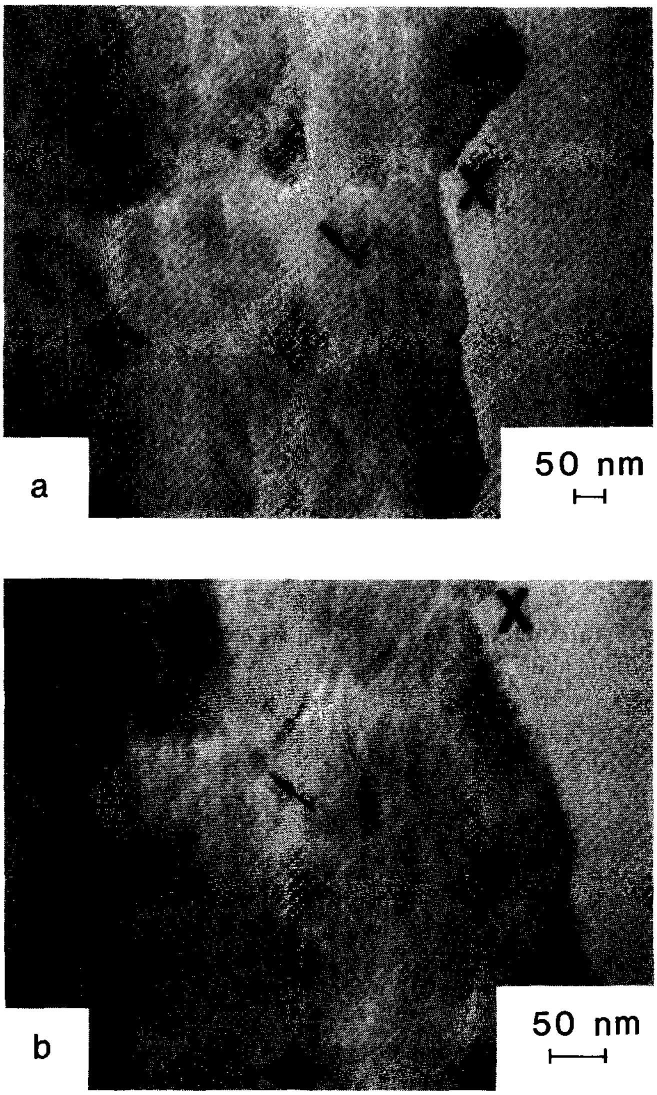


FIG. 2. A series of micrographs taken in one region of a molybdenum/alumina specimen treated in 5% H_2S/H_2 at (a) 705 K, (b) 815 K, (c) 875 K, and (d) reoxidation in oxygen at 785 K. The growth of particles, indicated by arrows can be seen in frames a, b, and c and the disappearance of particles in frame d.

entation to the alumina crystallites. This could provide an explanation why not all alumina edges showed these wispy features, in that not all alumina edges had the proper orientation for MoS_2 growth perpendicular to the edges. It should be noted that sulfidation of a blank alumina specimen at 840 K showed no evidence for crystallite formation or the wispy texture observed for the Mo/Al specimen.

After cooling the specimen to 300 K in H_2S/H_2, the system was reoxidized in O_2 at temperatures up to 785 K. As the temperature was raised from 460 to 575 K, the electron scattering density of the individual MoS_2 crystallites decreased, and this feature was accompanied by an increase in their sizes (see Table 1), suggesting that the crystallites were spreading on the alumina support. On continued heating to 645 K,

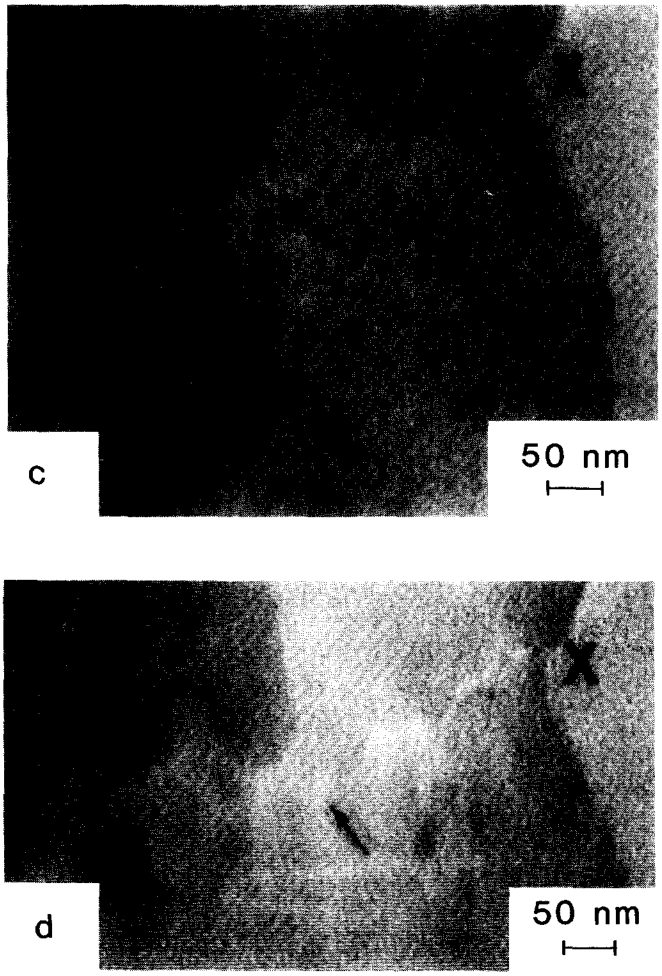


FIG. 2—*Continued.*

this behavior had progressed to such a stage that many of the crystallites had disappeared. After holding at this temperature for about 60 s, a survey of many regions of the surface revealed that almost all particles had completely redispersed on the alumina, in some instances leaving a shadowy cast to the featureless areas. It was also evident that during this period, the needle-shaped crystallites also disappeared from the edge regions of the alumina. This transformation in particle morphology can be seen in Figs. 2c and d and also in the sequence of Figs. 4a–d. An x is used to mark identical locations in each series of micrographs.

