

Studies of Molybdena-Alumina Catalysts

II. Kinetics and Stoichiometry of Reduction

F. E. MASSOTH

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

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Hydrogen reductions of molybdena-alumina catalysts were carried out in a flow microbalance reactor at atmospheric pressure. Extent of reduction of Mo(VI) oxide to lower valences was determined from weight loss measurements. The kinetics of reduction were studied over the temperature range 400-600°C.

Physical examinations of and butene adsorption on fresh (oxidized) catalysts indicated a high degree of dispersion of the molybdena on the alumina support. Catalyst reductions were slower and different in character than those of bulk MoO₃ and Al₂(MoO₄)₃. Extent of reduction increased with increase in Mo content, time of reaction, and temperature. Reduction data followed Elovich kinetics with a variable activation energy which increased with degree of reduction. Reoxidation of reduced catalysts with air revealed that appreciable hydrogen was retained on the reduced catalyst. In conjunction with independently derived values for Mo(V), individual Mo(VI) concentrations were calculated as a function of reduction time and temperature.

Results are interpreted in terms of a surface interaction compound between molybdena and the alumina surface, having a variable range of bond strengths. A mechanism for reduction is proposed, which includes hydroxylated intermediate states of molybdenum.

INTRODUCTION

Commercial catalysts used for hydrodesulfurization (HDS) are commonly based on molybdena supported on active alumina, promoted with lesser amounts of cobalt or nickel. Recent evidence (1) suggests that desulfurization activity derives from a reduced state of molybdenum on the catalyst. It thus seems worthwhile from both the basic and applied point of view to obtain a more detailed understanding of the reactions involved in catalyst reduction.

In the first part of this study (2), the formation and absolute measurement of molybdenum(V) during reduction of a molybdena-alumina catalyst was reported. The present paper describes the phase behavior of molybdena as characterized by detailed reduction studies. These studies, combined with other information in the

literature, provide a useful picture of the reduced molybdena surface. A following report will cover additional aspects of reduction as well as catalyst-activity measurements.

Sontag, Kim, and Marion (3) were the first to note the extreme difficulty of reducing in hydrogen molybdena supported on alumina compared with bulk molybdenum trioxide. They attributed this to an inhibition effect by water adsorbed on the alumina surface, which was suggested to arise from a localized surface equilibrium unfavorable to reduction. Kabe *et al.* (4) recently reported on the kinetics of reduction of molybdena-alumina. Reduction followed an Elovich-type equation and a variable activation energy was reported.

Several detailed structural studies have been carried out on cobalt-molybdena-alu-

mina catalysts. Using magnetic susceptibility measurements, Richardson (5) reported phases of MoO_3 , CoO , and CoAl_2O_4 in the fresh (calcined) catalysts. Lipsch and Schuit (6) found that all the molybdena was situated on the surface of the alumina as MoO_3 (octahedral coordination) and the cobalt to be distributed throughout the alumina. On the other hand, Ashley and Mitchell (7) claimed the molybdena was in tetrahedral coordination at the surface and the cobalt partly in octahedral and partly in tetrahedral coordination. The latter investigators found no evidence for any true compounds. Asmolov and Kyrlov (8) reported molybdena to be in tetrahedral coordination in the form of a 1:1 compound with the alumina. It is obvious that disagreement exists among the various workers as to the state of molybdena on alumina. Some of these differences may be reconciled by different molybdenum levels or supports used and preparation or calcination procedures adopted.

Concerning the molybdena catalyst, several facts emerge clearly from the prior work: (1) Mo on the calcined catalyst is in the hexavalent state; (2) the molybdena is difficult to reduce in H_2 compared with bulk MoO_3 ; (3) X-ray diffraction fails to detect any crystalline phases of Mo for levels up to 10–15 wt% Mo.

From these and other considerations, it seems reasonable to suppose that the molybdena is well dispersed over the alumina support in the form of a molybdena-alumina interaction. The present paper directs further attention to the nature of this interaction by means of detailed reduction studies, and proposes a mechanism for reduction.

EXPERIMENTAL

Materials

The $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts were prepared as described previously (2). A series containing nominally 2, 6, 8, 10, and 25% Mo on Davison high-purity eta-alumina (BET surface area 175 m^2/g , pore volume 0.26 ml/g) was used. A 10% Mo on Ketjen, thermally stabilized, gamma-alumina (191

m^2/g , 0.46 ml/g) was also tested. Catalysts were subjected to a final air calcination at 540°C for 20 hr. The 10% catalyst gave a diffraction (XRD) pattern typical of the η -alumina support; the 25% catalyst gave a sharp XRD pattern for MoO_3 .

Bulk MoO_3 was prepared by heating ammonium paramolybdate in air at 540°C for 20 hr; it had a surface area of 1.6 m^2/g .

Stoichiometric aluminum molybdate, $\text{Al}_2(\text{MoO}_4)_3$, was prepared by mixing finely divided MoO_3 and $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in a molar ratio of 5 to 1, followed by calcination in air at 750°C for 16 hr. Under these conditions, the excess MoO_3 vaporized, leaving only the desired compound. X-ray diffraction analysis identified the compound as $\text{Al}_2(\text{MoO}_4)_3$ (9) (orthorhombic, $a \sim b = 9.0$, $c = 12.56 \text{ \AA}$), and showed no evidence for MoO_3 or Al_2O_3 . Chemical analysis confirmed the stoichiometry (Mo: 54.0%, analysis; 53.9%, theory). The compound had a surface area of 5 m^2/g .

