JOURNAL OF CATALYSIS 96, 276–284 (1985)

Activity and Structure of Sulfided Molybdena–Alumina Catalysts

D. A. SCARPIELLO,[1] A. A. MONTAGNA,[2] AND J. FREEL

Gulf Research & Development Company, P.O. Drawer 2038, Pittsburgh, Pennsylvania 15230

Received January 31, 1985; revised June 8, 1985

The effect of molybdenum content on the activity of sulfided molybdena–alumina for furnace oil desulfurization showed two distinct regions. Percentage desulfurization increased rapidly with molybdenum content up to about 8 wt% molybdenum, but showed no further increase when up to 30 wt% molybdenum was incorporated in the catalyst. These two regimes were shown to result from two different solid phases. About 8–12% molybdenum appeared to interact with the alumina during impregnation, so that a discrete molybdenum phase could not be observed by electron microscopy upon subsequent calcination, reduction, or sulfiding. In samples containing 20 or 30% molybdenum, however, much of the excess molybdenum was precipitated at the periphery of the catalyst pellets yielding large (1 μm) molybdena crystals upon calcination. S^{35} exchange between hydrogen sulfide and the solid was explored as a means of measuring molybdenum dispersion on alumina. Exchange data at 100°C reflected the two-phase nature of the system and paralleled catalytic activity fairly well. However, only about 8% of the irreversibly bound sulfur was exchanged at 100°C and only 30% exchanged at 400°C. It is concluded that the sulfided molybdena–alumina phase is complex and not simply MoS_2 crystallites supported on alumina. Incorporation of 1.5 wt% nickel into 8 wt% molybdenum–alumina doubled the exchangeable sulfur at 315°C. © 1985 Academic Press, Inc.

INTRODUCTION

Supported molybdenum catalysts are used in the hydrogenation, denitrogenation, and desulfurization of petroleum stocks. Their structure has been one of the most widely investigated and debated questions in heterogeneous catalysis (*1*, *2*). The consensus seems to be that molybdena in the calcined (oxidized) form of the catalyst is disordered and highly dispersed. Lipsch and Schuit suggested that molybdena forms a monolayer on the alumina surface (*3*). More recent work provides evidence that raft-like molybdena species may be present (*4*, *5*), and that the alumina is incompletely covered. Some believe that molybdenum in the sulfided catalyst is converted to supported MoS_2 crystallites (*1*, *6*, *7*). Others prefer a model in which the molybdena–alumina precursor is converted to a mixed oxysulfide which retains strong bonding between the molybdenum and alumina phases (*8*). Recent studies using Raman spectroscopy (*5*, *9*) and EXAFS (*10*) suggest that sulfidation produces an MoS_2 phase at high temperatures (300–400°C), but that oxysulfide precursors predominate at less severe conditions. The MoS_2 formed appears to be highly disordered (*5*, *9*) or of very small crystallite size (*10*).

There is no generally accepted method of measuring the dispersion of supported metal sulfides, in the way that Group VIII metal dispersion can be obtained by gas chemisorption. It has been suggested that oxygen chemisorption (*11*, *12*) occurs at edge sites in MoS_2 and thereby correlates with the hydrodesulfurization activity of supported catalysts; but this interpretation is open to question (*13*, *14*).

The present work explores isotopic exchange as a means of probing the surface of

---

[1] Current address: Gas Research Institute, 8600 West Bryn Mawr, Chicago, Ill. 60631.

[2] Current address: Exxon Research and Engineering Company, P.O. Box 45, Linden, N.J. 07036.

0021-9517/85 $3.00

the sulfided catalyst. Lukens *et al.* (*15*) studied the exchange of radioactive H_2S with metal sulfides, and equated the sulfur exchange at room temperature with surface as opposed to bulk sulfide ion. They also studied the exchange reaction on sulfided NiMo–W on alumina at different metal loadings. They assumed that a crystalline metal sulfide phase would be present and concluded from their results that the metal sulfide crystallites were small (~30 Å) at low metal loadings, and much larger at high loadings. The latter could be detected by X-ray diffraction (XRD). Seshadri *et al.* (*16*) detected a crystalline molybdenum phase by XRD on a molybdena–alumina catalyst containing 16 wt% molybdenum but not on catalysts with lower molybdenum levels. More recently, Pollack *et al.* (*17*) detected MoS_2 crystallites on some sulfided catalysts and estimated their size by XRD line broadening. However, it seems agreed that crystalline MoS_2, detectable by XRD, is not the primary form of molybdenum in sulfided molybdena–alumina catalysts.