The second sulfidation treatment of oxidized molybdenum/alumina specimens gave trends qualitatively similar to those of the first sulfidation. Formation of crystallites occurred in the same temperature range (between 740 and 775 K) and they increased in size as the temperature was raised to 895 K. Unlike the first sulfidation, however, the particles were generally larger (see Table 1) and there was a greater preference for particles to be bonded along defects in the alumina such as grain boundaries (see Fig. 5). Many of these latter particles had elongated shapes because they were bonded along and had assumed the shapes of the grain boundaries (see the fea-

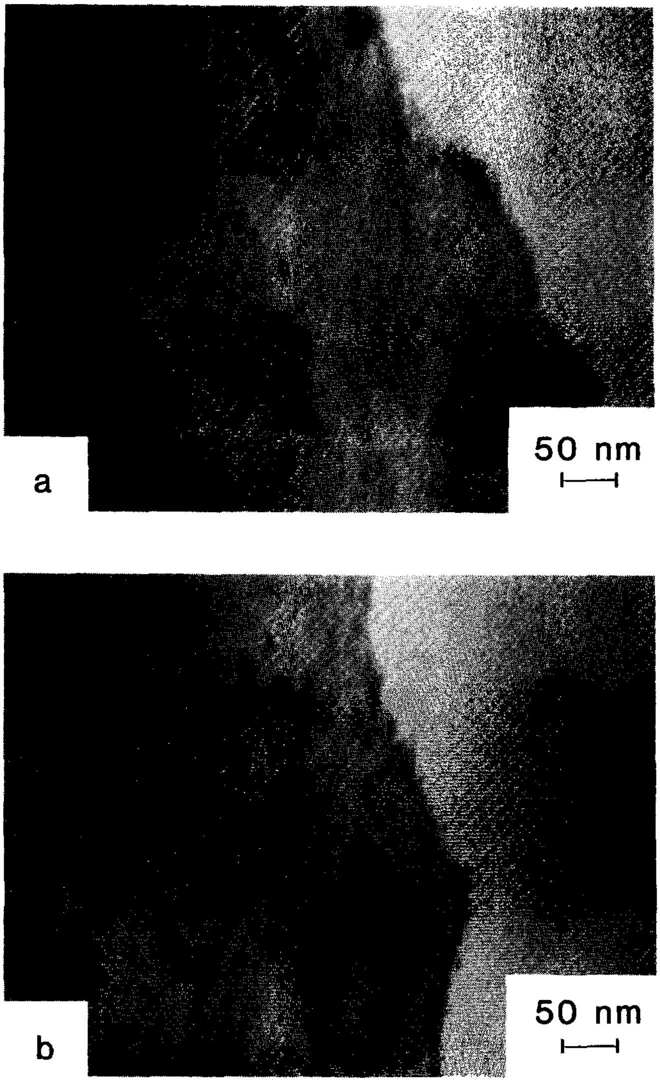


FIG. 3. Micrographs of various regions of a molybdenum/alumina specimen during treatment in 5% H_2S/H_2 at 875 K.

ture marked 1 in Fig. 5a). Also, the edges of the alumina examined did not contain any spikes or surface roughness observed in the first sulfidation, although it is possible that those edges examined in the second sulfidation were not of the proper orientation to permit observation of fine edge structure.

The second sulfidation also involved heating to higher temperatures than the first, and an additional transition in particle morphology was observed. After heating to temperatures between 895 and 995 K, the average particle size decreased by a factor of 2 (see Table 1). Upon cooling in H_2S/H_2 from 1020 to 802 K, the average particle size increased slightly, although the sizes at 802 K after the high-temperature transition were smaller than those before this transition. The positions of the particles remained the same during all of the aforementioned treatments in H_2S/H_2.

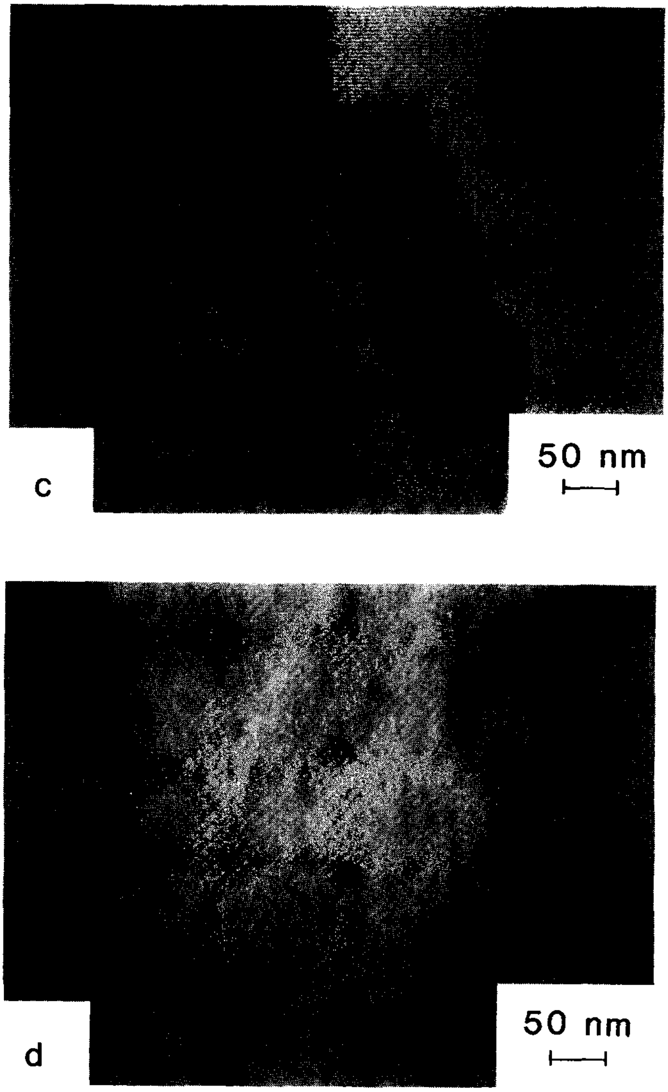


FIG. 3—*Continued.*

Molybdenum/Alumina–Graphite

In these experiments, fields of view were selected so that the behavior of molybdenum species could be continuously monitored on alumina, graphite, and the interfacial region of the two supports. As with the previous system, specimens were subjected to two cycles of treatments in O_2 and 5% H_2S/H_2.

The first oxidation sequence involved heating the specimen in incremental steps to a maximum temperature of 960 K. As with the molybdenum/alumina specimens, no particles could be distinguished on the alumina-support region of the specimen at any temperature in O_2. The formation of particles on the graphite was first observed during the heating step from 635 to 710 K, and both the size and number of particles increased as the temperature was raised. The particles were irregularly shaped when first formed, but on increasing the temperature to 870 K they developed a globular out-

