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Studies of Molybdena–Alumina Catalysts

IV. Rates and Stoichiometry of Sulfidation

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Molybdena–alumina catalysts were sulfided with H_2S/H_2 blends either directly from the calcined (oxidized) state or after prereduction with H_2. The course of the reaction was followed gravimetrically; sulfur analyses at the end of a run permitted material balance calculations to be made on the end state of the catalyst. Sulfided and reduced catalysts were additionally characterized by NH_3 adsorption and D_2 exchange.

Catalyst sulfiding occurred readily above 300°C. Extent of sulfiding increased with temperature. However, a limiting catalyst sulfur content was obtained at a given temperature; neither increase in H_2S partial pressure nor time much affected the sulfur level. The predominant reaction was exchange of oxygen associated with the molybdena (reactive oxygen) for sulfur, with formation of water. At higher temperatures, some additional reactive oxygen was lost due to a reductive reaction (also forming water), which presumably created anion vacancies. Prereduced catalysts sulfided to a lesser extent, even though some sulfur apparently added to anion vacancies present after the prereduction. Ammonia adsorption on sulfided and reduced catalysts showed a correlation with anion vacancy concentration. Exchange measurements with D_2 revealed that the sulfided catalyst irreversibly retained appreciable hydrogen, probably as -SH groups on the surface; the magnitude of the retained H was far greater than that found for reduced catalysts. The Al_2O_3 portion of the catalyst appeared to contain less hydrogen than that characteristic of the pure Al_2O_3 base.

A model of the catalyst surface, consisting of one-dimensional, chain-like groupings of MoO_2 over the Al_2O_3 substrate, is proposed to explain the results.

NOMENCLATURE

H_{Al}	hydrogen content of Al_2O_3 phase
H_I	irreversibly adsorbed hydrogen on Mo phase
H_R	reversibly adsorbed hydrogen on Mo phase
H_T	total hydrogen content of catalyst
O_A	excess water adsorbed on sulfided catalyst
O_E	reactive oxygen exchanged for sulfur
O_L	reactive oxygen lost as gaseous water
O_R	reactive oxygen remaining after reduction
O_{Rs}	reactive surface oxygen remaining after reduction
O_S	reactive oxygen remaining after sulfidation
O_T	total reactive oxygen on oxidized catalyst
O_{Ts}	total reactive surface oxygen on oxidized catalyst
S	total sulfur added to catalyst
S_E	exchange sulfur added to catalyst
S_I	incorporated sulfur added to catalyst
W_M	weight of molybdenum
W_O^0	weight of reactive oxygen on calcined catalyst

W_O^R	weight of reactive oxygen left on reduced catalyst
W_O^S	weight of reactive oxygen left on sulfided catalyst
W_{O_A}	weight of excess water adsorbed on sulfided catalyst
W_{O_E}	weight of oxygen lost through exchange with sulfur
W_S	weight of total sulfur
W_{S_E}	weight of exchanged sulfur
W_{S_I}	weight of incorporated sulfur
ΔW_{O_R}	weight loss in reduction of oxidized catalyst
ΔW_{O_S}	weight gain in sulfidation of oxidized catalyst
ΔW_{R_S}	weight gain in sulfidation of reduced catalyst
$\square_R$	anion vacancies present after reduction
$\square_S$	anion vacancies present after sulfidation

INTRODUCTION

Previous publications in this series (*1–3*) have dealt with reduction characteristics of molybdena–alumina catalysts. Since these catalysts are exposed to a sulfiding atmosphere when employed for hydrodesulfurization of sulfur-containing feedstocks, it becomes germane to characterize the state of the sulfided catalyst, especially as the catalyst is commonly presulfided prior to use. It is the latter process that is the main concern of the present report, namely, reactivity of a Mo/Al_2O_3 catalyst to an H_2S environment and characterization of the resultant sulfided catalyst.

It is surprising that despite all the work done with sulfided molybdena catalysts, the stoichiometry of the sulfided catalyst has not been investigated in any detail. The assumption has generally been made that MoS_2 is present, despite the fact that it is not observed by X-ray diffraction analysis (XRD). This view is probably engendered by the known hydrodesulfurization activity of unsupported MoS_2 (*4,5*) and the nonexistence of any known stable molybdenum oxysulfide. Against this trend, Armour, Ashley and Mitchell (*6*) presented evidence for a surface molybdenum oxysulfide on alumina, and Schuit and Gates (*7*) proposed a detailed surface model involving oxygen and sulfur; neither work, however, provided quantitative data on sulfided catalyst stoichiometries. Kabe *et al.* (*8*), in a limited study, reported a sulfided catalyst stoichiometry of $MoO_{1.5}S_{1.1\text{-}1.5}$. The present paper deals with this problem in detail as well as rates of sulfiding. From these and prior studies, a clearer picture of the structure of the Mo/Al_2O_3 catalyst should emerge.

EXPERIMENTAL METHODS

Catalyst supports used were a Davison high-purity η-alumina (BET surface area, 175 m^2/g; pore volume, 0.26 cm^3/g) and a Ketjen thermally stabilized γ-alumina (191 m^2/g, 0.46 cm^3/g). Catalysts were prepared by impregnation of the support with ammonium paramolybdate solution followed by calcination in air at 540°C for 16 hr. Molybdenum content and surface area of the calcined catalysts were: 8.5% and 166 m^2/g for the η-Al_2O_3; and 8.1% and 185 m^2/g for the γ-Al_2O_3. Catalysts were sized to 20 to 40 mesh.

A flow microbalance reactor was used to follow weight changes accompanying catalyst reduction or sulfidation. The apparatus has been described previously (*2*). In order to prevent reaction of the H_2S with the electrobalance (Cahn) components, a positive flow of N_2 through the balance case was maintained; back diffusion of H_2S from the reactor was avoided by means of a long, narrow tube carrying the N_2 from the balance case into the top of the reactor. The reactive gases entered from the bottom of the reactor, past the catalyst in a quartz bucket, and exited together with the top N_2 purge at the top of the reactor. The H_2S was supplied from a prepared mixture containing 9 vol % H_2S in H_2. Various H_2S partial pressures in H_2 were achieved by flow mixing the H_2S/H_2 blend with extra H_2 by use of standard rotameters. All runs were conducted at atmospheric pressure. Air, N_2 and H_2 were predried by passing through 4A molecular sieves. N_2 was passed through hot copper turnings and H_2 through a Deoxo unit prior to the sieves.

Catalyst charges of 300–400 mg were used. The catalyst was first heated in an air flow overnight at the temperature of the run to attain a constant weight. After flushing the reactor with N_2, the H_2S/H_2 mixture was admitted for a given reaction time, followed by another N_2 purge to constant weight. When catalyst prereduction was desired, a H_2 exposure (followed by N_2 purge) preceded the H_2S/H_2 step. Weight changes were corrected for gas buoyancy by reference to N_2 at the same temperature. Sulfur content of catalysts was determined by a high temperature combustion method.

Ammonia adsorption measurements were made on oxidized, reduced, and sulfided catalysts to determine the effect of the catalyst state on adsorption of a strong base. The same flow microbalance apparatus was used. After the appropriate reaction was carried out and the catalyst was purged with N_2 for 1 hr, the temperature was adjusted to 343°C. A 1% NH_3 in N_2 blend was passed over the catalyst for about 1 hr, followed by a N_2 purge for 1 hr. Comparison runs were made with the Al_2O_3 support. The sulfided catalysts were analyzed for sulfur after NH_3 adsorption.

Deuterium exchange experiments were made on Al_2O_3 support and catalysts which had been previously reduced or sulfided. The object of these experiments was twofold: (a) to estimate the H content associated with the free Al_2O_3 portion of the Mo/Al_2O_3 catalyst, and (b) to estimate the H content associated with the molybdenum phase on the sulfided catalyst. The H content associated with the molybdenum on reduced catalysts had been previously measured (*3*).

A conventional vacuum, circulating system similar to that used earlier (*3*) was employed in conjunction with a Veeco analyzer for following changes in H_2, HD, and D_2 concentrations in the gas-phase attending exchange. A capillary tube leak continuously bled off a small fraction of the gas-phase into an intermediate vacuum (about 10^{-3} Torr), followed by a variable leak controller into the mass spectrometer (about 10^{-7} Torr). The time response of a measurement was less than 15 sec with this arrangement. A correction for mass discrimination in the capillary was made by resort to calibrated mixtures of H_2 and D_2 in the approximate concentrations encountered in the experiments. Exchange was carried out at 350–400°C and 70-100 Torr pressure. Equilibrium between the gas-phase and catalyst was taken to be complete when no further change in gas-phase composition took place. Gas-phase equilibration was rapid, being complete within 10–15 min as judged by the closeness of the calculated equilibrium constant to the theoretical value (*9*). Equilibrium with the catalyst was usually achieved within 0.5–1 hr.