This study was undertaken to extend the previous work of Lukens *et al.* to higher temperatures, where sulfide ion mobility is of greater interest to catalysis. The effect of molybdenum content on catalyst properties was reexamined by studying a series of sulfided molybdena–aluminas containing 4–30 wt% molybdenum. Exchange of sulfur between H_2S/H_2 mixtures and the sulfided catalysts was investigated at various temperatures between 100 and 400°C. These results were compared with structural information obtained from electron microscopy and electron probe microanalysis to determine whether the exchange data defined a molybdenum sulfide which could be observed by electron microscopy. The exchange data were also compared with activity for hydrodesulfurization of a furnace oil.

The catalytic properties of molybdena–alumina are known to vary with molybdenum content. For example, as molybdenum content is increased, the activity of molybdena–alumina catalysts goes through a maximum in naphtha reforming reactions (*18*). Related changes also occur in various physicochemical parameters. Thus, SO_2 adsorption decreases with increasing Mo content and finally ceases when the alumina surface is completely covered by MoO_3 (*18*). Other work indicates the Mo(V) content in reduced catalysts follows molybdenum content in the same way as catalytic activity for an aldol condensation reaction, both going through a maximum at about the same molybdenum level (*19*).

METHODS

Apparatus

The exchange of sulfur-35 between H_2S and sulfur present on the sulfided catalysts was measured by continuously monitoring the decrease in radioactivity of a 10 : 1 hydrogen/hydrogen sulfide gas phase with a lithium-doped glass scintillation detector (*20*). Pulses produced by the β-radiation were counted using a digital ratemeter. Exchange experiments were carried out in an all-glass circulation system which included a Pyrex reactor heated by a conventional tubular furnace. The system was mercury-free and Teflon-to-glass stopcocks were used throughout. A small electromagnetic pump circulated the gas over the catalyst during the course of the exchange reaction. A glass Bourdon gauge and cathetometer were employed for measurement of pressure.

The supported molybdenum catalysts were sulfided in a separate flow system at atmospheric pressure. The H_2S/H_2 mixture and N_2 flows were controlled using calibrated rotometers. The same glass reactor was used in both the sulfiding and exchange experiments.

The hydrodesulfurization activities of the catalysts were measured in a fixed-bed reactor of conventional design. The liquid hydrocarbon was pumped and metered with a minipump. Hydrogen was metered through a stainless-steel capillary tube coupled with a differential pressure gauge. The reactor consisted of a stainless-steel tube equipped with an axial thermowell. A Nichrome wire-wound, tubular furnace was used to heat the reactor to the desired test temperature.

Transmission electron micrographs were obtained at 100 KV on a Phillips EM-300 instrument. Standard techniques for dispersing catalyst specimens were used. Scanning electron microscopy and microprobe studies were carried out using a JEOLCO JSM U-3 scanning microscope equipped with a JEOLCO crystal spectrometer. Sulfur and molybdenum were detected using the K_α and L_α lines, respectively.

Procedure

Sulfidation. The calcined catalyst was heated slowly in N_2 in the flow system at 200 ml/min over a period of 3 h to the sulfiding temperature. A 10% H_2S/H_2 mixture was then passed over the catalyst (~2.5 g) for 1 h at 100 ml/min. After cooling to room temperature, the flow was stopped and the reactor stopcocks closed. The reactor was then removed from the flow system and attached to the high-vacuum system.