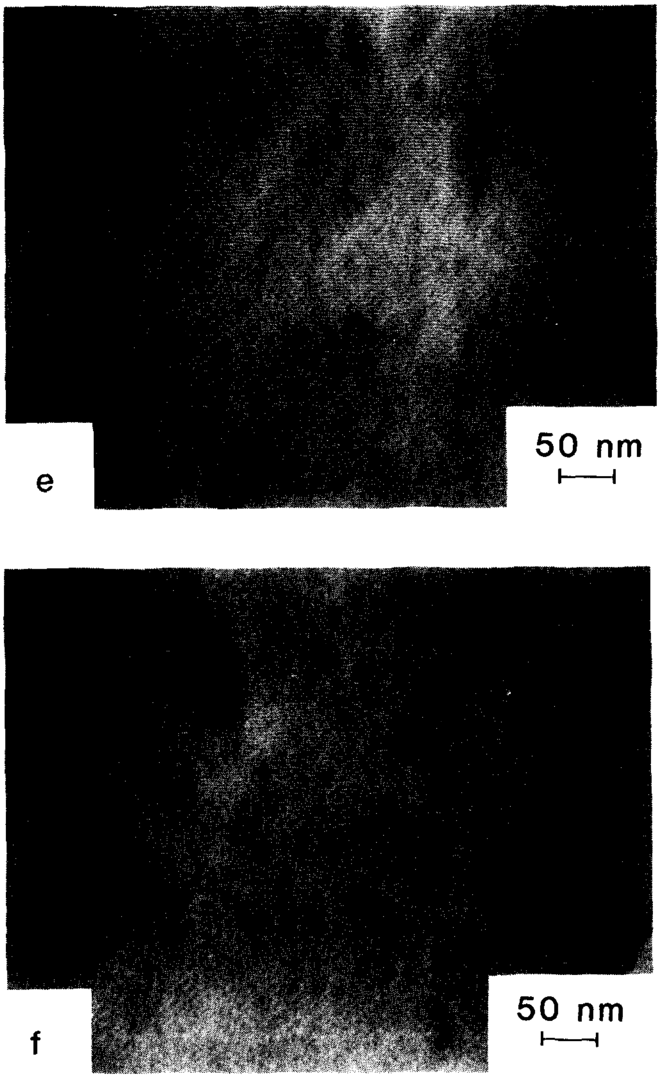


FIG. 3—*Continued.*

line. Also at this temperature inspection of the graphite edge regions showed that catalytic gasification was occurring, an effect which has been reported previously (*20*). At a slightly higher temperature of 935 K the droplike particles located on the graphite basal plane started to exhibit mobility and this resulted in an increase in the rate of particle growth due to coalescence (see the particle marked 2 in Fig. 6). In addition, particles in the graphite–alumina boundary region were observed to move from the graphite support, to come into contact with the alumina support, and to undergo a spreading action that caused the particles to disappear from the bright-field image. Examples of this behavior can be seen in the sequence presented in Fig. 6, where the particle marked 1, initially located on the light background, graphite, comes into contact with the darker contrast material, alumina. In all cases, after the particle encountered the alumina edge, it became smaller and darker, and gradually disappeared.

After cooling in O_2 the specimens were sulfided to a maximum temperature of 1050

K in 5% H_2S/H_2. Examination of the particles remaining on the graphite showed that they exhibited a change in morphology from a globular to a toroidal form at 475 K. On continued heating, these structures gradually transformed into a collection of interwoven fibers, as shown in Fig. 7. These irregular structures are characteristic of the formation of the poorly crystalline "rag phase" of MoS_2 (*21*). No further change in the appearance of the graphite support regions of the specimen was observed until the temperature was increased to 855 K, at which point small, dense particles (about 5 nm in diameter) started to collect on the irregular fibrous structures. Inspection of the alumina-support region of the specimen at 900 K showed the presence of small, dense particles, preferentially located at the alumina grain boundaries.

After cooling to 300 K in 5% H_2S/H_2, the specimen was reoxidized in O_2 up to 1105 K. In contrast to the first oxidation step, no particle mobility on the graphite support region was observed, and furthermore there was no change in morphology of the molybdenum species, indicating that the sulfidation had an irreversible influence on the system; e.g., a metal sulfide–support interaction is produced, which is not broken by subsequent treatment in O_2.

Cobalt/Alumina

This system was treated in one O_2 and 5% H_2S/H_2 cycle. Treatment in O_2 up to 815 K produced little change in the appearance of the specimen, except for the existence of some dark, irregularly shaped islands, which are indicated by arrows in Fig. 8a. These islands ranged from 30 to 100 nm in size and they could be attributable either to Co_3O_4 or features in the alumina.

Following treatment in O_2, the specimens were cooled and then treated in 5% H_2S/H_2 (see Fig. 8b). It was significant that the particles only grew to an average size of 5 nm, and they were considerably smaller than those formed from molybdenum/alumina under comparable conditions. In addition to the formation of particles on the alumina plane, a survey of the alumina edges showed the presence of small, needlelike structures in some of these regions.

Cobalt–Molybdenum/Alumina

As with the previous system, no evidence for particle formation was found when cobalt–molybdenum/alumina specimens were treated in O_2 at temperatures up to 775 K. However, when the system was subsequently heated in 5% H_2S/H_2, needlelike structures were formed on some of the alumina edges at 660 K and particle nucleation on the alumina surface was observed over the temperature range from 705 to 775 K. The rate of particle growth increased significantly as the temperature was raised to 840 K; particles reached an average size of 15 nm after only a few minutes of reaction at this temperature. Figure 9 is a sequence showing the change in appearance of a cobalt–molybdenum/alumina specimen as it was heated from 800 to 840 K in 5% H_2S/H_2. The particle growth characteristics were similar to those observed in molybdenum/alumina, but quite different from the cobalt/alumina system.

Finally the system was reoxidized in O_2 at temperatures up to 815 K. At 600 K, the needlelike structures began to disappear from the alumina edges and particles located on the alumina surface underwent a spreading action on the alumina support. Complete transformation in particle morphology was achieved on raising the temperature to 815 K, a condition where all edges had a relatively smooth profile and the existence of indistinct gray islands marked the initial locations of some of the particles.

DISCUSSION

The interaction of small particles with the surface of a carrier such as alumina controls both the stability of the catalyst and the shape of the supported particles. In agreement with other findings (*14*), when molybdenum/alumina specimens are

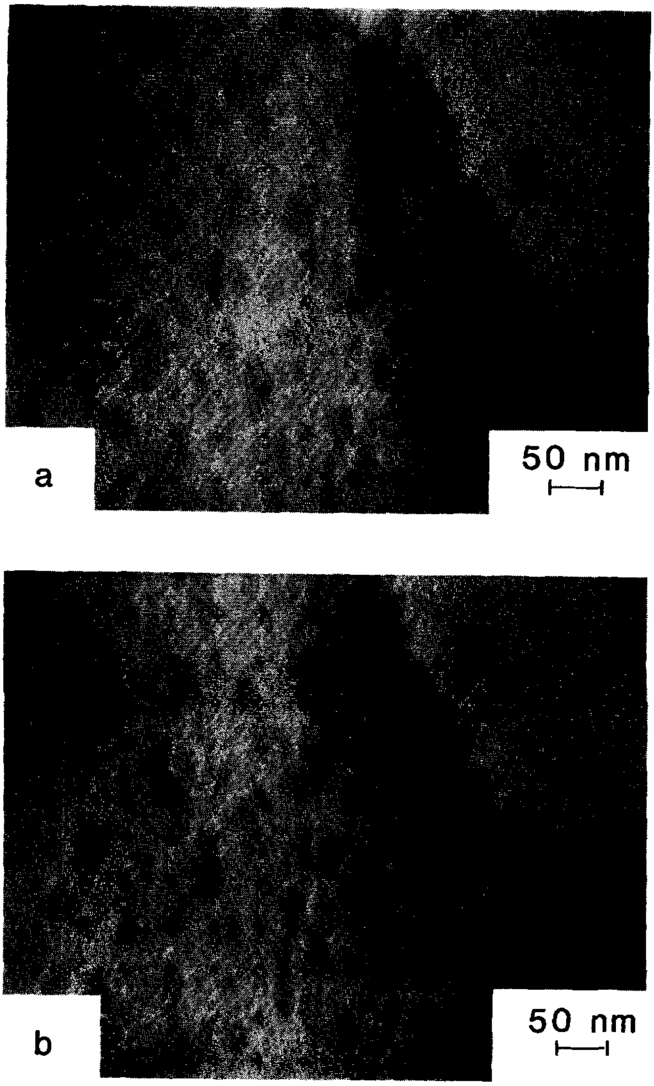
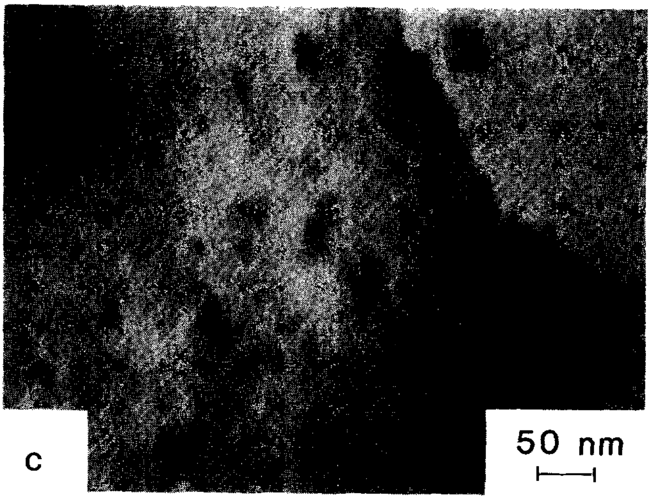