Apparatus and Procedures

A flow microbalance reactor was used to follow weight changes attending catalyst reduction or oxidation (10). The apparatus consisted of: a Cahn RG electrobalance, a quartz-tube reactor heated by a split-shell furnace, a quartz bucket for the catalyst sample and auxiliary equipment for introduction and metering of gas flows. Gases used were purified by passing through the following traps: N_2 -hot copper turnings followed by 4A molecular sieves; H_2 -Deoxo unit followed by sieves; and air-sieves. 1-Butene was used directly from the cylinder.

Catalyst charges of 200 mg to 1 g were used. For isothermal runs, the catalyst was pretreated in air for an overnight period at the reduction temperature to attain a constant weight. After flushing the reactor with N_2 , H_2 was admitted for a given period of time, the weight loss being automatically recorded on a strip-chart recorder. A final reduction value was obtained in nitrogen. Buoyancy corrections were applied to the reduction data using previously determined buoyancy changes determined with a quartz charge.

Extent of reduction was calculated from

weight change data, assuming loss of oxygen as water. This assumes that the water formed from reduction is not retained by the alumina support. Little difficulty was experienced above 400°C in maintaining equilibrium water content levels of the catalysts. Reoxidation under these conditions returned the catalysts to their initial oxidized weight. However, at 300°C, some retention of the water produced was noted, thus affecting the calculated degree of reduction. This was shown by intermittent reductions, in which an extended nitrogen purge was inserted between periods of reduction. During the nitrogen purge, the catalyst lost weight due to stripping of excess water held by the alumina.

For temperature-programmed reductions (TGA) of catalysts, the catalyst was first heated in air at the maximum temperature to be employed until the weight became constant. The temperature was then lowered to 50°C in N₂, after which the N₂ was replaced with H₂ and the temperature programming started.

In some cases, the effluent gas stream from the microbalance was monitored for water with a duPont Water Analyzer.

RESULTS

Butene Adsorption

In order to assess the extent of dispersion of the molybdena on the fresh catalyst, the amount of 1-butene chemisorption was measured. An adsorption temperature of 100°C was chosen on the basis of the following facts: (1) at room temperature, 1-butene polymerized on the catalyst as attested by excessive weight gain; (2) at 175°C, partial reduction of the catalyst occurred as evidenced by water in the effluent product stream; (3) at 100°C, neither of these was observed; but a weak ESR signal for Mo(V) was detected, probably from partial charge transfer accompanying chemisorption (11). Duplicate experiments were made with both the 10% Mo/Al₂O₃ and the γ -Al₂O₃ support, the results of which are given in Table 1. After adsorption for four hours, continued weight gain became negligible and the samples were flushed with

TABLE 1
BUTENE ADSORPTION ON Mo/Al₂O₃ CATALYST^a

Sample	Weight, mg/g catalyst		
	Adsorbed ^b	Desorbed ^c	Retained
10% Mo/ γ -Al ₂ O ₃	60	21	39
	62	21	41
γ -Al ₂ O ₃	23	21	2
	25	21	4

^a Temperature: 100°C; 1-Butene: 1 atm.

^b In four hours.

^c In twenty hours.

nitrogen for 20 hr. The butene retained on the support was small, whereas that on the catalyst was substantial, representing a butene-to-molybdena molar ratio of 0.63. If all the molybdena were available on the surface for adsorption of butene, and taking a surface area for MoO₄²⁻ of 25 Å² (7), and a molecular area for butene of 39 Å², the molar ratio of adsorbed butene to surface molybdena would be 0.64, close to the experimental value. This suggests that virtually all of the molybdena is as a monolayer on the alumina surface.

That the residual weight after desorption was in fact strongly chemisorbed butene and not carbonaceous residue resulting from polymerization was demonstrated by subsequently heating of the catalyst in a stream of nitrogen and monitoring the sample weight and evolved gaseous products. At 540°C, over 90% of the adsorbed weight had been lost, predominately as the original butene (although some higher molecular weight olefins were detected), according to gas chromatographic analysis.

Temperature-Programmed Reductions

Aluminum molybdate, Al₂(MoO₄)₃, is the only well-characterized compound between molybdenum and aluminum oxides known. Its reducibility was tested to ascertain whether it could account for the difficulty in reducing molybdena on alumina. A series of temperature-programmed (TGA) reductions in H₂ was made using Al₂(MoO₄)₃, MoO₃ + α -Al₂O₃, 6% Mo/Al₂O₃, and 10% Mo/Al₂O₃. The results are shown in Fig. 1, where the O/Mo ratio cal-

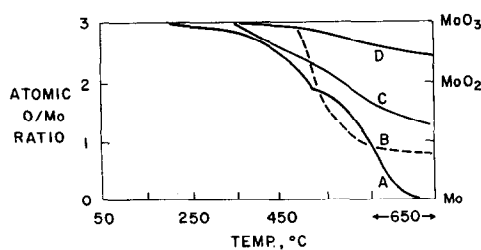


FIG. 1. TGA reductions in H_2 . Heating rate $5^\circ C/min$. (A) $MoO_3 + \alpha-Al_2O_3$, (B) $Al_2(MoO_4)_3$, (C) 10% Mo/Al_2O_3 , (D) 6% Mo/Al_2O_3 .

culated from weight loss measurements is plotted against the temperature. A programming rate of $5^\circ C/min$ was employed up to $650^\circ C$, after which the temperature was maintained constant. The results show that ease of reduction decreased in the order: $MoO_3 > Al_2(MoO_4)_3 > 10\% Mo/Al_2O_3 > 6\% Mo/Al_2O_3$. Actually some crossover was obtained in that the 10% Mo/Al_2O_3 catalyst commenced reduction at a lower temperature than the $Al_2(MoO_4)_3$, but reduced slower at higher temperature.