Sulfur exchange. In some preliminary experiments, the sulfided catalyst was evacuated, the H_2/H_2S exchange mixture made up in a loop isolated from the catalyst, and the experiment begun by opening this loop to the reactor. Much of the H_2S quickly disappeared from the gas phase under these circumstances, indicating significant adsorption of H_2S on the evacuated catalyst. The following procedure was therefore adopted in all subsequent experiments. After evacuation of the connections, the reactor was heated to the desired exchange temperature and held there for a period of about 2 h. The gases in equilibrium with the catalyst were expanded into the evacuated circulation loop and circulation was continued for about an hour to establish an initial equilibrium. The reactor was then isolated from the calibrated loop volume, the number of molecules of H_2S present in the loop determined by a pressure measurement after pumping off hydrogen at −196°C, and the number of H_2S molecules in the reactor calculated from the ratio of reactor-to-loop volumes. H_2S in the loop was pumped off and tagged H_2S/H_2 added so that the number of H_2S molecules was approximately the same as before. The partial pressure of H_2S in both volumes was about 0.1 atm. An initial counting rate was determined and the loop opened to the reactor. Counts per second were recorded at selected time intervals during the course of the exchange reaction which was continued for an overnight period to establish a final equilibrium value. The amount of H_2S at the conclusion of the experiment was measured as mentioned previously and a final specific activity determined.

Activity measurements. Ten milliliters of catalyst (20 × 40 mesh particles) were loaded into the reactor. The catalyst was heated in flowing N_2 and sulfided at 315°C according to the procedure used in pretreating the samples prior to sulfur-35 exchange. The furnace oil and hydrogen mixture was admitted at 315°C; then the reactor system was adjusted to the desired run conditions: 3.5 MPa, 315°C, 3 LHSV, and 445 ml (STP)/min of hydrogen. Since the steady-state activity of the catalyst was of interest, the first 2-h product was discarded. The product of the next two, 2-h periods was analyzed for sulfur by a conventional combustion technique. Preliminary runs had shown that steady state was reached in 2 h.

Catalysts

The molybdenum catalysts were prepared by impregnation of 20 × 40 mesh γ-alumina (Filtrol Grade 86) with a solution of ammonium paramolybdate. This was followed by oven drying at 120°C overnight and calcining in air at 540°C for 16 h. Physical properties are given in Table 1.

Materials

Five milliCuries of sulfur-35 as hydrogen sulfide gas were obtained from the Mathe-

TABLE 1

Physical Properties of Catalysts Used

Catalyst	BET S.A. (m^2/g)	Pore volume (cm^3/g)	Average pore radius (Å)
γ-Al_2O_3	282	0.63	45
4% Mo/Al_2O_3	240	0.57	48
8% Mo/Al_2O_3	217	0.55	51
12% Mo/Al_2O_3	203	0.48	48
20% Mo/Al_2O_3	157	0.40	51
30% Mo/Al_2O_3	99	0.25	50

son Company. This was diluted with C.P. grade H_2S gas (water-free) to yield a specific activity of 0.375 mCi/mmol. Prepurified H_2 and N_2 (Matheson) were used as received.

The petroleum stock used in the desulfurization activity tests was an FCC furnace oil boiling between 195 and 345°C, having a specific gravity of 0.92 at 0°C and containing 0.84% S, 335 ppm N, and 75% aromatics.

RESULTS

Exchange Experiments

Preliminary experiments showed that room-temperature exchange would be difficult to follow in the present apparatus. The volume of H_2S adsorbed on the sample at 25°C was so large that isotopic exchange was due mainly to extremely fast displacement exchange with the adsorbed gas. Since exchange between gas-phase H_2S and sulfur bound irreversibly to the molybdenum was of primary concern, experiments were therefore carried out at a minimum temperature of 100°C.

The amount of exchangeable sulfur at equilibrium, $N_{S\infty}$, was calculated as

$$N_{S\infty} = \frac{C_0 - C_\infty}{C_\infty} \times N_{H_2S}, \qquad (1)$$

where N_{H_2S} is the number of hydrogen sulfide molecules in the gas phase, C_0 and C_∞ the initial and final counting rates, respectively. In addition, the exchange rates were calculated in terms of N_S versus time, where N_S was obtained by substituting the counting rate at time t for C_∞ in Eq. (1). This permits a comparison of both reaction rates and the equilibria to which they pertain.

Figure 1 shows the extent of exchange with time on 12 wt% molybdenum–alumina when the presulfiding and exchange temperatures were varied. Sample weight was 2.79 g. Exchangeable sulfur increased significantly as the exchange temperature was raised from 100 to 400°C. In addition, the sulfur exchanged at 100°C was slightly higher after presulfidation at 315 versus 400°C.