Catalysts were reduced or sulfided by flow of H_2 or H_2S/H_2 mixture at atmospheric pressure, followed by a 1-hr purge in N_2. Prior to exposure to D_2, the catalysts were evacuated to below 1 μm pressure for at least 1 hr. In some runs, water generated from reduction or sulfidation was collected in a liquid N_2 or dry ice trap, respectively, allowing independent calculation of catalyst stoichiometry. During D_2 exchange, H_2O and/or H_2S desorption was experimentally determined to be small (< 5% of D_2) and was ignored in calculations.

Calculations of the H-content of catalysts were made according to the method of Cheselske, Wallace and Hall (*10*). The following formula was employed:

$$n_H = \left(\frac{X_e}{1 - X_e}\right) n_D{}^0,$$

where n_H is the moles of H on the catalyst, $n_D{}^0$ is the moles of D in the starting D_2 gas phase, and X_e is the atom fraction of H in the gas-phase at equilibrium.

TREATMENT OF DATA

Two types of sulfiding experiments were made: (a) direct sulfiding of the calcined catalyst, and (b) sulfiding of a prereduced catalyst. Data analysis basically consists of a material balance around catalyst oxygen and sulfur, after reaching a constant final weight in the N_2 purge. Therefore, the analysis pertains to the final stable catalyst state, exclusive of readily desorbed products. Of course, the latter are determined directly by the weight loss during the N_2 purge.

The following assumptions are made:

1. The only reactive O is that associated with the Mo in the catalyst and is in the ratio of O/Mo = 3 for the oxidized catalyst, i.e., Mo valence is +6.
2. Sulfur added is associated with the Mo.
3. The sulfur valence is always −2.
4. The weight of H retained after reduction or sulfidation is negligible.
5. Adsorbed water remaining from reduction or sulfidation reactions is negligible after N_2 purge.

Assumptions 1 and 2 require that the Al_2O_3 in the catalyst does not partake in reduction or sulfidation reactions. Liu, Chuang and Dalla Lana (*11*) reported the presence of adsorbed oxygen on oxidized Al_2O_3, which presumably could undergo reaction with H_2 or H_2S. The maximum extents of these reactions are small compared to those reported in the present investigation. Control runs on the Al_2O_3 support alone confirmed relatively small reactivities for both reactions. Assumption 3 excludes free sulfur being present on the catalyst, a remote possibility since this would require an oxidation of sulfide sulfur in a reducing atmosphere. Assumptions 4 and 5 have been found to be valid for reduction (*2,3*) and are considered reasonable for sulfidation also (see Appendix).

Direct Sulfiding

Sulfiding of the oxidized catalyst always resulted in a net weight gain. This is the difference between the S added and the O removed. A separate analysis for S allows calculation of the weight of reactive O left after sulfiding, $W_O{}^S$, according to the equation,

$$W_O{}^S = W_O{}^0 + \Delta W_{O_S} - W_S, \qquad (1)$$

where $W_O{}^0$ is the original weight of reactive O, ΔW_{O_S} is the weight change between the oxidized and sulfided catalyst, and W_S is the weight of S added. Stoichiometric ratios on the sulfided catalyst are given by,

$$O_S/Mo = 95.9\, W_{O_S}/16.0\, W_M, \qquad (2)$$

$$S/Mo = 95.9\, W_S/32.0\, W_M, \qquad (3)$$

where O_S/Mo is the moles of O left after sulfiding per mole of Mo, S/Mo the moles of S added per mole of Mo, and W_M is the weight of Mo.

During sulfiding, additional O may be lost by reduction of the catalyst. The number of anion vacancies created is the difference between the reactive O on the catalyst before and the sum of the S and O_S left after sulfiding. Thus,

$$\Box_S/Mo = 3 - (S + O_S)/Mo, \qquad (4)$$

where $\Box_S/Mo$ is the moles of anion vacancies on the sulfided catalyst per mole of Mo. This vacancy concentration can be simply considered as the fraction of reactive O lost without being replaced by S.

Prereduction Followed by Sulfiding

For reduction of the catalyst in H_2, the weight change directly reflects loss of oxygen. Therefore, the weight of O left after reduction, $W_O{}^R$, is given by,

$$W_O{}^R = W_O{}^0 - \Delta W_{O_R}, \qquad (5)$$

where ΔW_{O_R} is the weight loss upon reduction. Similarly, the moles of O left after reduction per mole Mo, O_R/Mo, and the moles of vacancies per mole Mo, $\Box_R$/Mo, are given by,

$$O_R/\mathrm{Mo} = 95.9\, W_O{}^R/16.0\, W_M, \qquad (6)$$

$$\Box_R/\mathrm{Mo} = 3 - O_R/\mathrm{Mo}. \qquad (7)$$

Upon sulfiding the prereduced catalyst, two modes of S addition may occur: (a) exchange with reactive O left, and (b) incorporation into anion vacancies. Without specifying mechanistic details at present, an overall material balance yields,

$$W_O{}^S = W_O{}^R + \Delta W_{R_S} - W_S. \qquad (8)$$

Here, $W_O{}^S$, $W_O{}^R$ and W_S are defined as before for the prereduced-sulfided catalyst, and ΔW_{R_S} is the weight gain in going from the reduced to sulfided state. Now Eqs. (2)–(4) apply for calculating the stoichiometry of the prereduced-sulfided catalyst state.

Further refinements are possible because of the manner in which the reduction–sulfidation experiments were made. Prereduction was generally carried out at elevated temperatures in order to achieve appreciable reduction; whereas, the subsequent sulfidation was done at lower temperature. As a consequence, additional loss of O due to direct reduction during the sulfiding was negligible. Therefore, the O loss in sulfiding can be considered to be due exclusively to exchange with S. In addition, the assumption that H_2O generated by the sulfiding reaction is not adsorbed on the catalyst may not be valid; this is because the Al_2O_3 water content had been equilibrated at the higher reduction temperature while the sulfidation was carried out at lower temperature, and the Al_2O_3 could thus retain additional water formed from the sulfiding reaction at this lower temperature.

With the above in mind, we separate the sulfur on the catalyst into exchanged, S_E, and incorporated, S_I. The latter is considered equivalent to irreversibly chemisorbed H_2S (see Discussion). In terms of weights,

$$W_S = W_{S_I} + W_{S_E}. \qquad (9)$$

Since the O removed in sulfidation is due exclusively to exchange with S,

$$O_E = S_E \qquad (10)$$

and since some exchange O may remain as adsorbed H_2O,

$$O_E = O_L + O_A, \qquad (11)$$

where O_E is the total reactive O exchanged, O_L that part lost as gaseous H_2O and O_A that remaining on the catalyst as adsorbed H_2O. Now, the weight change will be given by,

$$\Delta W_{R_S} = \left(\frac{34.0}{32.0}\right) W_{S_I} + W_{S_E} - W_{O_E} + \left(\frac{18.0}{16.0}\right) W_{O_A}. \qquad (12)$$

But, from Eq. (10),

$$W_{O_E} = \left(\frac{16.0}{32.0}\right) W_{S_E}. \qquad (13)$$

Combination of Eqs. (9), (12) and (13) yields,

$$W_S \underset{\mathrm{I}}{+} 2W_{O_A} = \left(\frac{8}{9}\right) [2\,\Delta W_{R_S} - W_S], \qquad (14)$$

$$W_{S_E} - 2W_{O_A} = \left(\frac{17}{9}\right) \left[W_S - \frac{16}{17}\,\Delta W_{R_S}\right]. \qquad (15)$$

These two equations contain three unknowns and consequently cannot be explicitly solved. However, analysis of the data showed that the adsorbed water on the sulfided catalyst was negligible when it had received a mild prereduction (see Appendix for calculation). Since in this case, the amount of water generated from reaction was the greatest; it was assumed that W_{O_A} was approximately zero for all prereduction conditions. Hence, W_{S_I} and W_{S_E} were calculated by Eqs. (14) and (15) omitting the W_{O_A} term, and S_I and S_E by,

$$S_I = 95.9\ W_{S_I}/32.0\ W_M, \quad (16)$$

$$S_E = 95.9\ W_{S_E}/32.0\ W_M. \quad (17)$$

RESULTS

Direct Sulfiding

Figure 1 displays actual weight change data obtained in sulfiding the calcined η-Al_2O_3 catalyst with a 1/10 mixture of H_2S/H_2 at 400°C and 1 atm under flow conditions. Four runs, each using a separate catalyst charge, were made at different durations of sulfiding. The curves show the degree of reproducibility of the sulfiding reaction. Each sample was purged with N_2 to constant weight (about 1 hr) and subsequently analyzed for sulfur content. The difference between the maximum weight gain at the end of the sulfiding time (corrected for gas buoyancy) and the final lined-out value in N_2 represents reversibly adsorbed H_2S and/or H_2O. The amount desorbed decreased with length of sulfiding treatment. It is probable that at short times, the desorption product was mainly H_2O (generated from the sulfiding reaction) which had not yet had time to desorb, whereas at long times it was H_2S since the sulfiding reaction was proceeding slowly.