The above experiment would seem to indicate that bulk aluminum molybdate is not present on the catalyst; if it were present as small discrete crystallites (undetectable by X ray), it should reduce faster than the bulk $Al_2(MoO_4)_3$, which consists of relatively large crystals, since reactivity in gas-solid reactions invariably increases with decreasing particle size; or

if it were present as an amorphous precursor, this also should be more reactive towards reduction, having a defective structure (12).

Effect of Mo Concentration on Reduction

The wide variation in reducibility shown in Fig. 1 between the two catalysts is due to the difference in Mo contents. Figure 2 presents isothermal reductions for a series of catalysts of varying Mo level from 2 to 25%. The degree of reduction, expressed as fraction of equivalent MoO_3 reduced to Mo, is plotted against time. Also shown is the comparable reduction of bulk MoO_3 . It is clear that the fractional reduction rate diminished as the Mo content of the catalysts was lowered. We take this as evidence of an interaction between the molybdena and the support for the following reasons: (1) the opposite should be true if the same number but smaller particles of MoO_3 were formed with decreasing Mo content; or (2) no change in rate should occur if the same size but a lesser number of particles were formed.

No evidence of a break in the reduction curves at about MoO_2 reduction state was observed in any of the catalysts, which is additional evidence that a true MoO_3 phase does not exist on the catalyst. Such a break was obtained for bulk MoO_3 , as would be expected from the greater reducibility of MoO_3 compared to MoO_2 (13).

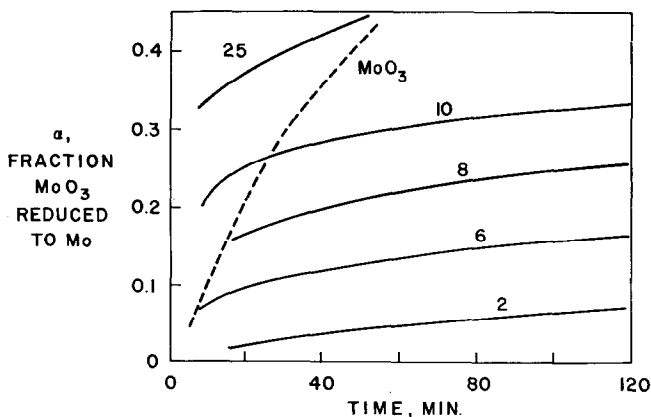


FIG. 2. Effect of Mo level on reduction of $Mo/\eta-Al_2O_3$ catalysts at $500^\circ C$, 1 atm H_2 . Numbers refer to wt% Mo.

It may be noted from Fig. 2 that the extents of reduction at short times for the 10% and 25% Mo catalysts are actually greater than for bulk MoO₃. In the case of the 25% Mo catalyst, XRD showed MoO₃ to be present. The MoO₃ on the catalyst would be expected to be more reactive, having a smaller particle size than the low area bulk MoO₃. The case of the 10% catalyst, in which no MoO₃ was detected by XRD, is discussed later.

Kinetics of Reduction

For a given Mo concentration, extent of reduction increased with increase in temperature and hydrogen partial pressure. This is illustrated in Fig. 3, where the fractional reduction is plotted against time on a semilogarithmic scale to show conformity to an Elovich-type kinetic equation. Again, it is obvious that the catalyst reduced quite differently from that of bulk MoO₃, the latter showing two curves, both non-Elovichian. Von Destinon-Forstmann (13) reported the kinetics of reduction of MoO₃ to follow a contracting sphere model with interface-reaction controlling for conversion of MoO₃ to MoO₂ (fast) and a linear rate law for conversion of MoO₂ to Mo (slow). The slopes of the Elovich plots increase with increase in reduction temperature. At constant temperature, however, the slopes remained constant with changing hydrogen

partial pressure, although the extent of reduction increased with hydrogen pressure.

The Elovich equation has been widely applied to surface phenomena (mostly adsorption). For surface reaction it takes the form,

$$d\alpha/dt = a \exp(-b\alpha), \quad (1)$$

where α is the extent of reduction, t is time, and a and b are constants. For weight change measurements, $\alpha = \Delta W/\Delta W^*$, where ΔW is the weight loss at time t and ΔW^* is the hypothetical weight loss for complete conversion of MoO₃ to Mo.

The integrated form of Eq. (1) is (14),

$$\alpha = -(1/b) \ln t_0 + (1/b) \ln(t + t_0), \quad (2)$$

where $t_0 = 1/ab$.

The data given in Fig. 3 show conformance to equation (2) for $t_0 \ll t$ at $t > 5$ min.