The effect of molybdenum content on exchangeable sulfur was therefore studied at 100°C after presulfidation at 315°C. The 100°C exchange temperature was selected to confine exchange to the surface in the event that discrete MoS_2 crystallites were present. As shown in Fig. 2, exchange on the alumina base at 100°C lined out rapidly in comparison with the molybdenum-containing catalysts. Figure 2 also shows the increase in exchangeable sulfur at 100°C as the concentration of molybdenum was increased, the corresponding values of $N_{S\infty}$ being given in Table 2. An approximately

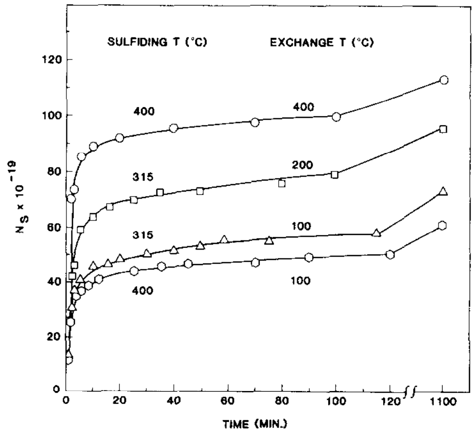

FIG. 1. Exchange of sulfur with time for 12 wt% molybdenum–alumina as a function of presulfiding and exchange temperature. Sample size 2.79 g.

TABLE 2

Sulfur Exchanged at 100°C in Sulfided Catalysts

Catalyst	Sample wt. (g)	$N_{S\infty}$/g cat. ($\times 10^{-19}$)	Total run time (min)
Al_2O_3	2.5883	8.2	1070
4% Mo	2.6914	13.2	1068
8% Mo	2.6791	18.8	1048
12% Mo	2.7860	26.0	1165
20% Mo	2.7387	26.3	1045
30% Mo	2.6683	23.4	1110

linear increase in exchangeable sulfur was observed up to 12 wt% molybdenum. The rates of exchange and the equilibria obtained were nearly identical at 12 and 20 wt% molybdenum, while exchange on the 30 wt% molybdenum sample was lower than on either of these.

The kinetics of exchange at 100°C were complex. As indicated in Fig. 2, the initial reaction was fast and limitations on circulating pump speed prevented kinetic analysis. However, this rapid reaction could be tentatively identified with a displacement exchange of reversibly adsorbed H_2S by means of evacuation experiments. After the exchange reaction reached equilibrium, the catalyst was evacuated for several hours at exchange temperature and the number of H_2S molecules desorbed and trapped at −196°C was measured. Results for the 8 wt% Mo/Al_2O_3 catalyst are shown in Table 3. If it is assumed that this quantity of H_2S corresponds to reversibly adsorbed gas in the original experiment, then the total exchange observed ($N_{S\infty}$) can be separated into exchange with reversibly adsorbed H_2S, N_S(ads), and exchange with a more strongly bound sulfur, probably Mo–S, [N_S(Mo–S)]. At 100°C, approximately 50% of the total exchange measured was with reversibly adsorbed H_2S. As temperature was increased, the amount of reversibly adsorbed H_2S decreased, and the major quantity of sulfur exchanged was of the strongly bound form at 315–400°C (Table 3). It is noteworthy that the value of N_S(ads) for 8 wt% molybdenum–alumina was comparable to the fast exchange observed with alumina itself (Table 2).

When the two types of reaction were differentiated by subtracting out the rapid exchange according to the volume of evacuable H_2S, the kinetics of the slower reaction were of the Elovich type.

The catalysts sulfided at 315°C were analyzed for total sulfur present by a combustion method. The data are shown in Table 4. Net sulfur contents, obtained by sub-

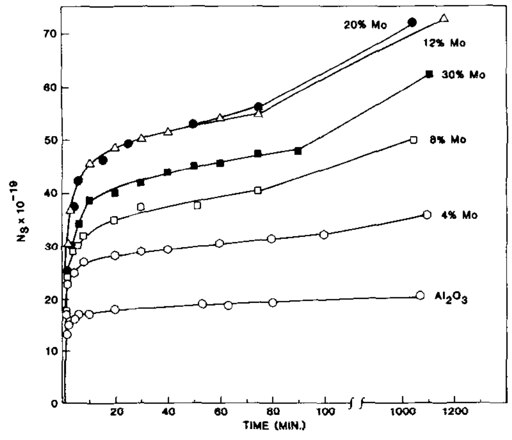

FIG. 2. The effect of molybdenum content on exchangeable sulfur at 100°C. Sample size approximately 2.5 g.