FIG. 4. A series of micrographs taken in one region of a sulfided molybdenum/alumina specimen during treatment in oxygen at (a) 480 K, (b) 515 K, (c) 645 K, and (d) 720 K.

heated in oxygen, the supported particles undergo a spreading action to form a well-dispersed molybdenum oxide phase. This behavior points to the existence of a strong oxide–oxide interaction.

This concept was proposed by Lund and Dumesic (*22*) who found that silica did not behave as an inert carrier for the preparation of supported Fe_3O_4 catalysts. Specifically, Si^{4+} substituted for Fe^{3+} cations in octahedral sites over the entire surface of the Fe_3O_4 particles. Other workers (*23–25*) have reported that spreading of oxidized metal particles occurred when silica- and alumina-supported noble metal systems were treated in oxygen, indicating the existence of a strong oxide–oxide interaction. Other examples of this type of phenomenon include the interaction of tungsten oxide (*26, 27*), iron oxide (*28*), and molybdenum oxide (*29*) with alumina, which has been shown to alter the physical and chemical properties of both major component and support oxides.



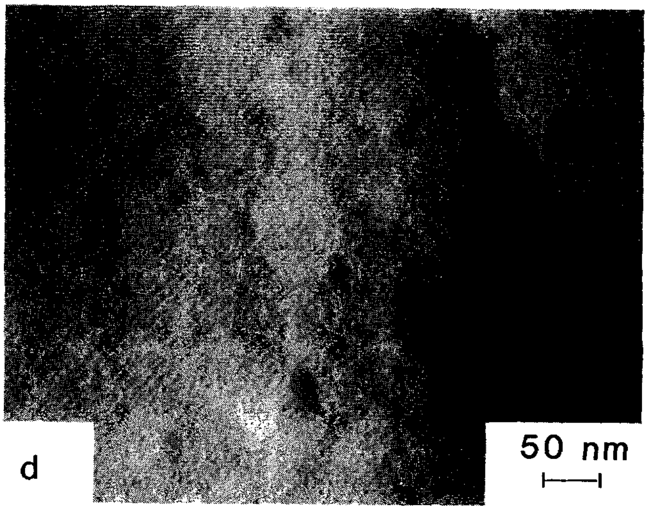


FIG. 4—*Continued.*

The difference in behavior of molybdenum oxide particles on alumina and graphite when heated in oxygen highlights the difference in the strength of the interaction of molybdenum oxide with these two supports. It is probable that at temperatures higher than 870 K, the molybdenum is present as molybdenum trioxide and the observed mobility on the graphite support at 933 K is characteristic of a material above its Tammann temperature (calculated as one-half the bulk melting point, this value being 535 K for MoO_3). This indicates that there is little interaction between MoO_3 particles and the basal plane of graphite. When the mobile MoO_3 particles encounter the alumina edges, they wet the support and spread over it. This change in particle morphology can be understood from a consideration of the interfacial energies, γ, prevailing in the two MoO_3/support systems. Using available interfacial tension data (alumina and molybdenum trioxide have values of 780 and 70 erg cm^{-2} at 935 K, respectively (*30*), and the graphite basal plane has a value of about 100 erg cm^{-2}),

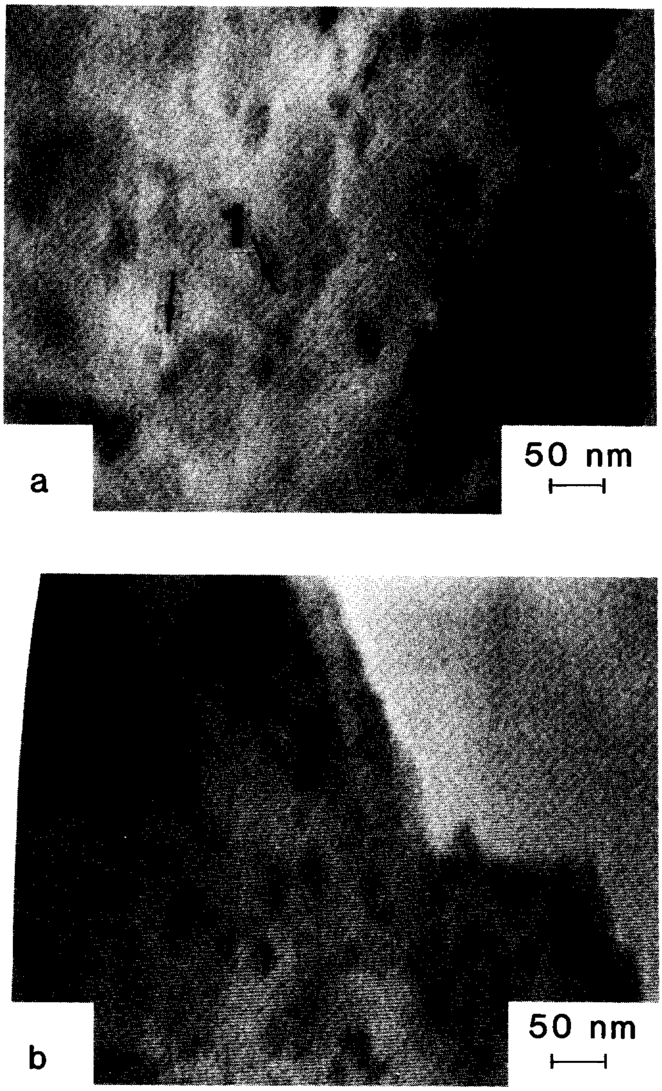


FIG. 5. Different regions of a molybdena/alumina specimen resulfided in 5% H_2S/H_2 at ca. 830 K. These micrographs show the preference for particles to be located at defect alumina sites such as grain boundaries (see arrows and feature at 1) and the alumina edge (see feature at 2).

one finds the following sequence:

$$\gamma_{Al_2O_3} \geqslant \gamma_{MoO_3} \cong \gamma_{graphite}.$$

This suggests that molybdenum trioxide will spread over alumina but not over graphite.