The Elovich equation has been justified on either of two theoretical models, viz. the variable site mechanism and the variable activation energy mechanism (14). The former requires that reaction at one site affects reactivity of neighboring sites with a single activation energy for reaction. In this case, the mathematics necessitate that the slope ($1/b$) should be independent of temperature, which is not in accord with the data of Fig. 3. The second model presumes a variable activation energy with

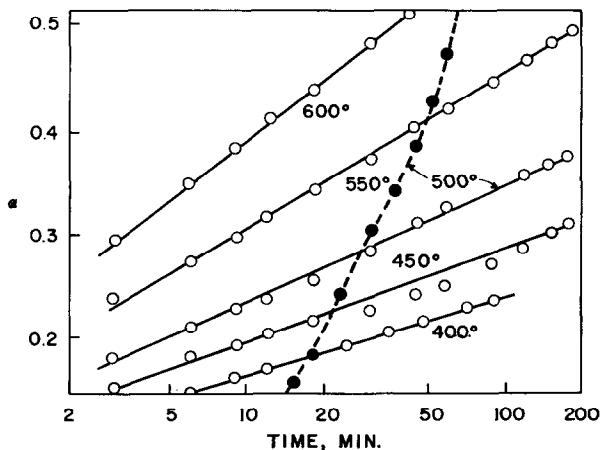


FIG. 3. Elovich plots for reduction of 10% Mo/ η -Al₂O₃ at various temperatures and 1 atm H₂. Solid points are for bulk MoO₃.

extent of reaction. A linear function is usually assumed for simplicity. Thus,

$$E_a = E_0 + c\alpha, \quad (3)$$

where E_a is the activation energy at any degree of reduction, α , and E_0 is the activation energy at the start of reaction; c is a constant. The constants a and b now take on the following relationships,

$$a = (kRT/c) \exp(-E_0/RT), \quad (4)$$

$$b = c/RT, \quad (5)$$

where k is a pressure dependent constant, R is the gas constant, and T is absolute temperature. Now the slope of Eq. (2), $1/b$, will increase with T , as observed in the plots of Fig. 3.

In order to evaluate the activation energies for reduction, Eqs. (1, 3-5) were combined and cast into logarithmic form to obtain,

$$\log(da/dt) = \log(kRT/c) - (E_a/2.303RT). \quad (6)$$

Rates of reduction at discrete values of α were obtained from the slopes of the original weight-time recorder tracings, and plotted against $1/T$ according to Eq. (6). E_a values were extracted from the slopes and plotted against α according to Eq. (3). The resultant correlation is given in Fig. 4. Extrapolation to $\alpha = 0$ gives $E_0 = 10$ kcal/mole.

Analysis showed the rate of reduction to be approximately proportional to the hy-

drogen partial pressure. Little significance attaches to this result for our purpose.

Overall Course of Reduction

Hydrogen reduction of the $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst as determined by weight-loss measurements entails loss of oxygen (as water) from the molybdena, with concomitant reduction of molybdenum valence. In the first part of this study (2), Mo^{5+} concentrations were determined by ESR measurements on the same catalysts and under the same reduction conditions as those employed here. By combining the weight loss data, which give average Mo valence states, with the Mo(V) found by ESR, the amounts of Mo(IV), Mo(V) and Mo(VI) can be calculated at any time. We make the following assumptions: (1) reduction of Mo(VI) to Mo(V) and Mo(IV) is accompanied by their respective stoichiometric oxygen loss required to maintain charge neutrality; and (2) no Mo valence below Mo(IV) are formed. Then material and charge balance considerations give:

$$\alpha = [\text{Mo(V)}]/6 + [\text{Mo(IV)}]/3 \quad (7)$$

$$1 = [\text{Mo(VI)}] + [\text{Mo(V)}] + [\text{Mo(IV)}], \quad (8)$$

where α is as defined previously, and $[\text{Mo(IV)}]$, $[\text{Mo(V)}]$ and $[\text{Mo(VI)}]$ are mole fractions. Independent determinations of α and Mo(V) then allow calculation of $[\text{Mo(IV)}]$ and $[\text{Mo(VI)}]$ according to Eqs. (7 and 8). These equations apply for $\alpha < 0.33$; above this value, lower valence Mo species must be included and hence individual Mo fractions cannot be explicitly determined. Although $\alpha < 0.33$ is a necessary criterion, it is not sufficient to establish that Mo valences lower than 4+ are not present. Nevertheless, in view of the slow reduction rate of the molybdena-alumina and the relatively slow reduction of bulk MoO_2 compared to MoO_3 , it is felt that this assumption is reasonable for low α values. Also, implicit in this analysis is that the ESR technique used measured all the Mo(V) present. It is possible that some Mo(V) escaped detection due to symmetry considerations (see "Discussion").

The results of this analysis on a 10%

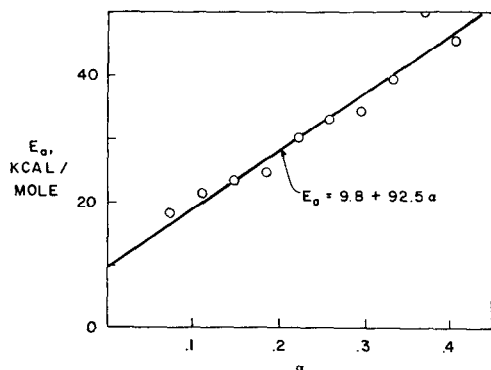


FIG. 4. Variation of activation energy with degree of reduction.

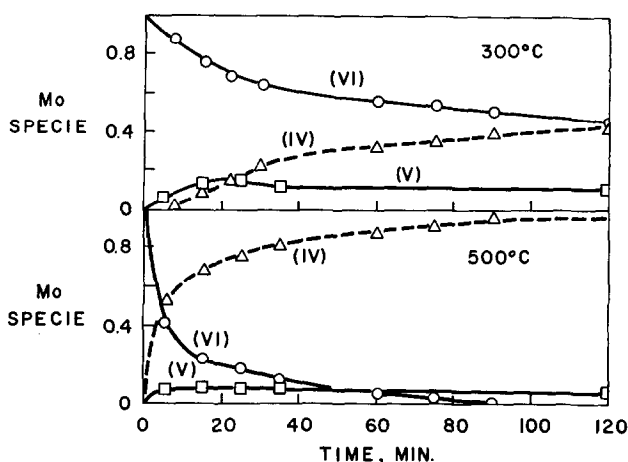


FIG. 5. Change in Mo species during reduction.