TABLE 3

Exchange and Evacuation Experiments on 8 wt% Mo/Al_2O_3 as a Function of Temperature

$N_{S\infty} = N_S(\text{ads}) + N_S(\text{Mo–S})$

T_{exchg} (°C)	$N_{S\infty}$/g[a] ($\times 10^{-19}$)	N_S(ads)/g[b] ($\times 10^{-19}$)	N_S(Mo–S)/g[c] ($\times 10^{-19}$)
100	18.8	8.5	10.3
315	24.4	3.0	21.4
400	36.0	2.4	33.6

[a] Experimentally determined exchangeable sulfur.

[b] Reversibly adsorbed H_2S, removable by evacuation after the exchange experiment.

[c] $N_{S\infty} - N_S$(ads).

TABLE 4

Percentage of Sulfur Exchanged at 100°C

Catalyst	wt% Sulfur by combustion	Net[a] wt% sulfur	S/Mo	% Total[b] sulfur exchanged	% Net[c] sulfur exchanged
Al_2O_3	2.46				
4% Mo	4.80	2.39	1.79	14.6	29.4
8% Mo	7.10	4.86	1.82	14.1	20.6
12% Mo	9.17	7.00	1.74	15.1	19.8
20% Mo	13.98	12.16	1.82	10.1	11.5
30% Mo	12.80	11.40	1.14	9.7	10.9

[a] Net sulfur equals sulfur analyzed less the sulfur blank on the alumina, which includes 1.1% sulfate impurity.

[b] $N_{S\infty}$ as percentage of gross sulfur content.

[c] $N_{S\infty}$ as percentage of net sulfur content.

tracting the alumina blank, are also given. The S/Mo ratio was fairly constant (1.8), up to 20 wt% molybdenum using the net values. It decreased to 1.1 at 30 wt% molybdenum.

Table 4 also shows exchangeable sulfur as a percentage of sulfur content in this series of catalysts. The quantity of sulfide ion bound to molybdenum is experimentally inaccessible. The net sulfur contents given in Table 4 probably approximate this quantity. In subtracting the alumina blank, however, no allowance is made for the fact that molybdena coats the alumina surface, which may reduce sulfur pickup by the alumina during sulfiding. For this reason, the true value for sulfide ion associated with molybdenum may be somewhat higher than the net values of Table 4.

The exchangeable sulfur ($N_{S\infty}$) was roughly 15% of the gross sulfur content and 20% of the net value in catalysts containing 4 to 12 wt% molybdenum. (Exchangeable sulfur was ~30% of net sulfur content in the 4 wt% Mo catalyst, where use of an overly large blank would be expected to introduce the greatest error.) Exchange with strongly bound sulfur, N_S(Mo–S) must therefore involve some 8–10% of the net sulfur content, since roughly half of the exchange observed at 100°C was with reversibly adsorbed H_2S (Table 3). At 400°C, the exchangeable sulfur was about 30% of the net sulfur content of the 8 and 12 wt% molybdenum catalysts.

As shown in Table 4, the fractional exchange at 100°C was significantly lower in the 20 and 30 wt% molybdenum catalysts.

Exchange data were also obtained for a 1.5 wt% nickel–8.0 wt% molybdenum alumina catalyst. The extent of exchange at 100°C was identical to that found with 8 wt% molybdenum alone. However, when the exchange temperature was increased to 315°C for direct comparison with the temperature of the desulfurization reaction, the nickel–molybdenum catalyst showed a twofold increase in exchangeable sulfur over the molybdenum catalyst (Table 5).

Electron Microscopy and Microprobe Studies

Up to 12 wt% molybdenum, the transmission electron microscope revealed essentially no difference between the appearance of the calcined molybdenum catalysts and that of the alumina alone. A few widely scattered metal oxide microcrystals were observed on the 8 and 12 wt% samples, but it was clear that most of the molybdenum content was unresolved. Samples of the 12 wt% molybdenum–alumina were also examined after sulfidation and after overnight reduction in hydrogen at 500°C. Discrete crystallites of the molybdenum phase were not observed in either case.

