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Highly Reduced MoO_3/Al_2O_3 Catalysts

I. Characterization

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MoO_3/Al_2O_3 containing 0.89–7.4% Mo and reduced at 950°C by H_2 (MoO_3/Al_2O_3;H_2;950°) is Mo(0)/Al_2O_3. It has been studied and compared with Mo(0)/Al_2O_3 prepared by $Mo(CO)_6$/dehydroxylated Al_2O_3;He,300–500°;H_2,650–950° and found to be essentially equivalent in chemisorptive behavior. MoO_3/Al_2O_3;H_2,650° has also received some attention. The high purity alumina support treated H_2,950° becomes gray and is reduced by an amount representable as $Al^{2+}/Al^{3+} = 0.0012$. It is reoxidized to white material by O_2,800° but not by O_2,650°. Content in O_2 must be kept below 0.03 ppm in the other gases if a clean metallic molybdenum surface is to be maintained for a reasonable period of time. The amount of CO adsorbed at 25°C appears to be a measure of the percentage exposed of Mo(0)/Al_2O_3. If a molecule of CO is taken to occupy 1.5 sites, the percentage exposed of Mo varied from 25 to 58%. At 25°C, H_2 is chemisorbed rapidly but rather weakly on Mo(0)/Al_2O_3, and at least two forms of activated adsorption exist at higher temperatures. Under the conditions of this work the Mo particles in the samples of Mo(0)/Al_2O_3 are not carbide but rather, as evidenced by high resolution TEM and EXAFS, metallic bcc Mo. © 1989 Academic Press, Inc.

INTRODUCTION

Metallic molybdenum supported on alumina (Mo(0)/Al_2O_3) has been prepared in two quite different fashions. In the earlier preparation, $Mo(CO)_6$/DA (for DA, see Table 1) was treated He,300–500°;H_2,650°–950° (for the treatment code see Table 1). Mo(0)/Al_2O_3 so prepared exhibited some reremarkable catalytic activity and had been characterized moderately well both physically and catalytically. In the second preparation, MoO_3/HA was reduced with flowing H_2 at 950°C. The Mo(0)/Al_2O_3 so prepared had been examined in much less detail.

Physical characterization and catalytic activity of MoO_3/Al_2O_3 catalysts reduced by H_2 at up to about 500°C have been widely studied and particularly extensively by W. K. Hall and co-workers (*1*, *2*). Reduction at about 500°C of MoO_3/Al_2O_3 with monolayer or submonolayer coverages by MoO_3 results in an average oxidation number (O.N.) of Mo of 4 or a little larger (*1*, *3*). However, it has been reported that somewhat higher temperatures of reduction, up to 600°C, generate somewhat lower O.N., in particular, average O.N. = 3.8 (*4*). However, no studies of the catalytic activities of such more highly reduced materials have been reported.

Decomposition of $Mo(CO)_6$/PDA (Table 1) in flowing helium at about 300°C leads to the liberation of CO, H_2, and a little methane and leaves a material in which the average O.N. of Mo is about +2 (*5*). In this process, the original O.N. of zero is increased to +2 by the σ-OH groups of PDA acting as oxidizing agents primarily by the reaction

$$Mo(O) + 2\sigma\text{-}OH \rightarrow Mo^{2+} + 2\sigma\text{-}O^- + H_2$$

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TABLE 1

Terminology

σ-OH	Surface OH groups of alumina.
HA	Hydroxylated alumina, ~14 σ-OH nm^{-2}.
PDA	Alumina partially dehydroxylated at 475°C, ~4 σ-OH nm^{-2}.
DA	Alumina dehydroxylated at 950°C, ~0.1 σ-OH nm^{-2}.
O_2,500°,1;He,500°,1	The pretreatment in which flowing oxygen is passed over the catalyst at 500°C for 1 h and then flowing helium is passed at 500°C for 1 h. Gas flow rates were near 45 cm^3 min^{-1}.
O.N.	Average oxidation number of molybdenum.
MoO_3/HA	The 0.9, 5, and 8% Mo/Al_2O_3 catalysts as prepared by impregnation. They were pretreated O_2,500°,1;He,500°,1 upon insertion into the apparatus.

If $Mo(CO)_6$/DA is heated in helium to 300–500°C, CO is liberated and molybdenum is left along with 0.3 C per Mo and presumably an equal amount of oxygen (5). Since the surface concentration of σ-OH on DA is very low, little oxidation by σ-OH occurs. Exposure to flowing H_2 at 650°C liberates methane and reduces C/Mo to 0.01;H_2 at 950°C reduces C/Mo to 0.00 (5, 6). These materials were the first supported molybdenum catalysts in which the O.N. of the Mo was near zero and $Mo(CO)_6/Al_2O_3$;He,300–500°;H_2,650–950° was the first supported metallic molybdenum catalyst. $Mo(0)/Al_2O_3$ had a number of unusual and interesting catalytic properties (7) which are described in the following paper. A particularly striking feature of this catalyst was that, after exposure to oxygen or other contaminants, H_2,950° led to complete regeneration with no loss of the original metal surface area or catalytic activity (5, 6). Chemisorption of CO at 25°C gave CO/Mo of about 0.17 whence it was concluded that the fraction exposed of Mo was between 0.17 (simple chemisorption) and 0.34 (dissociative chemisorption).