Analysis of the final weight gain and sulfur data according to Eqs. (1)–(3), gave the results shown in Fig. 2A. Here the ratio of S/Mo, O_S/Mo and $(S + O_S)$/Mo are plotted against the time of sulfiding. Sulfur addition proceeded relatively rapidly and then tended to level out after 1–2 hr. A similar trend was obtained for oxygen loss by the catalyst. The sum of the sulfur added and the oxygen left was about the same, independent of reaction time, and was slightly lower than the total reactive oxygen content of the starting catalyst. This indicates that a constant anion vacancy concentration was rapidly produced prior to, or concomitant with, the sulfiding reaction. The significant finding of this experiment is that at 400°C, sulfiding of the catalyst resulted predominantly in exchange of catalyst oxygen by sulfur with

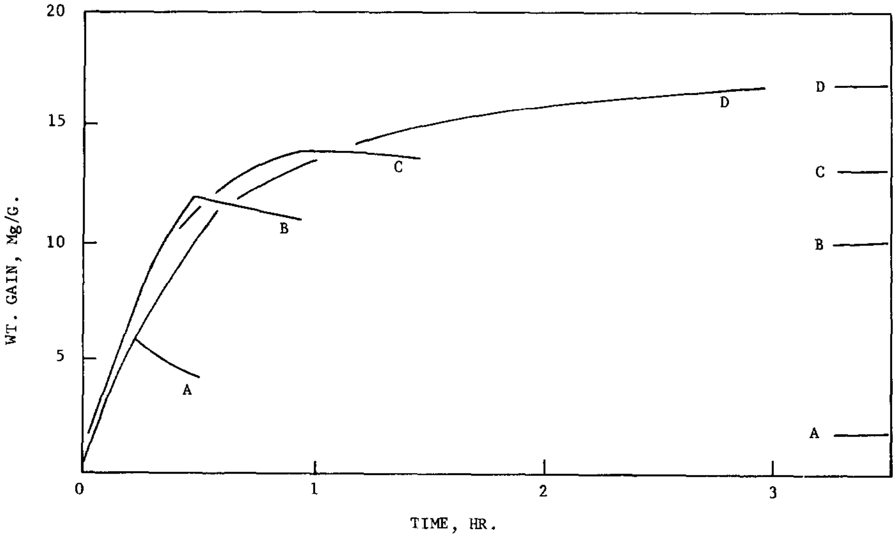


FIG. 1. Catalyst weight changes versus sulfiding time. 8% Mo/η-Al_2O_3, 400°C, H_2S/H_2 = 1/10. Curves are repeat runs terminated at: (A) 1/4, (B) 1/2, (C) 1, and (D) 4 hr; lines at extreme right are weights after 1 hr N_2 purge.

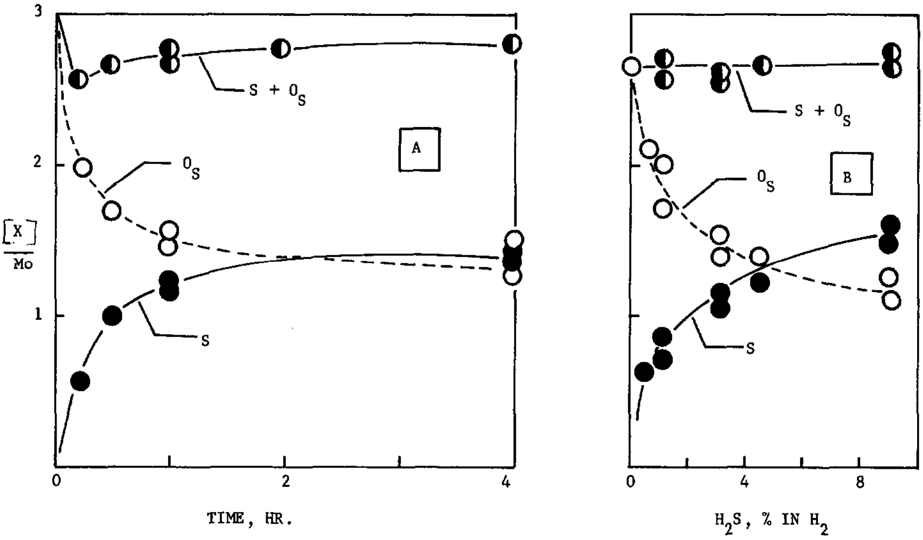


FIG. 2. Effect of time and H_2S partial pressure on catalyst stoichiometry. 8% Mo/η-Al_2O_3, 400°C. [*X*] = S (●), O_S (○), S + O_S (◐). (A) 9% H_2S in H_2, (B) 2 hr.

little net loss in total oxygen plus sulfur. In other words, the vacancy concentration remained low ($\square_S$/Mo about 0.3) despite appreciable sulfiding.

Another series of runs was carried out varying the H_2S partial pressure (balance H_2), maintaining constant temperature (400°C) and sulfiding time (2 hr). The results of the analyses of the separate runs are given in Fig. 2B. A similar trend as found for sulfiding time was obtained. There is an indication that greater concentrations of H_2S would give somewhat higher sulfur values, but the leveling out trend is apparent. Again, the vacancy concentration of the catalyst was constant throughout the H_2S partial pressure range, even at relatively high H_2/H_2S ratios.

The effect of temperature on the sulfidability was more pronounced. Figure 3 presents the results obtained over an extensive temperature range for both the η- and γ-Al_2O_3 catalysts. The most significant finding was that as temperature of sulfiding increased, extent of vacancies increased. Thus, as the S content increased with temperature, the remaining O content decreased more rapidly.

Considering the data for the η-Al_2O_3 catalyst, which covered a larger temperature range, it can be seen that appreciable sulfiding with little vacancy formation occurred at low temperature. Sulfur content increased gradually with temperature, approaching a limiting value close to S/Mo = 2 at very high temperature. At the highest temperatures, the remaining oxygen content dropped below 1 O_S/Mo. The 650°C sulfided catalyst was analyzed for the presence of MoS_2 by XRD; no evidence of any molybdenum compounds was obtained.

The sulfiding data for the γ-Al_2O_3 catalyst followed the same general trend as for the η-Al_2O_3 catalyst, but the γ-Al_2O_3 catalyst was more reactive towards sulfiding, reaching equivalent sulfur levels at much lower temperatures. Not only the sulfur levels, but also the vacancy formation was greater for the γ-Al_2O_3 catalyst at comparable conditions. At 500°C, very little reactive oxygen was left (0.3 O_S/Mo), and the sulfur level was close to 2 S/Mo. In no case was it found that the combined sulfur plus residual reactive oxygen ever fell below 2.

The temperature region of interest in commercial hydrodesulfurization is be-

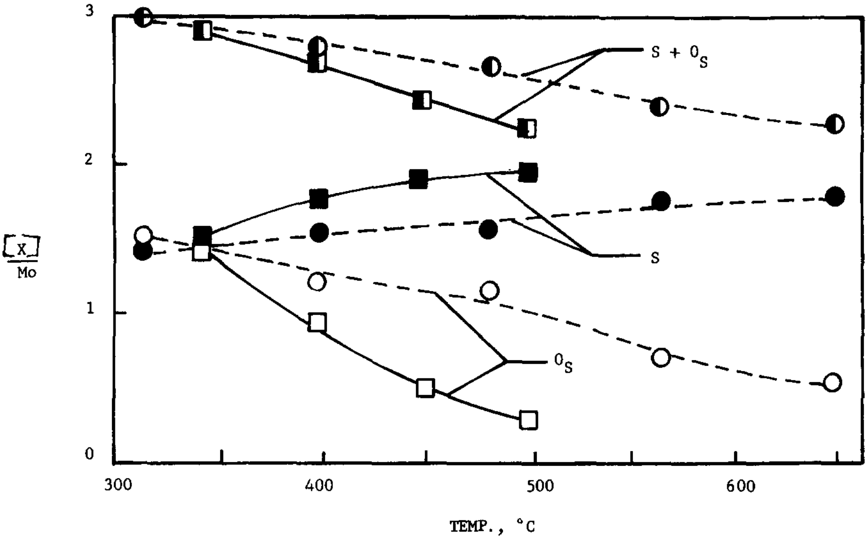


FIG. 3. Variation in catalyst stoichiometry with temperature. Circles: 8 Mo/η-Al_2O_3; squares: 8 Mo/γ-Al_2O_3; other symbols as in Fig. 2.

tween 350 and 420°C. In this regime, extensive sulfiding of the γ-Al_2O_3 catalyst occurs, but the catalyst is not completely sulfided by any means, i.e., appreciable reactive oxygen still remains. The predominant reaction is exchange of oxygen by sulfur.