On the 20 and 30 wt% Mo/Al_2O_3 catalysts, micrometer-size platelets of MoO_3

TABLE 5

Effect of Nickel Addition on Hydrodesulfurization Activity and Sulfur-35 Exchange

$NiMo/Al_2O_3$ vs Mo/Al_2O_3

Catalyst	T_{exchg} (°C)	$N_{S\infty}/g$ ($\times 10^{-19}$)	% Desulf. (315°C)
8 wt% Mo	100	18.8	
	315	24.4	40
1.5 wt% Ni; 8 wt% Mo	100	18.7	
	315	44.8	80

were observed by transmission electron microscopy and identified by electron diffraction. Scanning electron micrographs of exterior and interior surfaces of the catalyst pellets showed that these large molybdena crystals were confined to the geometric surface of the pellets. Clusters of molybdena platelets were readily observable in scanning electron micrographs of the pellet surface while the internal surfaces of fractured pellets could not be distinguished from those of alumina itself.

This precipitation of excess molybdenum on the exterior surface was confirmed by electron probe microanalysis. The molybdenum profiles of sulfided pellets containing 20 and 30 wt% molybdenum showed high molybdenum concentrations at the exterior surface. Significantly, the peak for sulfur was not correspondingly intense, indicating that these large aggregates of molydena crystals did not sulfide as readily as the well-dispersed molybdenum. This probably accounts for the decline in sulfur-to-molybdenum ratio at high molybdenum content (Table 4). Microprobe analysis also showed that molybdenum concentration on the interior of the 20 wt% molybdenum alumina sample was similar to that on the interior of the 12 wt% molybdenum sample. The interior concentration was somewhat higher on the 30 wt% molybdenum sample.

Catalytic activity. The same series of catalysts was sulfided under identical conditions in a flow microreactor and evaluated for the desulfurization of a furnace oil at 315°C. The activity data, based on a constant volume of catalyst, were converted to a weight basis by using measured bulk densities. The relationship to the sulfur exchange data is displayed in Fig. 3. Since the reactions were carried out in a large excess of hydrogen and the feedstock contained only 0.84 wt% sulfur, the H_2S/H_2 ratio should have been essentially constant for all runs and, therefore, should not have affected the level of desulfurization. The increase in desulfurization activity with increasing molybdenum content up to 8 wt% molybdenum paralleled the linear increase in the total number of sulfide ions exchanged. Catalytic activity appeared to maximize at 8 wt% molybdenum, however, with little improvement noted at higher concentrations.

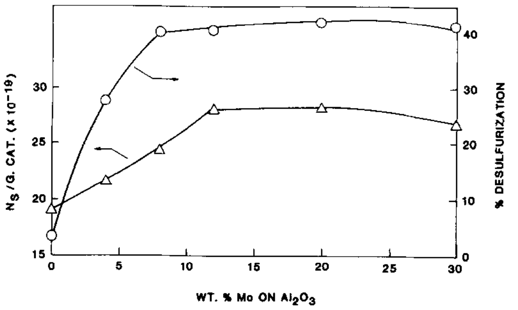

FIG. 3. Effect of molybdenum content on exchangeable sulfur (100°C) and desulfurization activity.

The addition of Ni to the molybdena–alumina catalyst resulted in a dramatic increase in desulfurization activity. As shown in Table 5, the extent of desulfurization with the Ni, Mo/Al_2O_3 catalyst was 80% compared to 40% with the corresponding Mo/Al_2O_3 catalyst.

DISCUSSION

The relative activities of the present series of catalysts for hydrodesulfurization were similar to the data reported by Russell and Stokes (*21*) for the dehydrocyclization of *n*-heptane to toluene. Catalytic activity increased rapidly with added molybdenum up to a certain point, and remained constant when molybdenum was added beyond that value. Molybdenum content had a different effect on aldol condensation (*19*) and on gasoline yield in reforming (*18*). In these reactions, product yield increased with molybdenum content, reached a maximum, and declined rapidly upon the addition of further molybdenum. In each case, however, the relationship between catalytic activity and molybdenum content changed markedly at about 8–12 wt% molybdenum, a value which Russell and Stokes equated with monolayer coverage of the alumina by the molybdenum phase.