When oxidized molybdenum/alumina specimens were treated in 5% H_2S/H_2, small particles were observed to form on the support at ca. 750 K. In a separate study (*14*), particles forming in the same temperature range were identified as MoS_2 by microdiffraction analysis. This transformation in particle morphology upon switching from oxidizing to sulfiding conditions indicates that the latter treatment induces a weakening in the strength of the interaction between the particles and the support. Unfortunately, appropriate interfacial energy data are not available on metal sulfides to allow us to rationalize this behavior.

The finding that the average MoS_2 parti-

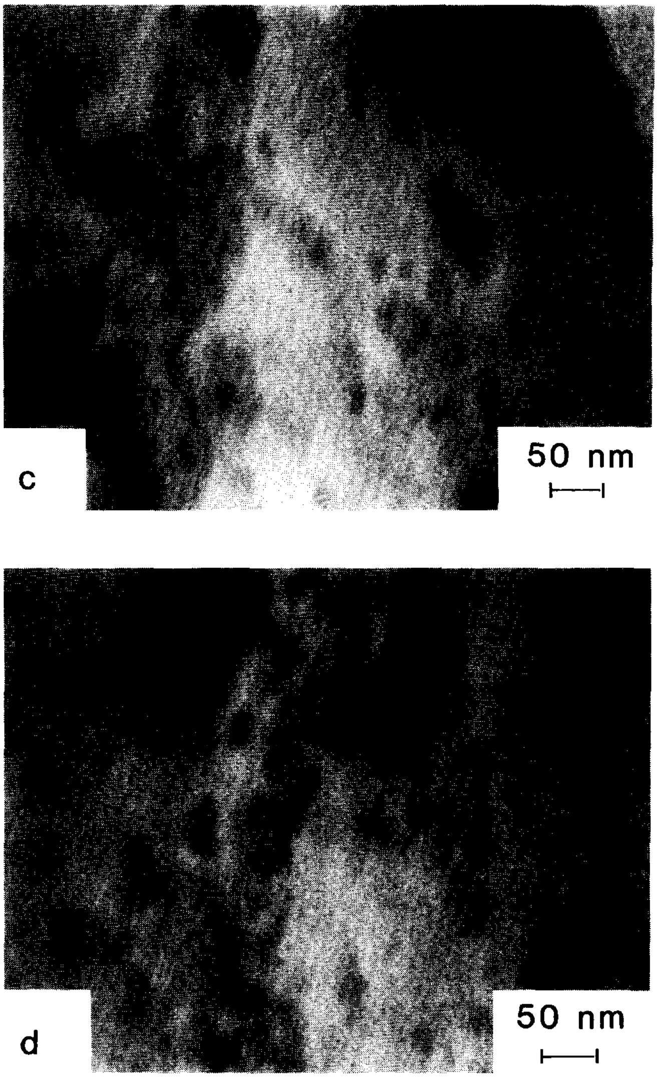


FIG. 5—*Continued.*

cle size increased after the second oxidation–sulfidation cycle suggests that the catalyst properties are a function of the temperature history and the number of such cycles that the catalyst has undergone. Although the spreading behavior of the molybdenum oxide particles is reproducible in consecutive oxidation treatments, the temperature of the preceding sulfidation appears to produce irreversible changes in morphology of the MoS_2 crystallites formed in subsequent resulfidation steps. In recent studies of the effects of sulfiding temperature it was suggested that a low concentration of strong Al–O–Mo (possibly Al–S–Mo) bonds are produced which anchor the MoS_2 crystallites to the support surface (*10, 15*). Evidence for molybdenum oxysulfide species in molybdenum/alumina catalysts has been found from S/Mo chemical analysis (*3, 31*) and Raman spectroscopy (*32*). Also, in a separate study (*14*), the observation that MoS_2 crystallites exhibited various orientations with respect to the alumina surface was explained by the notion that the crystallites were attached to the

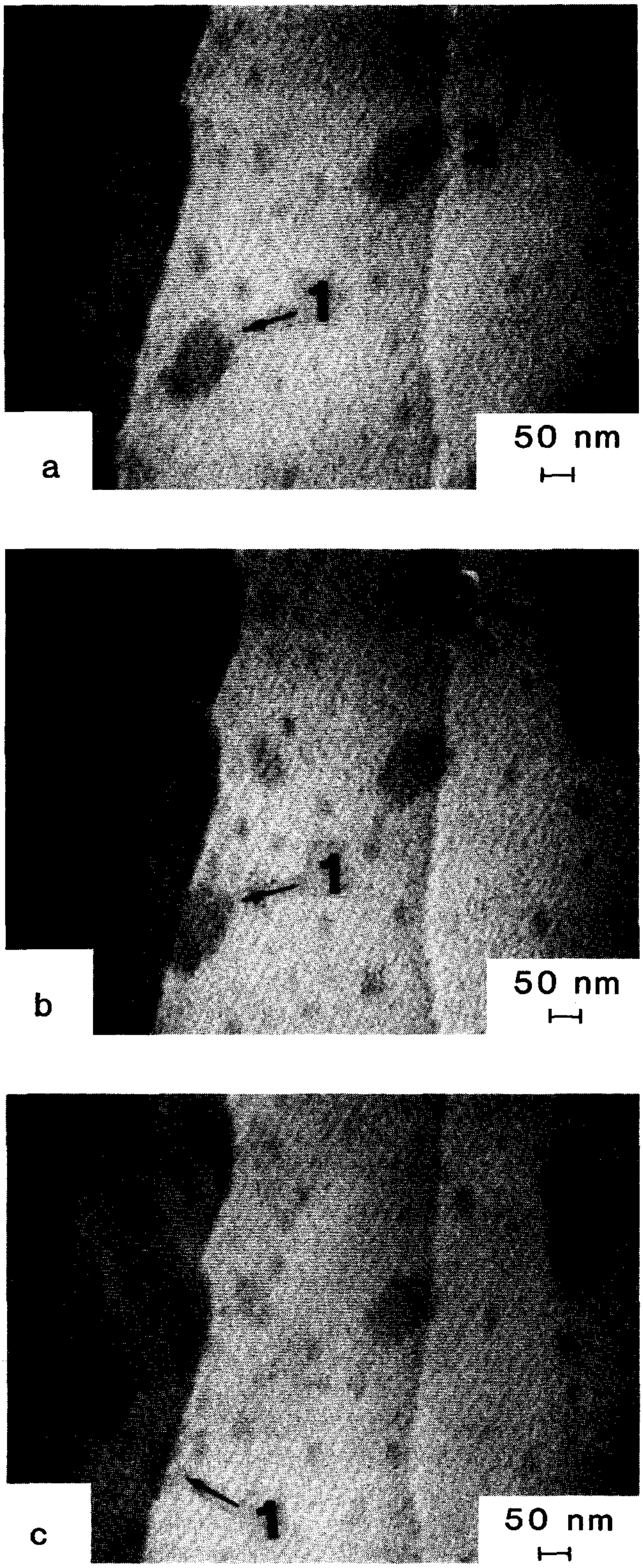


FIG. 6. A sequence of micrographs taken from a molybdenum/alumina/graphite specimen during treatment in oxygen at 960 K. Particle 1 is moving from the graphite support to the alumina edge and eventually spreads over the alumina.