Sulfiding with Prereduction

Runs in which the catalyst was prereduced prior to sulfiding were done exclusively on the Mo/γ-Al_2O_3 catalyst. In order that the catalyst did not undergo additional reduction during the sulfiding step, sulfiding was carried out at 300°C, where no net reduction was obtained. Prereductions in H_2 were conducted at increasingly higher temperatures to achieve increased extents of reduction.

The two modes of sulfiding on the reduced catalyst can be determined at the end of the reaction by knowledge of the final weight change and a separate sulfur analysis of the resultant catalyst, as described in the Treatment of Data Section. Figure 4 depicts the results obtained in terms of exchanged sulfur, S_E, incorporated sulfur, S_I, and remaining oxygen, O_S, versus the vacancy concentrations of the catalyst. The diagonal, broken line represents the reactive oxygen content, O_R, left after the prereduction but before the subsequent sulfiding of the catalyst.

Variation in the sulfided catalyst stoichiometry with degree of sulfiding followed a complex pattern. The total sulfur content, $S_E + S_I$, decreased regularly; but this was made up of a combination of a decrease in S_E and an increase in S_I with increasing prereduction. On the other hand, the residual O_S went through a maximum. Finally, the total $S + O_S$ on the sulfided catalyst remained approximately constant and then dropped off with degree of prereduction. It should be remembered that the overall extent of reduction of the sulfided catalyst is given by the difference between the total $S + O_S$ and 3. However, $S + O_S$ was always greater than O_R, indicating a partial occupation of vacancies present on the reduced catalyst.

Returning to the makeup of the retained sulfur on the prereduced and sulfided catalyst, since S_E decreased while S_I increased with extent of prereduction, an attempt was made to correlate them with different catalyst parameters. Since S_E represents the sulfur that exchanged with oxygen of

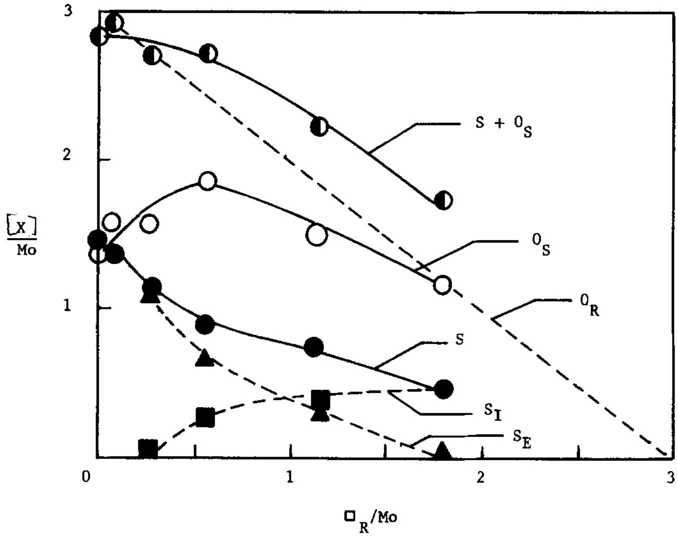


FIG. 4. Effect of prereduction on catalyst sulfiding. 8 Mo/γ-Al_2O_3. Prereduction: H_2 at various temperatures and times. Sulfidation: 2% H_2S in H_2, 300°C, 2 hr.

the catalyst, the former was plotted against the active O content of the prereduced catalyst. Figure 5A shows that S_E decreased in a nonlinear manner with decrease in O_R. The shape of the curve indicates that sulfur exchange is more pronounced at higher O_R levels. This is better illustrated in Fig. 5B, where the fraction of the surface active oxygen (O_{Rs}) which has exchanged, O_E/O_{Rs}, is plotted versus O_{Rs}. (Here it is assumed that $O_{Ts}/Mo = 2$. It should be recalled that $O_E = S_E$ by definition.) The linear relationship obtained indicates that the fraction of O_{Rs} exchanged decreased regularly with O_{Rs} left. In other words, sulfiding via oxygen exchange became progressively more difficult with lesser levels of oxygen left after reduction.

Turning to the sulfur added by incorporation, S_I, this is presumed to irreversibly adsorb on the catalyst without oxygen loss. A natural correlation in this case would consider S_I as a function of the degree of prereduction of the catalyst. This has been done in Fig. 5C, where a linear relationship is seen to obtain, lending support to the idea that S_I adsorbs on vacancies created in the prereduction. However, the quantitative relationship is quite far removed from 1 $S_I/\square_R$. Other factors may come into play here, e.g., temperature, H_2S partial pressure, which could alter the relative coverage of S_I.

Adsorbed H_2S

During the course of a sulfiding run, the weight of desorbed products obtained in the N_2 purge subsequent to sulfiding was automatically recorded. For run durations of 2 hr, the main desorbed product was H_2S and we equate this with reversibly adsorbed H_2S. Desorption ranged from 1 to 3.5 mg/g catalyst, and appeared to be independent of the number of vacancies on the sulfided catalyst. Rather, desorption correlated in a nonlinear manner with the sulfur content of the catalyst; highly sulfided catalysts exhibited nonproportionally higher reversibly adsorbed H_2S than moderately sulfided ones. Of significance, the γ-Al_2O_3 support alone, although sulfiding very little (0.2% S), desorbed 3.2 mg/g, comparable to the highly sulfided catalysts.

Ammonia Adsorption

Ammonia adsorption was relatively fast, a weight line out being established within 15 min. However, a true equilibrium was

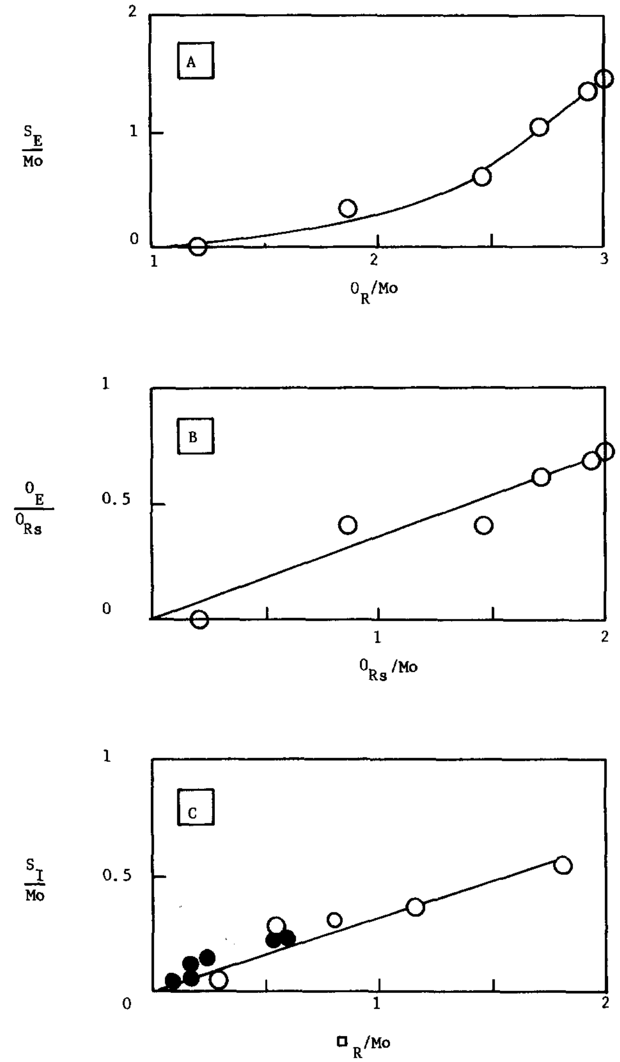


FIG. 5. Relationships between sulfided and prereduced catalyst states. (●) H_R/Mo vs $(□)_R/Mo$ data from Ref. (*3*).

not achieved, as evidenced by lack of complete reversibility. About one-half of the NH_3 adsorbed was irreversibly retained by the catalyst. The reversible part desorbed rapidly.

The results of adsorption of NH_3 on a series of reduced and sulfided catalysts are given in Table 1. The oxidized catalyst gave the lowest adsorption, about two-thirds of that of the Al_2O_3 support itself. A slow weight loss with time of NH_3 exposure was noted for the oxidized but not the reduced or sulfided catalyst, possibly due to slow reduction of the catalyst by NH_3 or displacement of water (*12*). The loss became more pronounced at 400°C, mitigating use of NH_3 for adsorption measurements at temperatures above 350°C.