Mo/ η -Al₂O₃ catalyst are illustrated in Fig. 5, where the calculated Mo species are plotted against time of reduction for two temperatures. The fraction of Mo(V) in relation to the total Mo is seen to be small. Although not clearly shown here, the Mo(V) concentration increases rapidly to a maximum, then decays and reaches a plateau with continued reaction time (2). Mo(VI) and Mo(IV) display reverse, monotonic variations with time of reduction. At the higher temperature, appreciable Mo(IV) is formed early in the reduction. In fact, at the end of 2 hr, practically no Mo(VI) is left. At the lower temperature, however, the Mo(V) forms early while the Mo(IV) only increases slowly with time.

Differences in overall reducibility between eta- and gamma-Al₂O₃ catalysts were minimal. At 500°C, virtually identical results were obtained; whereas at 300°C, the eta-Al₂O₃ catalyst showed slightly greater reduction to Mo(IV) at the expense of Mo(V).

Reoxidation with Air-Hydrogen Retention on Reduced Catalyst

Reoxidation of reduced catalysts with air was essentially instantaneous. At temperatures above 400°C, catalyst weights returned to their original values before reduction. However, at 400° or below, reoxidation caused a rapid weight increase above the starting oxidized state which was

followed by a slow decay to the initial state (Fig. 6a). Concomitantly, water was detected in the effluent air stream, the water concentration gradually diminishing as the catalyst weight returned to its initial level. The water must arise from oxidation of hydrogen held on the reduced catalyst. This hydrogen, which we will call "retained H," must be chemically combined on the reduced molybdena phase since it persisted even after several hours of N₂ purging (to constant weight) and was not present when the Al₂O₃ support alone was

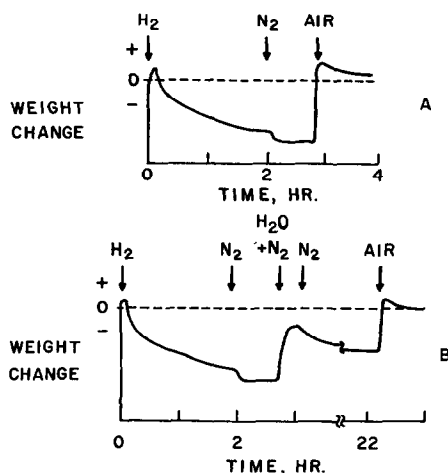


FIG. 6. Reoxidation of reduced catalyst. 8% Mo/ η -Al₂O₃, 400°C. (A) air reoxidation, (B) water reoxidation.

run through the same cycle. During oxidation, the retained H reacts with O₂ forming water, some of which is liberated and some of which is temporarily adsorbed by the catalyst; the latter is then slowly desorbed.

Analyses of several reoxidation runs are given in Table 2 in terms of H retained at the end of the reduction period (after N₂ purging to constant weight). Estimates of H retained were made as follows: water was measured in the effluent air stream with the water analyzer for 1–2 hr; when the water analyzer reading was too low for accurate reading, additional water loss was determined from catalyst weight loss over an overnight period. The sum of these two was used to calculate the retained H on the catalyst prior to the oxidation.

The results of Table 2 show that appreciable H is retained on the reduced catalyst. For example, H retained is of the same order of magnitude as oxygen removed in the reduction in three of the four experiments suggesting that H retained may be related to degree of reduction. The present data do not permit a more detailed consideration of this relationship owing to the

limited scope of reductions and low accuracy of the measurements.

It should be noted that although significant H was retained compared to O lost on a molar basis, the calculated degree of reduction, α , based on O loss, is little affected due to the low (molecular) weight of H compared to O. Of somewhat greater consequence is the possibility that Mo(V) formation may arise from H addition rather than O loss (see "Discussion"), in which case the [Mo(V)] term in Eq. (7) should be deleted, and a slightly larger [Mo(IV)] value will be calculated. For these reasons, the results given in Fig. 5 should be considered semiquantitative in nature, but nevertheless indicative of the overall course of the reduction.

Reoxidation with Water

To check the reversibility of the reduction process wherein water is the major gaseous product, a catalyst reduced at 400°C was subjected to a stream of N₂ saturated with H₂O. The addition of H₂O resulted in an immediate weight gain, as shown in Fig. 6b. After stripping off the

TABLE 2
ANALYSIS OF H RETAINED ON REDUCED CATALYST^a

Run number	1	2	3	4
<i>Reduction</i>				
H ₂ /N ₂ ratio	1/0	1/0	1/7	1/1
Time, min	125	90	70	90
Weight loss, mg	3.32	2.95	1.85	2.45
α^b	0.202	0.180	0.113	0.149
<i>Oxidation (Air)</i>				
H ₂ O evolved, ^c mmole	0.054	0.069	0.045	0.069
Extra weight loss, ^d mmole	0.019	0.014	0.008	0.011
Total H ₂ O lost, mmole	0.073	0.083	0.053	0.080
H retained, ^e mmole	0.146	0.166	0.106	0.160
Corrected O loss, ^f mg	3.47	3.12	1.96	2.61
Corrected α	0.211	0.190	0.119	0.160
O loss/H retained	1.49	1.17	1.16	1.02

^a 10% Mo/ γ -Al₂O₃, 1 g charge, 400°C, 1 atm.