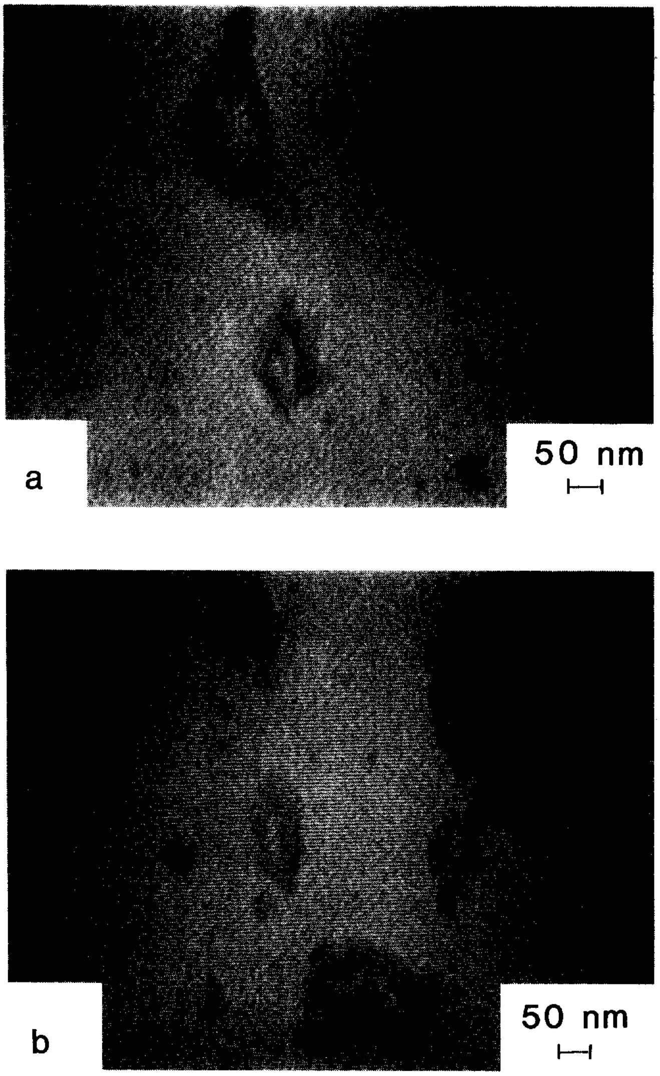


FIG. 7. Appearance of molybdenum species on the graphite support regions during treatment in 5% H_2S/H_2 at 475 K. These fibrous structures are indicative of MoS_2 formation.

alumina by differing numbers of anchor bonds; those crystallites which were oriented with their basal planes perpendicular to the support surface had a smaller number of anchor bonds. As the sulfiding temperature is raised, anchor bonds to the support are broken, and ultimately only the stronger ones remain. This behavior explains the finding of the present study that during the second sulfidation there is a greater preference for particles to become bonded to high-energy, alumina defect sites. Such alumina sites would be expected to give rise to particularly strong Al–O–Mo anchor bonds. Furthermore, the lack of needle and spike features on alumina edge in the second sulfidation may suggest that the alumina edge regions do not form strong Al–O–Mo anchor bonds.

It is probable that the sintering behavior observed during high-temperature sulfiding is a result of some of the MoS_2 particles losing all their anchor bonds, becoming mobile, and eventually combining with other

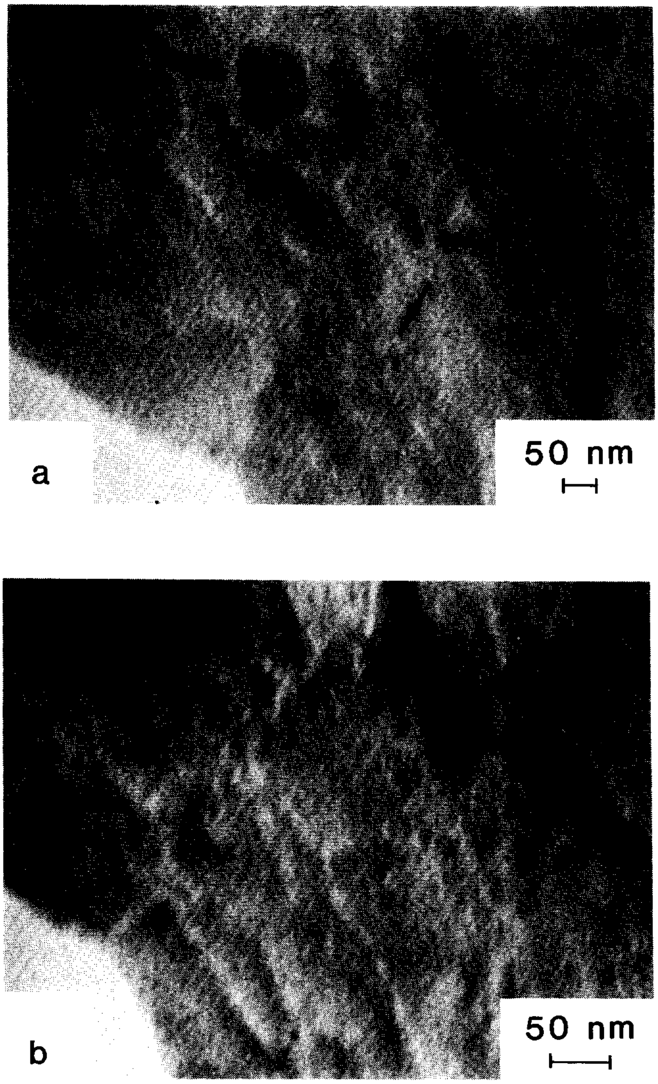


FIG. 8. Appearance of a cobalt/alumina specimen after (a) treatment in O_2 at 815 K and (b) the same area of the oxidized catalyst after treatment in 5% H_2S/H_2 at 840 K.

particles which remain anchored to the support. When these crystallites are redispersed on alumina during a subsequent oxygen treatment, they apparently form thin islands of oxide rather than individual MoO_x moieties. Hence, during a second sulfidation step the sintering process continues at a point in particle size where the first sulfidation was terminated.