In Fig. 6, the total NH_3 adsorbed is plotted against the vacancy concentration of the catalyst. A reasonably good linear relationship obtains, indicating that NH_3 adsorption is related to some property of the reduced state of the catalyst. The close agreement between the sulfided and reduced catalyst would seem to indicate that

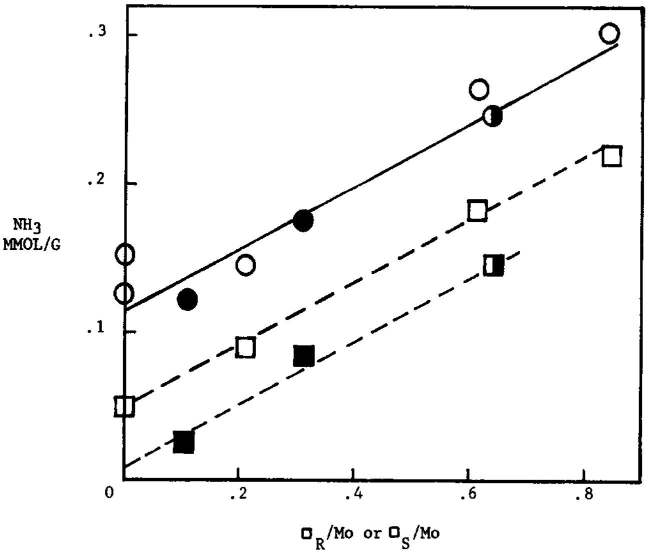


FIG. 6. Ammonia adsorption on reduced and sulfided 8 Mo/γ-Al_2O_3 catalysts. (○) Total adsorption; (□) net adsorption; (○) reduced; (●) sulfided; (◑) prereduced and sulfided.

TABLE 1
AMMONIA ADSORPTION ON TREATED Mo/γ-Al_2O_3 CATALYST

Treatment	Temp (°C)	NH_3 (mmol/g) Total	Net	□/Mo	%S
None[a]	–	0.186	0.105	–	–
Sulfided[a]	400	0.181	0.081	–	0.22
None	–	0.127	0.048	0	–
Reduced	400	0.144	0.090	0.22[b]	–
	500	0.267	0.182	0.62[b]	–
	550	0.304	0.219	0.84[b]	–
Sulfided	345	0.120	0.024	0.10[c]	4.44
	400	0.175	0.084	0.32[c]	4.71
Reduced/ Sulfided	450/345	0.245	0.145	0.65[c]	5.16

[a] γ-support alone.
[b] $□_R$/Mo.
[c] $□_S$/Mo.

NH_3 adsorption is not influenced by the type of surface anions present in the Mo-phase, inasmuch as the reduced phase contained all O^{2-} anions; whereas, the sulfided phase contained a predominance of S^{2-} anions.

Deuterium Exchange

The results of the D_2-exchange experiments on reduced and sulfided catalysts, as well as the γ-Al_2O_3 support are presented in Table 2. In order to ensure that all the H had been exchanged from the catalyst, after equilibrium had been attained, the exchange temperature was raised to 600°C in run 6; no change in the gas-phase composition took place.

It was necessary to check the effect of reduction and sulfiding conditions employed with the catalyst on the H content of the γ-Al_2O_3. Runs 1 and 2 yielded H content values in close agreement with H_2O content values given by MacIver, Tobin and Barth (*13*) for a γ-Al_2O_3 closely resembling the one used here, viz, 14.8 mg/g vs 16 at 400°C and 11.5 vs 11 at 500°C. The H held on Al_2O_3 is predominantly as terminal hydroxyl groups. As such, the concentrations found calculate to 5.2×10^4 OH/cm^2 at 400°C, and 4.0×10^{14} at 500°C, which values fall in the range generally found for aluminas (*14*). Exposing the Al_2O_3 to H_2 resulted in no detectable H_2 consumption or water formation. Sulfiding the Al_2O_3 likewise did not appreciably effect the H content of the Al_2O_3 as shown by the good agreement between runs 1 and 3, although a small amount of sulfur was irreversibly adsorbed.

TABLE 2

D_2 EXCHANGE ON REDUCED AND SULFIDED CATALYSTS

Run No.:	1	2	3	4	5	6	7	8
Catalyst:	γ-Al_2O_3			8 Mo/γ-Al_2O_3				
Temp (°C)								
Calcine	400	500	400	500	500	500	400	500
Treatment[a]	400R	500R	400S	–	500R	500R	400S	500R/400S
Exchange	400	400	350	400	400	400	350	350
H Content (mmol H/g)	1.65	1.28	1.71	0.34	0.64	0.71	1.47	1.57
H_T/Mo (atom/atom)				0.40	0.76	0.84	1.74	1.86
H_I/Mo (atom/atom)				0	0.46	(0.47)[c]	1.26	1.51
H_{Al}/Mo (atom/atom)				0.40	0.30	0.37	0.48	0.35
H_{Al} Content (mmol H/g Al_2O_3)	1.65	1.28	1.71	0.39	0.29	0.35	0.46[f]	0.35[d]
H_{Al} Ratio[b]				0.30[d]	0.23[d]	0.27[d]	(0.27)[e]	(0.27)[e]
$\square_R$/Mo				0	0.39	0.27	–	0.43
S/Mo							1.74	1.34
O_S/Mo							0.99	1.30
$\square_S$/Mo							(0.27)[c]	0.36

[a] R refers to reduction and S to sulfiding.

[b] Ratio of H_{Al} on catalyst to that on pure support.

[c] Value assumed from other runs under identical conditions.

[d] Based on run 2.

[e] Average of runs 4–6 used.

[f] Based on run 3.

The oxidized catalyst had a low H content compared with the support (run 4 vs run 2). Since some reduction with H_2O formation occurred during D_2 exchange, which could complicate the results, two reduced catalysts were run (runs 5 and 6). Here, additional catalyst reduction in D_2 was minimal. For the reduced catalysts, it was necessary to correct for the irreversible H content (H_I) associated with the reduced Mo phase of the catalyst. The value of H_I for run 5 was independently determined by measuring the H_2 consumed and H_2O formed during the reduction and the O_2 consumed during oxidation after the D_2 exchange had been accomplished [see Ref. (*3*) for calculations]. For run 5, a maximum value was assumed from prior work (*3*) based on the extent of reduction. As shown, all three runs yielded approximately the same H content for the Al_2O_3 portion of the catalyst, which was appreciably lower than that obtained for the γ-Al_2O_3 support alone.

The sulfided catalysts gave completely different results. Total H content was high, comparable to the Al_2O_3 alone (runs 7 and 8 vs run 3). But, we have just shown that the Al_2O_3 does not increase in H content on sulfiding, and the Al_2O_3 portion of the catalyst has a low H content. Therefore, the bulk of the H held on the sulfided catalyst must be ascribed to the sulfided Mo phase of the catalyst. In order to estimate this value, the following calculations were made for run 7:

1. The average percentage of free Al_2O_3 on the catalyst, as determined in the reduction runs, was multiplied by the H content of the sulfided Al_2O_3 support to obtain the H content of the Al_2O_3 portion of the sulfided catalyst. Thus,

$$H_{Al}/Al_2O_3 = 0.27 \times 1.71$$
$$= 0.46 \text{ mmol H/g } Al_2O_3.$$

2. This was converted to a per millimole Mo basis and subtracted from the total H content per Mo to obtain the H_I content

associated with the Mo, viz,

$$H_I/Mo = 1.74 - 0.46 \times 0.88/0.844 = 1.26.$$

In a similar manner, H_I/Mo was calculated for run 8. Here, the H content of the Al_2O_3 was taken from run 2 since the catalyst had been prereduced at 500°C. The resulting value of 1.51 H_I/Mo is also high. These values are about three times the H content of the reduced catalysts.

DISCUSSION

Detailed discussion of reduced Mo/Al_2O_3 catalysts have already been presented (*2,3*). The salient findings pertinent to the present discussion may be summarized as follows:

1. Molybdena is extremely well-dispersed on the alumina surface, most likely as a monolayer.
2. A strong interaction between the molybdena and the alumina is manifested in a distribution of bonding strengths of the terminal (Mo) oxide ions.
3. The reduced catalyst retains irreversibly adsorbed hydrogen, probably as surface hydroxyl groups associated with molybdenum. The ratio of irreversibly adsorbed hydrogen (H_I) to oxide anion vacancies ($\square_R$) is close to 2 at low reduction, but H_I reaches a limiting value at moderate reduction at about 0.5 H_I/Mo.
4. The reduced catalyst shows the presence of some Mo^{5+}, as well as lower valences of Mo. Anion vacancies are believed to be balanced by exposed Mo^{4+} cations, and the Mo^{5+} to arise from addition of an H to a $Mo^{6+}O^{2-}$ grouping, forming Mo^{5+}-OH^-.

Nature of the Sulfiding Reaction

The course of sulfiding of a Mo/Al_2O_3 catalyst occurs quite differently from that of bulk MoO_3. Whereas bulk MoO_3 (and Mo-SiO_2 catalyst) undergoes a rapid reduction to MoO_2 followed by a slow sulfiding to MoS_2 in an H_2S/H_2 atmosphere (*15*), the Mo/Al_2O_3 catalyst showed an immediate weight gain and rapid addition of sulfur. The most significant finding is that at moderate temperatures, the *predominant reaction is exchange of catalyst reactive oxygen for sulfur.* The overall stoichiometry was closer to MoO_xS_y, where $x + y = 3$, than $MoO_2 + MoS_2$, as found for bulk MoO_3. Certainly, description of the sulfided catalyst in terms of a MoS_2 phase is inaccurate.