^b Assumes all weight loss due to O loss only.

^c From water meter in 2 hr.

^d From additional weight loss overnight.

^e H retained on catalyst at end of reduction.

^f Sum of weight loss and H retained.

excess adsorbed water by a dry N_2 purge for overnight, a residual weight gain above the reduced value remained. This corresponded to about 40% return of catalyst back to the oxidized weight. Oxidation in air finally returned the catalyst to its original oxidized state.

In contrast to the reduced catalyst, a similar water treatment of the fresh catalyst (oxidized state) resulted in a small weight gain followed by an immediate weight loss upon N_2 purging. The catalyst weight returned to its initial value after purging overnight. Thus, water does not irreversibly react with the oxidized molybdena as it does with the reduced catalyst.

DISCUSSION

State of Molybdena on Alumina

Much evidence exists which argues for a high degree of dispersion of molybdena on activated alumina. The following observations may be listed:

(1) X-ray diffraction analyses have consistently failed to detect discrete phases or particles due to Mo compounds for Mo levels up to about 10–15% Mo. High resolution transmission EM investigation (15) of 8 and 12% Mo catalysts revealed a few isolated microcrystals, representing less than 10% of the Mo content. These were not observed on lower-level Mo catalysts. A lower limit of detection by these methods may be considered to be in the vicinity of 30 Å, corresponding to a particle surface to total molar ratio of at least 0.3.

(2) Butene chemisorption indicates a very high ratio of surface-to-volume molybdenum sites, close to a monolayer. Although some of the assumptions inherent in the calculations may be subject to question, that a high degree of dispersion is present seems evident.

(3) Finally, the Elovich kinetics found for catalyst reduction provides indirect evidence suggesting a surface phenomenon. Elovich kinetics has been exclusively employed for correlation of surface reactions and has been put on a sound theoretical basis (14). Correlation of the reduction data to the variable activation energy

mechanism for the Elovich equation is good. This implies that all the molybdena is available to react with hydrogen, implying a monolayer surface phase for the molybdena. The rapid increase in activation energy with extent of reaction from 10 kcal/mole at zero extent of conversion to 50 at 0.4 conversion, indicates a large variation in bonding energies of the molybdena with the alumina substrate. Kabe *et al.* (4) found a similar correlation for reduction of 8% Mo on a γ - Al_2O_3 catalyst, except they report an E_0 of 30 kcal/mole. Although in the present investigation it was only possible to follow the reaction to about 50% reduction to Mo (average $MoO_{1.5}$), this limitation is due to the increased activation energy for reduction, rather than to a given fraction of the molybdena being on the surface, i.e., the amount of molybdena undergoing reduction does not appear to be limiting.

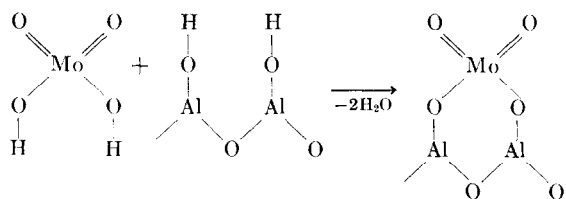
It should be mentioned that the logarithmic law found in oxidation of metals (16) is formally identical to the Elovich equation. The former law derives from a bulk diffusion mechanism through pores or defects in a solid. However, in that case, a constant activation energy is obtained representing activated diffusion contrary to the variable activation energy obtained with the catalyst.

That the well-dispersed molybdena on alumina is not present as free MoO_3 is evident from the reduction results. Thus, reduction rates were lower than for bulk MoO_3 and decreased with decrease in Mo content, contrary to expectation if free MoO_3 were present. Especially noteworthy was the absence of a break in the reduction curves at the MoO_2 stage, as is observed for bulk MoO_3 . Furthermore, reduction kinetics for the catalyst were totally different than those for bulk MoO_3 . The evidence, although not as conclusive, would seem to indicate that bulk $Al_2(MoO_4)_3$ is also not present on the catalyst.

The decreasing reduction rates with lower Mo concentrations may be rationalized on the basis of a variation in strengths of interaction between molybdena and alumina surface phases. The hetero-

generosity of high area alumina surfaces is well known. Thus, more active sites on the alumina may react preferentially with the molybdena, either by adsorption of molybdate ions from solution during impregnation or during calcination, forming a strong interaction compound. As the Mo level is increased, the less active alumina sites may form weaker interaction compounds. Thus, a spectrum of strengths of interaction compounds may be present on a 10% Mo catalyst. Such a condition would be manifested in the reduction kinetics as a variable activation energy, as found experimentally. Furthermore, the rapid initial reduction of the 10% Mo catalyst compared to bulk MoO_3 (see Fig. 2) is now explicable in terms of more ready reduction of the weaker interaction compounds. That short-time extent of reduction is actually greater for the catalyst compared to bulk MoO_3 does not invalidate our argument since reduction rates would be expected to be related to available surface areas, the former being essentially all available in a monolayer while the latter as discrete particles of low surface area. The lower reducibility of the stronger interaction compounds is clearly evidenced in the lower extents of reduction observed at longer times.

From the above arguments, it is concluded that molybdena is well dispersed, probably as a monolayer, on the alumina, and is strongly bonded to the alumina to render it less reactive towards reduction. Dufaux *et al.* (17) have suggested a surface interaction complex arising from an acid-base reaction during impregnation and subsequent calcination, viz.