These results are in agreement with a model based on evidence from solution impregnation of the oxide form of the catalyst, which proposes the existence of thin Mo oxide islands of different sizes bonded to the alumina support. Wang and Hall (*33*) reported that the number of Mo atoms in a Mo oxide cluster adsorbed on alumina depended on the pH of the solution and this structure was retained after calcination. Other workers (*34*) developed a model based on the assumption that the cluster size in the oxide form was retained in the sulfide form after mild sulfidation at 675 K. A greater degree of polymerization of Mo

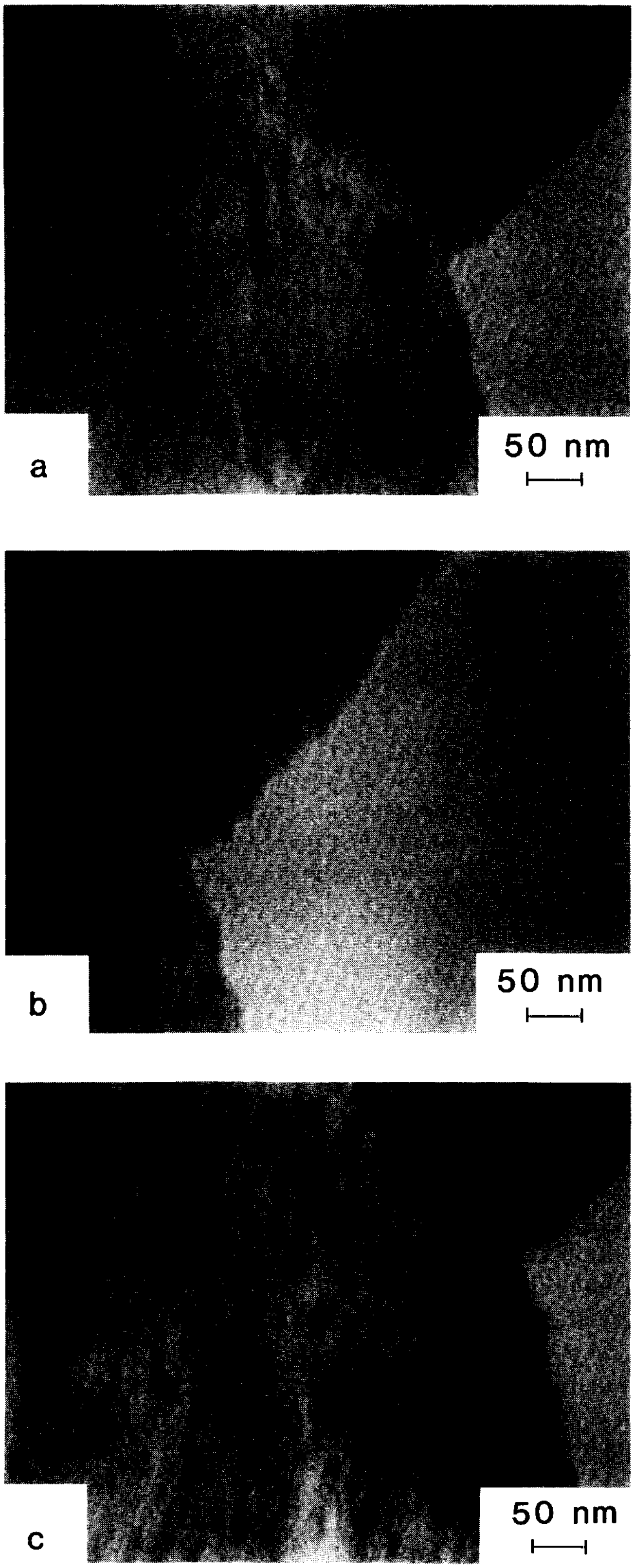


FIG. 9. Sequence of micrographs during the change in appearance of an oxidized cobalt–molybdenum/alumina specimen as it is heated in 5% H_2S/H_2 from 800 to 840 K.

oxide species after 670 K sulfiding has also been observed from Raman spectroscopy studies (*32*).

The extraordinary behavior of MoO_3/graphite specimens when treated in H_2S/H_2 highlights the difference in the nature of the interactions which exist in this and the alumina-supported system. It is possible that the toroidal structures observed at 475 K are an intermediate state consisting of a mixture of MoO_2 and MoS_2. Other workers (*35, 36*) have reported that the structure of catalyst particles prepared from the sulfidation of ammonium heptamolybdate at 675 K consists of a twisting MoS_2 surface "skin" encapsulating a core of crystalline MoO_2. The fibrous and toroidal structures observed in the present study indicate that the formation of the MoS_2 rag phase (*21*), if not complete, starts to form at low temperatures.

It is significant that the molybdenum sulfide species remained immobile on both support surfaces even at temperatures in excess of 900 K (since the Tammann temperature of MoS_2 is 730 K). This finding points to the existence of an interaction between the molybdenum species with both alumina and graphite in sulfiding atmospheres. However, as described previously, the strong sulfide–support interaction of the molybdenum/alumina system can be broken at very high sulfiding temperatures.

Because the small, dense particles observed in H_2S/H_2 at ca. 1000 K on graphite had a size and appearance similar to those formed on alumina, it is suggested that these particles are independent of the support. Although their identity is not known, they may be a reduced form of molybdenum sulfide, such as Mo_2S_3. Indeed, the most recent phase diagrams of the molybdenum–sulfur system (*37*) show that bulk Mo_2S_3 forms from molybdenum metal and MoS_2 at temperatures above 935 K, which is close to the high-temperature sulfiding transition observed on both graphite and alumina in this work. Another possibility is that the particles are metallic molybdenum formed by reduction of MoS_2. Such a transition is thermodynamically favorable for bulk MoS_2. Such a transition is thermodynamically favorable for bulk MoS_2 crystallites at about 1250 K in 5% H_2S/H_2 (*38*). The slight increase in particle size obtained for these small, dense particles on alumina after cooling in sulfiding atmospheres may indicate a resulfiding process back to MoS_2.

The similarity between particle sizes of cobalt–molybdenum/alumina and molybdenum/alumina following sulfidation at 840 K indicates that MoS_2 crystallites are formed in both systems. Candia *et al.* (*15*) reported only a slight difference in MoS_2 particle sizes for high sulfiding temperatures when cobalt is bonded to MoS_2 edges in the HDS-active Co–Mo–S phase.

The formation of a narrow distribution of small particles on cobalt/alumina (and probably on cobalt–molybdenum/alumina) following treatment in 5% H_2S/H_2 at 840 K suggests that these particles are Co_9S_8. Separate microdiffraction analysis of cobalt–molybdenum/alumina model catalysts sulfided at 800 K revealed the presence of a narrow size distribution of face-centered cubic Co_9S_8 particles (*18*). Previous work on high-surface-area powders has shown that Co_9S_8 is the stable bulk sulfide produced in sulfiding both Co_3O_4 and $CoMoO_4$, if either bulk crystallite is present in the molybdenum-oxide/γ-alumina catalyst (*39*).

CONCLUSIONS

When molybdenum oxide was supported on γ-alumina and heated in oxygen, a strong oxide–oxide interaction was observed, resulting in a highly dispersed phase. When supported on graphite, the support interaction was weak and bulk molybdenum oxide formed and became mobile on the surface at temperatures higher than 930 K. On mixed supports containing alumina and graphite regions, the mobile molybdenum oxide particles on graphite were observed to disappear when they contacted alumina edges due to rapid spreading of the molybdenum oxide over the alumina surface. This behavior was explained by the relatively low surface energy for MoO_3 compared to a high surface energy for Al_2O_3 and low surface energy for graphite.