The factors which affect the sulfur level of the catalyst are temperature, H_2S partial pressure and reaction time, in decreasing order of importance. A limiting sulfur content was obtained at a given temperature. This result is indicative of a surface reaction having a variable activation energy with extent of conversion, in agreement with earlier findings for reduction (*2*). Partial pressure of H_2S and time only affected the results in that lower values of these parameters gave catalyst sulfur contents below the limiting value. Although sufficient data were not obtained, it is probable that sulfiding follows logarithmic kinetics similar to that found for reduction (*2*), which would explain the relative insensitivity to reaction time. A logarithmic rate law has been found for the sulfidation of a tungsten silica–alumina catalyst (*16*).

Although sulfiding of the catalyst occurred predominantly by exchange, some net reduction, i.e., formation of anion vacancies, took place, especially at higher temperatures. However, even at the most extreme conditions employed, when S/Mo approached 2, some reactive catalyst oxygen still remained intact, and the vacancy concentration never exceeded one. In contrast, under reduction in H_2 alone, $\square/Mo$ approached two at high temperatures (*2*). Thus, it appears that the presence of H_2S (in H_2) prevents catalyst over-reduction.

Interaction of the molybdena with the support undoubtedly is of paramount importance in determining the degree of lability of the reactive oxygen. The catalyst supported on γ-Al_2O_3 was more reactive than that supported on η-Al_2O_3 towards sulfiding in both greater extent of sulfur exchange and of vacancy formation, suggesting a stronger bonding of the molybdena to the support for the η-Al_2O_3. This is in line with the greater strengths of the acid sites in η-Al_2O_3 compared to γ-Al_2O_3 (*13*), considering interaction to be the result of an acid-base reaction between the hydroxylated forms of Al_2O_3 and MoO_3 (*17*) during impregnation and/or subsequent calcination. However, both catalysts showed about the same response to reduction in H_2 (*2*), indicating this reaction to be less sensitive to differences in interbonding strengths between the aluminas.

The effect of prereduction on the course of sulfiding gives further insight into the catalyst surface structure. Ignoring for the moment the hydrogen content of the prereduced catalyst and mechanistic details of sulfiding two modes of sulfur addition are clearly indicated by the results. One, direct exchange with catalyst oxygen, prevails at low prereductions; the other, sulfur incorporation without concomitant oxygen loss, only becomes important at moderate to high prereductions. The total sulfur added plus oxygen remaining, $S + O_S$, was always equal to or greater than the oxygen left after the prereduction step, O_R, or $\square_R \geqslant \square_S$. In our analysis, we assume that S_I occupies vacancies. Hence, the vacancy concentration left after sulfiding is given by:

$$\square_S/Mo = \square_R/Mo - S_I/Mo. \tag{24}$$

The loss of vacancies due to sulfiding cannot, however, necessarily be equated with a real gain in the oxidation state of the Mo. In fact, there would be no change in Mo valence if the S_I existed as adsorbed H_2S_I or as $2H^+ + S_I^{2-}$, since in the latter case the net positive and negative charges balance each other. The only way the Mo valence could increase during sulfiding of the prereduced catalyst would be by formation of hydrogen, viz.

$$Mo^{4+} + \square + H_2S \rightarrow Mo^{6+} + S^{2-} + H_2. \tag{25}$$

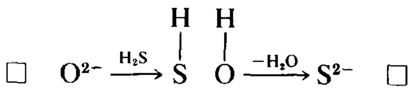
Although it cannot be dismissed out of hand, this reaction seems unlikely.

Mechanism of Sulfiding

Since a reducing atmosphere is present during sulfiding, it is reasonable to presume that a small number of vacancies are rapidly formed, even at moderately low sulfiding temperatures. Figure 2A shows that vacancies formed early in the reaction period and remained relatively constant during continued sulfur exchange. A direct replacement reaction between gaseous or adsorbed H_2S and oxide anions not involving vacancies, viz.

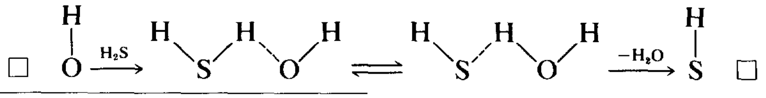
$$H_2S_a + O^{2-} \rightarrow S^{2-} + H_2O \tag{26}$$

is difficult to imagine. If vacancies are involved, two mechanisms may be envisioned. One involves a vacancy-oxide ion pair,



$$\square \quad O^{2-} \xrightarrow{H_2S} \overset{H}{\overset{|}{S}} \quad \overset{H}{\overset{|}{O}} \xrightarrow{-H_2O} S^{2-} \quad \square \tag{27}$$

and requires dissociative adsorption of H_2S followed by dehydroxylation. The second utilizes a vacancy-hydroxyl pair, similar to that proposed for sulfiding of Al_2O_3 (*18*), viz.



(28)

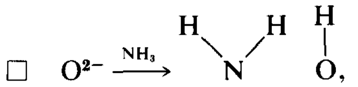
and involves molecular adsorption of H_2S, followed by bond shifting and desorption of H_2O. Both maintain the catalyst surface intact except for the exchange of sulfur for oxygen. Also, both involve vacancy migration, a necessary requirement to achieve high sulfur levels at low vacancy concentrations. Without vacancy migration, sulfiding via these mechanisms would cease after all oxide anions neighboring a vacancy have been exchanged by sulfur.

The results of sulfiding prereduced catalysts seem contrary to the vacancy mechanism proposed for direct sulfiding in that the prereduced catalysts, although having appreciably larger vacancy concentrations than the directly sulfided catalysts, sulfided to a lower extent. The explanation for this most likely resides in the heterogeneity of the strength of bonding of the active oxygen, i.e., the increasing activation energy for oxide removal with decreasing oxide concentration (*2*). Thus, at high degrees of prereduction, the weakly bonded oxygen has mostly all been removed; hence, only the strongly bonded oxygen is left, which oxygen is also difficultly exchanged by sulfur. On the other hand, at mild reductions, much easily reactive oxygen remains, and more sulfur exchange can occur. Of course, counter to this occurrence, more sulfur is added to vacancies (as S_I) at the higher reduction, but the net result on sulfur level is still a continuous decrease with increase in prereduction.

Nature of the Mo-Phase

The Mo-phase of the catalyst has been viewed as consisting of a monomolecular layer of MoO_3 over the Al_2O_3 support surface (*2,3*). The oxygen associated with the Mo is considered to be labile towards reduction or sulfidation. Thus, reduction in H_2 removes some reactive oxygen creating anion vacancies; sulfiding effects mostly exchange of reactive O^{2-} for S^{2-} and also creates some vacancies. The Mo cations associated with vacancies can be considered to be coordinately unsaturated (*19*), or Lewis acid type centers. Hence, electron-pair donor molecules may adsorb on them either associatively or dissociatively.

The NH_3 adsorption data show a correlation with vacancy concentration for both reduced and sulfided catalysts. Since total adsorption was independent of the type of anion present (O^{2-} or S^{2-}), adsorption must almost certainly occur at vacancy sites. It is not known whether adsorption is associative or dissociative; probably both types are present. Dissociative adsorption on a $\square\ O^{2-}$ or $\square\ S^{2-}$ pair, viz,



$$\square \quad O^{2-} \xrightarrow{NH_3} \overset{H\quad H}{N} \quad \overset{H}{O}, \qquad (29)$$

as suggested by Peri (*20*) for Al_2O_3 at elevated temperatures, may be responsible for the irreversibly retained NH_3. It also may account for the slight weight loss obtained with the oxidized catalyst via dehydroxylation of OH's formed via reaction (29) with adjacent OH's.

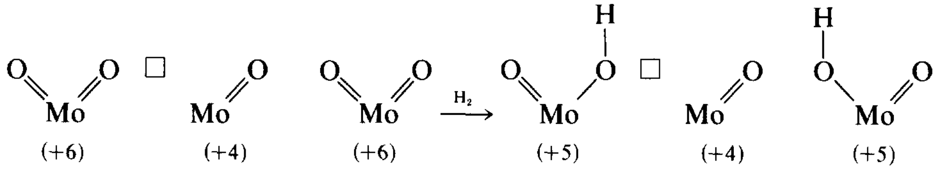
It is interesting to note that the net NH_3 adsorption after desorbing the reversibly adsorbed NH_3 is lower for the sulfided catalysts compared with the reduced catalysts; whereas, the total adsorption is the same. This would seem to imply that NH_3 is less strongly retained by a $\square$ S pair than a $\square$ O pair, the latter being a stronger Lewis acid site.