The present electron microscope and microprobe studies tend to confirm this picture. Discrete molybdena crystals were not observed on calcined catalysts containing 4, 8, or 12 wt% molybdenum. Transmission electron microscopy also failed to resolve the molybdenum phase in a sample of 12 wt% molybdenum–alumina which had been reduced overnight in hydrogen at 500°C or sulfided for 4 h at 500°C. In contrast, very large molybdena crystals were found in catalysts containing 20 and 30 wt% molybdenum and scanning electron microscopy showed that these crystals were located at the exterior of the catalyst pellets. Electron probe microanalysis confirmed the presence of excess molybdenum on the periphery of the catalyst pellets, and also showed that the molybdenum concentration within the pellets was fairly uniform and not very different in catalysts containing 12, 20, or 30 wt% molybdenum.

These results describe a system comprised of two distinct phases. They suggest that roughly 8–12 wt% molybdenum interacted with the alumina during impregnation so that subsequent calcination, reduction, or sulfiding did not yield a detectable, crystalline molybdenum phase. Further molybdenum added to the catalyst probably precipitated on the alumina during drying predominantly on the exterior of the catalyst pellets.

We conclude that S^{35} exchange between hydrogen sulfide and catalyst sulfur does not define a molybdenum sulfide surface in the sense that Lukens *et al.* (*15*) assumed, i.e., a single-phase system in which the size of metal sulfide crystallites increases with increasing molybdenum content. This is not consistent with the two-phase system observed by electron microscopy. The small fraction of available sulfur which exchanged with H_2S at all molybdenum levels in the present study is also inconsistent with such a model. The number of exchangeable sulfur atoms at 100°C was only 15% of the sulfur content measured by elemental analysis, and half of this amount was identified with displacement exchange of adsorbed hydrogen sulfide which could be removed from the surface by evacuation. Thus, in samples for which the atomic ratio of combined sulfur to molybdenum was approximately 1.8, only 8% of the irreversibly bound sulfur was exchanged at 100°C. Since Lukens *et al.* (*15*) showed that the entire surface sulfide ion in pure molybdenum disulfide exchanged at room temperature, molybdenum disulfide crystallites dispersed on the alumina would have to be at least 100 Å in size to give the low levels of exchangeable sulfur observed in the present study. MoS_2 crystallites of this size would be completely at odds with the disordered structures detected by Raman spectroscopy (*5*) and EXAFS (*10*). In addition, it seems likely that such crystallites would be observed in the transmission electron microscope, which they were not. Therefore, the low sulfur exchange found on sulfided molybdenum–alumina can be taken as further evidence for an Mo–S surface different than that found in molybdenum disulfide.

The increase in exchangeable sulfur with temperature between 100 and 400°C, coupled with the low percentage of bound sulfur exchanged even at 400°C (30%) suggests that the strength of molybdenum–sulfur bonds in the surface is very heterogeneous. The fact that the exchange observed at 100°C obeyed Elovich kinetics is consistent with this picture. Work with pure tungsten disulfide, which should be a reasonable analog for molybdenum disulfide, showed (*20*) that surface and bulk sulfide ion were readily distinguishable in this temperature range. Surface sulfide ion was exchangeable at 100°C, when no bulk exchange could be discerned. At 400°C, surface sulfide ion was exchanged very rapidly, while bulk exchange was extremely slow, in keeping with the Tamman temperature (about 600°C for both tungsten and molybdenum disulfides).

The effect of temperature on sulfur exchange in the molybdenum–alumina system showed no sharp distinction which could be attributed to surface versus bulk exchange in MoS_2 crystallites. It also seems unlikely that the present results could be obtained with a catalyst containing uniform 15-Å crystallites of MoS_2, as EXAFS studies have suggested for a cobalt–molybdenum alumina sulfided at 300–400°C (*10*). Essentially all the sulfide ion in such crystallites should be exchangeable at low temperatures, based on the work of Lukens *et al.* with unsupported MoS_2.