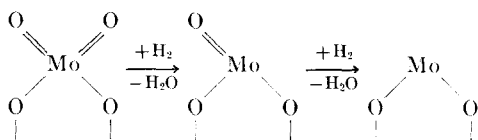
In the presence of water, the Al_2O_3 surface becomes highly hydroxylated. Upon heating, water is expelled and acid sites are

formed. These have a range of strengths as evidenced by adsorption and indicator studies (18). Interaction of these acid sites with the Mo could form interaction compounds having a range of strengths.

It seems significant that at even severe reduction conditions, the O/Mo atomic ratio did not go below unity. The data of Sontag *et al.* (3) also suggest a limiting reduction to O/Mo = 1. This would indicate that two of the three oxygen anions associated with Mo exhibit weaker bonding than the third. This is in accord with the structure given above, where the third oxygen is bonded through aluminum (the fourth oxygen also bonded through aluminum originally derived from the alumina).

Course of Reduction

Simple reduction may be equated to removal of surface oxide ions associated with the Mo, viz.



Such a sequence would involve reduction of the Mo valence from 6+ to 4+ to 2+. Intermediate states of reduction may also exist during reduction, such as 5+ or 3+, if isolated oxygen anions are removed from clusters of surface molybdena. Although reduction of bulk MoO_3 proceeds only through the sequence $\text{MoO}_3 \rightarrow \text{MoO}_2 \rightarrow \text{Mo}$ (13), compounds of molybdenum containing all integral valence states between 2+ and 6+ are known. Alumina appears to have the special property of stabilizing inter-

mediate Mo valence states, in particular, Mo^{3+} . Based on reflectance spectra of reduced $\text{Mo}/\text{Al}_2\text{O}_3$, Asmolov and Krylov

(19) concluded that molybdenum ions were present in different valence states and coordination.

In the early stages of reduction, reaction proceeds topochemically through the sequence $\text{Mo(VI)} \rightarrow \text{Mo(V)} \rightarrow \text{Mo(IV)}$. At longer times, Mo(V) remains essentially constant while Mo(VI) continues to decrease and Mo(IV) to increase. This may be due to a quasi steady-state concentration of the intermediate Mo(V) , or to a competitive direct reaction of $\text{Mo(VI)} \rightarrow \text{Mo(IV)}$. It is probable that both processes are occurring but on different sites.

Masson and Nechtshein (20) have postulated that the Mo(V) state is stabilized through a valence induction effect due to the alumina, and as such is confined to that layer of Mo immediately adjacent to the alumina surface. Additional layers of Mo act as free MoO_3 and reduce directly to MoO_2 . Using their concept, the surface model given in Fig. 7 is proposed to explain the reduction results. For simplicity, three Mo phases of differing reactivity are considered, although recognizing a spectrum of reactivities exist. The phases may all be located on the surface of the alumina as monolayer patches (complete Mo dispersion), or combined surface and bulk phases (partial Mo dispersion). Phase A is assumed to form an especially stable Mo(V) ; whereas Phase B initially forms Mo(V) , which then reduces further to Mo(IV) , depending on severity of reduction conditions. Phase C reduces directly to Mo(IV) .

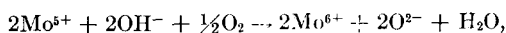
The overall reduction of each phase with times is shown below the model. At high temperatures, even lower reduced states

than Mo(IV) may be formed. This model qualitatively accounts for the Mo(V) maximum observed as well as its long-term stability by assuming different reduction rates of the phases according to reduction conditions.

Reduction Mechanism

Thus far, discussion has been confined to reduction states of molybdenum and a general model of surface reduction. The specific nature of these states as well as the mechanism of reduction is not precisely known at present. However, several facts emerging from this study permit reasonable proposals to be made.

The nature of the hydrogen retained on the reduced catalyst must first be discussed. It is not reversibly absorbed hydrogen, being still present after an overnight purge, nor is it as adsorbed water, since the addition of air causes an immediate evolution of water. It is associated with molybdenum, since it was not found on the alumina support alone. We, therefore, surmise that the retained hydrogen is present as a hydroxyl group associated with molybdenum. Furthermore, in order to account for its oxidation, the molybdenum must be in a lower valence state than $6+$. Taking as an example the pair Mo(V)-OH , oxidation could occur as follows:



regenerating the original oxidized state of the molybdena and forming water in the oxidation process. Obviously, hydroxyl groups associated with hexavalent molyb-

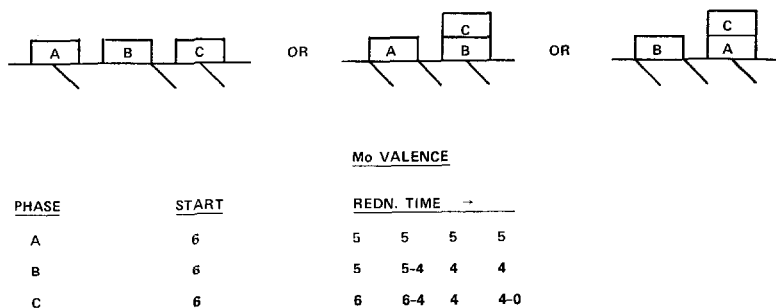


FIG. 7. Model for $\text{Mo/Al}_2\text{O}_3$ reduction.

denum or with alumina cannot undergo this type of oxidation.