Besides NH_3, irreversibly adsorbed H_2S (S_I) on the prereduced catalyst and reversibly adsorbed H_2 (H_R) also appear to correlate with vacancy concentration (Fig. 5C). DeRosset, Finstrom and Adams (*21*) concluded that H_2S adsorbs at Lewis acid sites on Al_2O_3; the vacancies of the Mo-phase of the catalyst should partake of a similar character but perhaps less acidic, since reversibly adsorbed H_2S does not correlate with vacancies. We have previously suggested that reversibly adsorbed H_2 may adsorb by heterolytic dissociation on vacancies on the reduced catalyst (*3*).

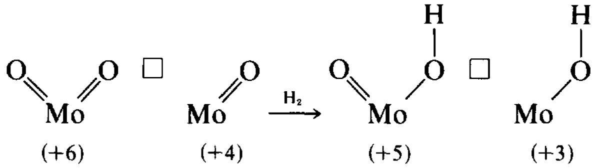
The D_2-exchange experiments demonstrate that the H content (H_I) of the sulfided catalyst is appreciably higher than a comparable reduced catalyst, exclusive of that present on the Al_2O_3 portion. It must be recalled that this H associated with the

Mo-phase is irreversibly retained (H_I) by the catalyst after a 1-hr evacuation. For the reduced catalyst, this H_I was suggested to be associated with a vacancy (*3*). Clearly, in the case of the sulfided catalyst, almost all of the surface S^{2-} anions must have an H_I associated with them. The reason for the greater retention of H_I by the sulfided catalyst is not known at present.

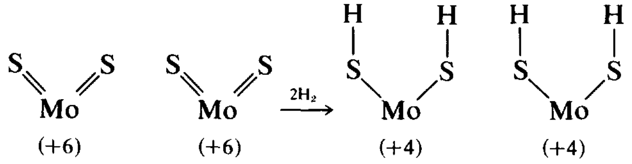
In this connection, the concentration of the Mo^{5+} species observed by ESR on a sulfided catalyst was appreciably lower than that found on a reduced catalyst treated under similar conditions (*15*). We proposed earlier that Mo^{5+} on the reduced catalyst resulted from the homolytic dissociation of H_2 with formation of OH groups adjacent to a vacancy. This irreversibly retained H should cause a proportional lowering in the Mo valence which may be depicted as,



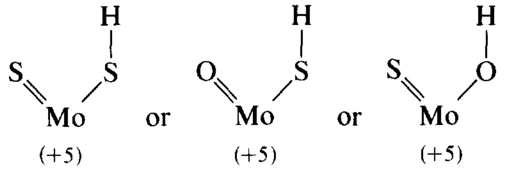
and/or,



On the other hand, in the case of the sulfided catalyst, the irreversibly retained H can no longer be considered to be associated with vacancies alone, in view of the fact that it can account for almost every surface anion as SH or OH groups. Therefore, the predominant state envisioned becomes,



and only a relatively small amount of Mo^{5+} as,



Nature of the Catalyst Support

Although this study has concentrated on the sulfiding reaction and properties of the sulfided catalyst, ancillary information regarding the Al_2O_3 phase of the catalyst was collected. If it is assumed that the Mo-phase is dispersed over the Al_2O_3 surface as a monolayer, the maximum surface covered by an epitaxial MoO_2 layer on top of a (110) γ-Al_2O_3 surface (see discussion under proposed model), using an oxide concentration of 9.1×10^{18} O^{2-} ions/m² (*22*), is for the 8% Mo/γ-Al_2O_3 catalyst,

maximum fraction MoO_2 coverage

$$= \frac{2 \times 0.844 \times 6 \times 10^{23}}{9.1 \times 10^{18} \times 185} = 0.60.$$

Therefore, the "free Al_2O_3 surface" will be at least 40% of the total surface of the catalyst. By free Al_2O_3 is meant that portion of the surface which exhibits characteristics of the Al_2O_3 support itself. Desorption of H_2S from mildly sulfided catalysts was appreciably lower than for the pure Al_2O_3 support, signifying a much reduced free Al_2O_3 area on the catalyst.

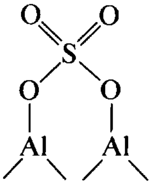
The NH_3 adsorption data showed that the oxidized catalyst adsorbed some 50–70% of that of the Al_2O_3 support alone. Thus, assuming that NH_3 adsorbs only on the Al_2O_3-free portion of the catalyst, it appears that the surface acidity of the Al_2O_3 portion of the catalyst has increased somewhat in the presence of the Mo-phase.

On the other hand, the D_2-exchange experiments showed that the OH concentration of the Al_2O_3 portion of the catalyst has decreased over that of the γ-Al_2O_3 support itself. Using an average fractional Al_2O_3 surface of 40%, the OH concentration is about one-half of that of the pure γ-Al_2O_3. We tentatively conclude, therefore, that the Al_2O_3 portion of the Mo/γ-Al_2O_3 catalyst exhibits a Lewis acidity higher than and a surface hydroxyl concentration lower than that of pure γ-Al_2O_3.

In addition to a lower OH concentration, there is evidence for a difference in type of OH present on the catalyst. In related work (*23*), in which pyridine adsorption was studied by infrared, evidence was found for the presence of Bronsted acid sites on the oxidized catalyst, as well as Lewis sites. The Al_2O_3 support alone exhibited only Lewis acidity. This would seem to indicate a weakening in the AlO–H bond in the catalyst, presumably influenced by the presence of the Mo-phase.

Additional confirmation of the changed nature of the Al_2O_3 support when molybdena is added comes from infrared studies (*24*). A pure η-Al_2O_3 exhibited five hydroxyl bands in the hydroxyl stretching region, similar to that reported by Peri (*25*), although not as distinct and shifted to lower frequencies. The infrared spectrum of a sample containing 3% Mo impregnated on the same η-Al_2O_3 showed that two of the OH bands of the η-Al_2O_3 had disappeared and one new absorption band appeared. These data do not reveal whether the new OH group on the Mo/η-Al_2O_3 sample was associated with the Mo-phase, or the Al_2O_3 phase modified by the adjacent Mo-phase, or an existing band shifted due to interaction with the Mo-phase. However, the new absorption band was shown to disappear upon the addition of pyridine indicating that it was a relatively strong protonic acid. Also, Sonnemans and Mars (*26*) report, for a 12% Mo/γ-Al_2O_3 catalyst prepared by a vapor-phase treatment, that the OH spectrum region was far less intense for the catalyst than for the Al_2O_3. Due to the high Mo level, this catalyst would be expected to have a proportionally smaller Al_2O_3-free surface.

An analogous system to the Mo/Al_2O_3 catalyst may be found in sulfated-alumina. The surface structure may be represented by,



which is formally identical to our proposed catalyst surface where S is replaced by Mo. It has been reported (*27*) that the effect of sulfate incorporation is to appreciably lower the surface OH concentration and raise the Lewis site concentration from that of the pure Al_2O_3, similar to that observed in the present work for the Mo/γ-Al_2O_3 catalyst.

Proposed Surface Model for Mo/γ-Al₂O₃ Catalyst

Very few detailed surface models for the Mo/γ-Al_2O_3 catalyst are found in the literature. Schuit and Gates (*7*) consider two terminal surface configurations arising from a two-dimensional monolayer of MoO_3 on top of a (110) Al_2O_3 substrate. Neither model can adequately account for the extensive catalyst sulfur exchange levels found in the present work, without appreciable disruption of the proposed structures. Kabe *et al.* (*8*) proposed a monolayer structure containing three terminal O atoms per two Mo atoms. Their sulfided catalyst also contained a maximum of 1.5 S/Mo. Incorporation of additional sulfur and/or vacancies as found in the present work is difficult to reconcile with their model.

It is generally accepted that the Mo-phase is extremely well dispersed over the Al_2O_3 surface of a Mo/γ-Al_2O_3 catalyst. However, controversy exists as to the exact nature and structure of the Mo-phase. One group of workers (*26,28,29*) holds to the tenet that a monolayer of MoO_3 covers the Al_2O_3 surface, the MoO_3 having bulk MoO_3 properties. Another group (*30–32*) espouses a surface interaction between the MoO_3 and the Al_2O_3. Recently (*33*), a combination of both has been proffered.

The results of the author tend to support the second school in that the reaction characteristics of the catalyst appear to be greatly different from those of bulk MoO_3 (*2*). Additionally, the characteristics of the support are changed in the presence of molybdenum, as discussed above.

Earlier, we proposed a model for the surface of the oxidized and partially reduced Mo/γ-Al_2O_3 catalyst (*3*), which consists of a two-dimensional, epitaxial monolayer of MoO_2 over a (110) γ-Al_2O_3 surface. The third O associated with the Mo^{6+} cation is located in the underlying oxide layer of the Al_2O_3 and is unreactive towards reduction. Loss of terminal oxide anions associated with Mo via reduction creates vacancies. At the same time, two protons (H_I) are added on adjacent oxide cations forming OH groups. The two $OH_I/\square$ relationship held only at low degrees of reduction. At higher reductions, the H_I content leveled out.