The exchange reactions observed on sulfided molybdenum–alumina seem more consistent with recent descriptions of the sulfided catalyst by Schrader and Cheng (*5*, *9*) or with concepts advanced by Massoth (*22*, *23*), i.e., the local environment of molybdenum in the sulfided catalyst is diverse, including complex oxysulfide species and disordered molybdenum sulfides which remain bound to the alumina by Mo–O–Al bonds. "True" MoS_2 crystallites may be present, but they are probably not an important feature of catalysts sulfided at commercial sulfiding conditions.

In spite of this complexity, the exchangeable sulfur at 100°C almost certainly involved molybdenum–sulfur bonds and correlated with dispersion of the active phase. The number of exchangeable sulfur atoms paralleled molybdenum content up to about 12 wt% molybdenum, leveling off at this point. For this reason, the exchange results also showed fair agreement with the desulfurization activity of this series of catalysts. However, the 12 wt% molybdenum catalyst contained substantially more exchangeable sulfur than the 8 wt% molybdenum sample, while the two had comparable desulfurization activity. The exchange results did parallel the general trend in activity in a way which molybdenum content, sulfur content, or BET area did not.

The exchange was studied at 100°C because distinction between surface and bulk exchange on pure tungsten disulfide was known to be good at this temperature (*20*). The exchangeable sulfur contents of the 8 wt% molybdenum and the 1.5 wt% nickel, 8 wt% molybdenum catalysts were identical at this temperature. At 315°C, however, there was twice as much exchangeable sulfur in the nickel-containing catalyst. This is an intriguing result, which we have been unable to pursue. Hopefully, it may stimulate others to investigate this exchange reaction, which appears to have been ignored since the early studies of Lukens *et al.* (*15*).

REFERENCES

1. Massoth, F. E., "Advances in Catalysis and Related Subjects," Vol. 27, p. 265. Academic Press, New York, 1978.
2. Furimsky, E., *Catal. Rev. Sci. Eng.* **22,** 371 (1980).
3. Lipsch, J. M. J. G., and Schuit, G. C. A., *J. Catal.* **15,** 174 (1969).
4. Hall, W. K., *in* "Proceedings, 4th International Conference on Chemistry and Uses of Molybdenum" (H. Barry, Ed.). Climax Molybdenum Co., Golden, Colorado, 1982.
5. Schrader, G. L., and Cheng, C. P., *J. Catal.* **80,** 369 (1983).
6. Voorhoove, R. J. H., and Stuiver, J. C. M., *J. Catal.* **23,** 228 (1971).
7. Parekh, B. S., and Weller, S. W., *J. Catal.* **65,** 263 (1980); **66,** 65 (1980).
8. Schuit, G. C. A., and Gates, B. C., *Amer. Inst. Chem. Eng. J.* **14,** 159 (1968).
9. Schrader, G. L., and Cheng, C. P., *J. Catal.* **85,** 488 (1984).
10. Parham, T. G., and Merrill, R. P., *J. Catal.* **85,** 295 (1984).
11. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
12. Tauster, S. J., and Riley, K. L., *J. Catal.* **67,** 250 (1981).
13. Zmierczak, W., Muralidhar, G., and Massoth, F. E., *J. Catal.* **77,** 432 (1982).
14. Fierro, J. L. G., Gonzalez Tejuca, L., Lopez Agudo, A., and Weller, S. W., *J. Catal.* **89,** 111 (1984).
15. Lukens, H. R., Meisenheimer, R. G., and Wilson, J. N., *J. Phys. Chem.* **66,** 469 (1962).
16. Seshadri, K. S., Massoth, F. E., and Petrakis, L., *J. Catal.* **19,** 95 (1970).
17. Pollack, S. S., Makovsky, L. E., and Brown, F. R., *J. Catal.* **59,** 452 (1979).
18. John, G. C., Den Herder, M. J., Mikovsky, R. J., and Waters, R. F., "Advances in Catalysis," Vol. 9, p. 252. Academic Press, New York, 1957.
19. Seshadri, K. S., and Petrakis, L., *J. Phys. Chem.* **74,** 4102 (1970).
20. Freel, J., Larson, J. G., and Adams, J. F., submitted for publication.
21. Russell, A. S., and Stokes, J. J., *Ind. Eng. Chem.* **38,** 1071 (1946).
22. Massoth, F. E., *J. Catal.* **36,** 164 (1975).
23. Massoth, F. E., *J. Less-Common Met.* **54,** 343 (1977).