On the alumina support, the strong oxide–oxide interaction was broken by sulfiding in 5% H_2S/H_2 at 740–755 K, with the formation of bulk crystallites of MoS_2 located at defect sites on alumina; larger crystallites were obtained at higher sulfiding temperatures. Reoxidation at temperatures greater than 645 K redispersed the crystallites due to spreading of molybdenum oxide over the support because of the previously described favorable surface energies. The MoS_2 particle size after sulfidation was dependent on the prior sulfidation temperature history of the catalyst. These results were consistent with a model in which strong Mo–O–Al linkages anchor the MoS_2 crystallites to the support, and these linkages become irreversibly broken during high-temperature sulfiding.

The behavior observed in this study of thin film, model catalytic materials is in agreement with the behavior of high surface area, supported molybdenum catalysts, as reviewed recently by Hall (*40*). Specifically, strong interactions between molybdenum oxide species and alumina supports have been documented, and these interactions are at least partially broken during reduction treatments.

On the graphite support, a MoS_2 rag phase was formed from the MoO_3 bulk crystallites and a strong sulfide–support interaction was formed. In addition, this strong support interaction was not broken by high-temperature oxidation, showing that the sulfidation had an irreversible effect on the Mo species in the catalyst. As on the alumina support, the MoS_2 crystallites congregated preferentially at defect sites on graphite. On both supports, sulfiding temperatures in excess of ca. 900 K resulted in a change in MoS_2 particle morphology that may be related to a transition to a reduced molybdenum sulfide species.

Sulfidation and reoxidation of a cobalt-promoted molybdenum/alumina catalyst showed behavior characteristic of MoS_2 particles on the unpromoted catalyst, indicating that MoS_2 particles were also formed on the $CoMo/Al_2O_3$ sample.

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REFERENCES

1. Massoth, F. E., *in* "Advances in Catalysis," Vol. 27, p. 265. Academic Press, New York, 1978.

2. Grange, P., *Catal. Rev. Sci. Eng.* **21,** 135 (1980).

3. Topsøe, H., and Clausen, B. S., *Catal. Rev. Sci. Eng.* **26,** 395 (1984).

4. Topsøe, H., Clausen, B. S., Topsøe, N.-Y., and Pedersen, E., *in* "ACS Miami Meeting, 1985," in press.

5. Breyssee, M., Bennett, B. A., Chadwick, D., and Vrinat, M., *Bull. Soc. Chim. Belg.* **90,** 1271 (1981).

6. Duchet, J. C., van Oers, E. M., deBeer, V. H. J., and Prins, R., *J. Catal.* **80,** 386 (1983).

7. Bridgewater, A. J., Burch, R., and Mitchell, P. C. H., *Appl. Catal.* **4,** 267 (1982).

8. Stevens, G. C., and Edmonds, T., *in* "Preparation of Catalysts, II" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 1979. Elsevier, Amsterdam, 1979.

9. Topsøe, H., Clausen, B. S., Burriesci, N., Candia, R., and Mørup, S., *in* "Preparation of Catalysts, II" (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 479. Elsevier, Amsterdam, 1979.

10. Topsøe, H., Candia, R., Topsøe, N.-Y., and Clausen, B. S., *Bull. Soc. Chim. Belg.* **93,** 783 (1984).

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

12. Hall, W. K., *in* "Proceedings, 4th International Conference on the Chemistry and Uses of Molybdenum," Golden, CO, 1982.

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

14. Hayden, T. F., and Dumesic, J. A., submitted for publication.

15. Candia, R., Sørensen, O., Villadsen, J., Topsøe, N.-Y., Clausen, B. S., and Topsøe, H., *Bull. Soc. Chim. Belg.* **93,** 763 (1984).

16. Candia, R., Topsøe, H., and Clausen, B. S., *in*

"Proceedings, 9th Iberoamerican Symposium on Catalysis," Lisbon, Portugal, 1984, p. 211.

17. Ruckenstein, E., and Malhotra, M. L., *J. Catal.* **41,** 303 (1976).
18. Hayden, T. F., Ph.D. dissertation, University of Wisconsin, Madison, 1986.
19. Hennig, G. R., *in* "Chemistry and Physics of Carbon" (P. L. Walker, Jr., Ed.), Vol. 2, p. 1. Dekker, New York, 1966.
20. Baker, R. T. K., Harris, P. S., Kemper, D. J., and Waite, R. J., *Carbon* **12,** 179 (1974).
21. Chianelli, R. R., Prestridge, E. B., Pecoraro, T. A., and deNeufville, J. P., *Science* **203,** 1105 (1979).
22. Lund, C. R. F., and Dumesic, J. A., *J. Phys. Chem.* **87,** 3175 (1981).
23. Chen, J. J., and Ruckenstein, C., *J. Catal.* **69,** 254 (1981).
24. Wang, T., and Schmidt, L. D., *J. Catal.* **70,** 187 (1981).
25. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29,** 224 (1973).
26. Thomas, R., Kerkhof, F. R. J. M., Moulijn, A. J., Medema, J., and deBeer, V. H. J., *J. Catal.* **61,** 559 (1980).
27. Murrell, L. L., Grenoble, D. C., Baker, R. T. K., Prestridge, E. B., Fung, S. C., Chinnelli, R. R., and Cramer, J. P., *J. Catal.* **79,** 203 (1983).
28. Sushumna, I., and Ruckenstein, E., *J. Catal.* **94,** 239 (1985).
29. Suarez, W., Dumesic, J. A., and Hill, C. G., Jr., *J. Catal.* **94,** 408 (1985).
30. Overburg, S. H., Bertrand, P. A., and Somerjai, G. A., *Chem. Rev.* **75,** 547 (1975).
31. Arnoldy, R., van den Heijkant, J. A. M., deBok, G. D., and Moulijn, J. A., *J. Catal.*, in press.
32. Schrader, G. L., and Cheng, C. P., *J. Catal.* **80,** 369 (1983).
33. Wang, L., and Hall, W. K., *J. Catal.* **77,** 232 (1982).
34. Chung, K. S., and Massoth, F. E., *J. Catal.* **64,** 332 (1980).
35. Sanders, J. V., *Chem. Scr.* **14,** 141 (1978).
36. Pratt, K. C. and Sanders, J. V., in "Proceedings, 7th International Congress on Catalysis," Tokyo, 1980 (T. Seiyama and K. Tanabe, Eds.), p. 1420. Kodansha, Ltd., Tokyo, 1981.
37. Brewer, L., and Lamareaux, R. H., *Atomic Energy Review,* Special Issue No. 7, p. 11 (1980).
38. McKinley, J. B., *in* "Catalysis" (P. H. Emmett, Ed.), p. 405. Reinhold, New York, 1957.
39. Chung, K. S., and Massoth, F. E., *J. Catal.* **64,** 320 (1980).
40. Hall, W. K., *in* "Chemistry and Physics of Solid Surfaces" (R. Vanselow and R. S. Howe, Eds.), Vol. VI. Springer-Verlag, New York/Berlin, in press.