The two-dimensional layer model must now be modified somewhat in view of the present sulfiding results showing extensive exchange of oxygen for sulfur. The significance of this lies in the fact that the S^{2-} anion is some 40% larger than the O^{2-} anion. Hence, a close-packed oxide layer, even a (110) surface, cannot undergo even moderate exchange with sulfur without appreciable disruption of the surface.

For the above reason, instead of an extensive two-dimensional layer or two-dimensional patches, a surface model consisting of one-dimensional chains of MoO_2 over the Al_2O_3 substrate is proposed. The third O associated with Mo is placed in vacancies in the Al_2O_3 substrate, as before. The model requires separation of the chains, with exposed Al_2O_3 substrate between chains. The relative amounts of the MoO_2 chains would, of course, be dictated by the Mo concentration of the catalyst.

A model of a hypothetical surface one-half covered with MoO_2 is illustrated in Fig. 7A. This idealized surface approximates the 8% Mo/γ-Al_2O_3 catalyst used in the present study. Although depicted as a regular chain superstructure of infinite length in only one direction, conceptually, the model does not preclude finite chains in random directions or interlaced networks, provided the overall one-dimensional character is not significantly altered.

Such a model permits extensive exchange of oxygen for sulfur without disruption of the surface configuration, as shown by Case C1 of Fig. 7, which represents run 7 of Table 2. Stages of partial reduction of the catalyst, as exemplified by Cases B1–B3, accurately reflect the H_I and $\square$ relationships obtained previously (*3*). Sulfiding of a prereduced catalyst can likewise be accommodated by the model, as shown by Case C2, which represents run 8 of Table 2.

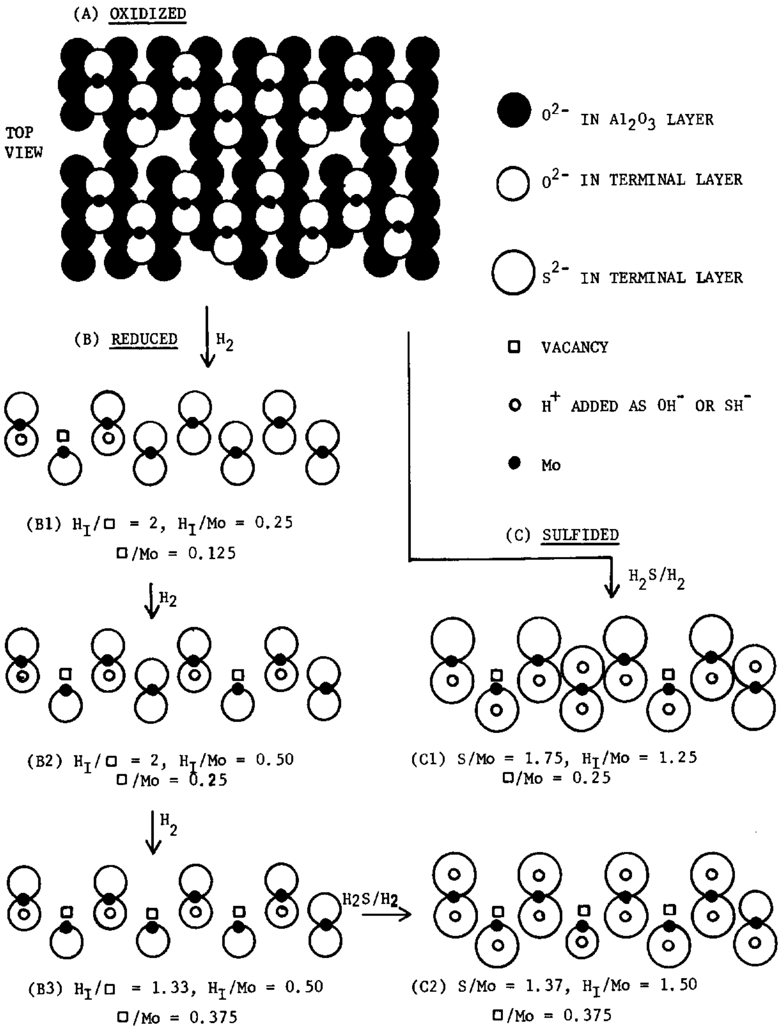


FIG. 7. Proposed surface model for Mo/γ-Al_2O_3 catalyst.

This model, based on two reactive oxygen anions per Mo, which can be removed by reduction or exchanged for sulfur, does not conveniently account for those sulfiding cases where more than two O/Mo are lost. Under those extreme sulfiding conditions (about 400°C for the γ-catalyst and 500°C for the η-catalyst), extensive vacancies are obtained and some exchange of oxygen in the underlying layer must occur or vacancies in the underlying layer must be assumed. Some disruption of the catalyst surface structure would be expected to occur. However, strain would be minimized at sites adjacent to a vacancy in the Al_2O_3 layer. The chain structure proposed would minimize such disruption compared to a two-dimensional model.

Aside from accounting for the reduction and sulfiding results obtained, the proposed chain model can also account for the unusual properties associated with the Al_2O_3 phase of the catalyst, since no characteristic, extensive, areas of free Al_2O_3 exist. The Al_2O_3 substrate surface exposed between MoO_2 chains would be expected to be modified from that of pure Al_2O_3 due to the close proximity of the MoO_2 and incorporation of the third oxygen of the Mo-phase into its structure. This is manifested in a lower OH content per unit surface area compared with the unmodified γ-Al_2O_3 surface. In addition, Bronsted acid sites develop on the catalyst. This may be rationalized as due to a weakening of the AlO–H bond by partial electron withdrawal caused by the neighboring MoO_2. Some vacancies in the Al_2O_3 phase would also be present after calcination. The exposed Al cations would act as Lewis sites for NH_3 adsorption.

CONCLUSIONS

The salient findings of this study relative to sulfiding of Mo/Al_2O_3 catalysts are:

1. Extent of sulfiding increased with temperature. A limiting catalyst sulfur content was obtained at a given temperature, neither increase in H_2S partial pressure nor time much affecting the sulfur level.
2. The predominant reaction was exchange of oxygen associated with molybdena for sulfur. At higher temperatures, some additional oxygen was lost via reduction, creating anion vacancies.
3. Prereduced catalysts sulfided to a lesser extent; some sulfur may have been added to vacancies present after the prereduction.
4. Ammonia adsorption on sulfided (and reduced) catalysts correlated with vacancy concentration.
5. The sulfided catalyst contained appreciable irreversibly adsorbed hydrogen, its magnitude being far greater than that found for reduced catalysts.
6. The Al_2O_3 portion of the catalyst appeared to contain appreciably less hydrogen and somewhat greater acidity than the support alone.

A model of the catalyst surface is proposed embodying one-dimensional, chain-like groupings of MoO_2 over the Al_2O_3 substrate surface, the third oxygen associated with the molybdena being located in the Al_2O_3 substrate layer. Sulfur exchange and vacancy formation are perceived to occur predominately at the two terminal oxygens associated with each Mo.

APPENDIX

Estimate of Water Adsorption on Al_2O_3 Portion of Prereduced and Sulfided Mo/γ-Al_2O_3 Catalyst

The catalyst was heated in air for 16 hr at 400°C, followed by N_2 for 1 hr and H_2 for 0.5 hr. The temperature was lowered to 300°C and the catalyst was sulfided with a 9% H_2S in H_2 mix for 2 hr. The sulfur content of the final catalyst was 31.2 mg/g. The weight changes after reduction and sulfidation were: −3.7 and 15.8 mg/g.

Assuming all the S exchanged for O, forming H_2O, and no additional reduction occurred during sulfidation,

$$H_2O \text{ liberated} = 31.2 \times \frac{18}{32} = 17.5 \text{ mg/g}.$$

From Ref. (12), for a γ-Al_2O_3 similar to that used here, it is estimated that 5.5 mg/g Al_2O_3 are lost by the Al_2O_3 in going from 300 to 400°C. Assuming one-half of the Al_2O_3 is actually exposed Al_2O_3 surface in the catalyst,

$$\text{max possible } H_2O \text{ pickup} = \frac{5.5}{2} = 2.75 \text{ mg/g}.$$

From Eq. (14),

$$W_{S_1} + 2W_{O_A} = \frac{8}{9}(2 \times 15.8 - 31.2) = 0.35 \text{ mg/g}.$$

The maximum amount adsorbed water, W_{O_A}, occurs when $W_{S_1} = 0$. Thus,

$$W_{O_A}\ (\text{max}) = 0.18 \text{ mg/g}.$$

Hence, the H_2O picked up by the catalyst in sulfiding at low temperature was negligible despite the fact that ample H_2O was liberated.

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