Lipsch and Schuit (1) found hydrogen chemisorption (activated type) on a reduced CoMo/Al₂O₃ catalyst, and concluded that H-H bond cleavage was involved. Their measurements were not quantitative. Further, they measured H₂ uptakes after flushing the reduced catalyst with argon for 4 hr at 500°C. On the other hand, our measurements of retained hydrogen apply to the amount of H remaining on the reduced catalyst (Mo/Al₂O₃) after a similar purge treatment. Assuming the presence of cobalt does not greatly affect the overall phenomena, we conclude that their reduced

and purged catalyst must have still contained appreciable H, which could only be removed by oxidation.

With the above discussion in mind, it is reasonable to suppose that initial reaction involves chemisorption of hydrogen on the nonbridged oxygen anions associated with the molybdena. A mechanism for reduction is proposed in Fig. 8. Initial hydrogen chemisorption is followed by transfer of an electron to the Mo(VI), forming Mo(V) and an OH group (Structure A). This step is probably at equilibrium and may account for any reversibly adsorbed hydrogen. Dehydroxylation will now lead to reduced Mo(IV), (B), or to an interme-

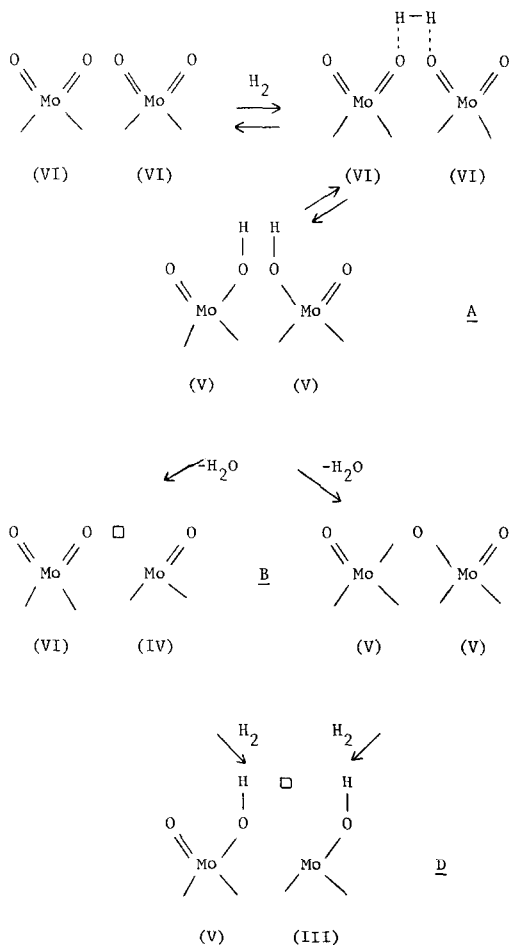
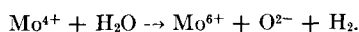


FIG. 8. Proposed reaction mechanism for reduction. Roman numerals under Mo indicate formal valence. □ is an anion vacancy.

diate Mo(V) pair, (C). Of especial interest catalytically, further hydrogenation of structures B or C can lead to a site containing a vacancy surrounded by two neighboring OH groups. A structure similar but not identical to D has been proposed by Lipsch and Schuit (1) as the active site for thiophene hydrodesulfurization over reduced CoMo/Al₂O₃ catalyst. Such hydrogen-containing sites should be particularly effective for exchanging hydrogen between gas and solid, a necessary requisite for desulfurization reactions. The relative amounts of the hydrogen-containing intermediates undoubtedly depend upon reduction conditions, higher temperatures favoring conversion to the lower oxidation states of molybdenum.

The structures having a formal valence of Mo(V) may or may not give rise to an ESR signal at room temperature depending upon the localized field symmetry (19). We can only speculate at present that a signal might not be detected for structure C because of pair symmetry quenching, whereas structure D might be detected. It should be noted that the companion Mo in structure D would have a formal valence of 3+. Although a valence state lower than Mo(IV) [including Mo(0)] has not been reported in the literature for reduced Mo/Al₂O₃ catalysts, this may be due to the fact that the catalysts were not reduced sufficiently far. However, when the average reduction state goes below Mo(IV) ($\alpha > 0.33$ in Fig. 3), charge balance requires that some lower Mo valence states must be present.

Addition of H₂O to the reduced catalyst presumably involves dissociative adsorption on vacant anion sites. Thus, a hydroxyl group can fill the vacancy and the associated proton adsorb on an adjacent free oxide site. The chemisorbed water is not removed even after overnight purging with N₂. A possible explanation for this stability, which does not occur with an oxidized catalyst, is that concomitant oxidation of the molybdenum occurs, viz.



Thus, the poisoning effect of water on thio-

phene desulfurization (1) may be ascribed to competitive adsorption on active sites or to reverse reactions leading to partial re-oxidation of molybdenum.

CONCLUSIONS

Reduction results, as well as other data, show that molybdenum supported on alumina is quite different in character from that of bulk MoO₃ or Al₂(MoO₄)₃. The molybdena is extremely well dispersed on the alumina surface, perhaps as a monolayer. Strong interaction between the molybdena and the alumina renders the former less reactive towards reduction. A surface interaction compound having a distribution of bonding strengths is suggested.

Partially reduced catalysts retain appreciable hydrogen, probably as surface hydroxyl groups associated with molybdenum. This hydrogen seems to be related in a yet undertermined way to the state of reduction of the catalyst. It is suggested that the molybdenum(V) observed by ESR measurements may be due to isolated molybdenum-hydroxyl groups.

Further quantitative study of the hydrogen content-state of reduction relationship, as well as correlation of catalyst activity for thiophene desulfurization with reduction properties, is currently underway and will be covered in a future report.

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