In the course of this work, reduction of MoO_3/HA at high temperatures was investigated. It was found that H_2,650° reduced MoO_3/HA to about $Mo(\sim 2+)/Al_2O_3$ and that H_2,950° reduced it to $Mo(0)/Al_2O_3$ (6, 8, 9). That H_2,950° leads to Mo with an O.N. near ~0 has been confirmed in other laboratories (*10–13*).

When this work commenced, a few catalytic runs had indicated that MoO_3/HA; H_2,950° had catalytic properties similar to those of $Mo(CO)_6$/DA;He,500°;H_2,650–950°, but no characterization of MoO_3/HA; H_2,950° had been attempted beyond measurement of O.N. (*6*). It therefore appeared desirable to attempt some characterization of this material for comparison with Mo(0)/DA prepared from $Mo(CO)_6$ and further to investigate its catalytic characteristics. This paper reports upon characterization and the following paper upon catalytic behavior.

EXPERIMENTAL

Experimental Techniques

The experimental techniques employed were, in general, the same as before (5, 6). At the entrance to the apparatus, high purity He and H_2 were passed through traps of Davison grade 62 silica gel at −196°C to reduce the concentrations of all gases except H_2, He, and Ne to below 0.03 ppm. Traps of MnO/SiO_2 just preceded the reactor to reduce the content in any O_2 which may have entered via microleaks to a few parts per billion (*14*). The Carle gas chromatographic injection valve used in pulse experiments and the Carle valve used to isolated and bypass the catalyst during desorption measurements were jacketed and purged with helium.

Gases such as CO and CH_4 liberated into hydrogen or helium streams were trapped on silica gel at −196°C. Warming the trap released a pulse for catharometric measurement. Sometimes the pulse was passed through a silica gel column for chromatographic separation. To measure CO_2 in a stream of oxygen, the CO_2 was isolated by trapping on silica gel at −120 to −130°C and released as a pulse for catharometry.

The absence of leaks was periodically confirmed by inserting a tube containing 0.5% MnO on SiO_2 gel in the reactor position, passing He, Ar, or H_2 through the system, and measuring the rate of advance of the green (unoxidized)–brown (oxidized) boundary. O_2 was kept less than 0.03 ppm.

Catalyst Preparation

PHF γ-Al_2O_3 of American Cyanamid (reported purity, 99.99%) was crushed carefully and sieved. The 80- to 100-mesh portion was washed with distilled water which had been passed through an ion-exchange purifier, 0.1 *M* nitric acid, and water. After drying, the alumina was heated in a flow of Matheson tank air at 570°C for 1.5 h, stored for 3 days in a desiccator over water, and then dried at 140°C to generate hydroxylated alumina, HA.

Following He,450° the specific area, specific pore volume, and average pore diameter of this alumina were 200 $m^2\ g^{-1}$, 0.58 $cm^3\ g^{-1}$, and 10 nm, respectively, as determined on the Omnisorp 300. After H_2,650°; vac,650°, the values were 170 $m^2\ g^{-1}$, 0.55 $cm^3\ g^{-1}$, and 10 nm, and after vac,950°, 146 $m^2\ g^{-1}$, 0.50 $cm^3\ g^{-1}$, and 10 nm (*15*).

Two catalysts, 0.89 and 7.4 wt% Mo/Al_2O_3, were prepared by impregnating alumina to incipient wetness with appropriate solutions of ammonium heptamolybdate. The alumina was contained in a beaker rotated at an angle of about 25° from the horizontal. While rotation continued, the beaker was heated by an infrared lamp until constant weight was achieved. After heating in an oven at 120°C overnight, the product was uniformly colored. However, if the product was placed in the oven before it had come near constant weight in the rotating beaker (which mixed the alumina continuously), a pepper and salt product resulted consequent to migration of solution to the surface of the pile of alumina during heating in the oven.

A 4.8% Mo/Al_2O_3 catalyst was prepared by the equilibrium method of Wang and Hall (*16*). Ten grams of Al_2O_3 was agitated periodically for 8 h in a solution of 4.34 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 cc of water adjusted to pH of 2.1 with nitric acid. It was filtered and dried as above in the rotating beaker and the oven. By atomic absorption spectroscopy, the Mo content was 4.8%. In this preparation there is a possibility that some of the molybdate may be present as a fine precipitate which is difficult to distinguish visually from the alumina (*17*). As will be seen in this and the following paper, the properties of the 4.8% Mo catalyst diverged a little from those of the 0.89 and the 7.4% Mo catalysts.

Unless otherwise specified, about 0.25 g of catalyst was used in an experiment. After initial insertion into the reactor, a catalyst was always exposed to O_2,500°,1;He, 500° before further pretreatment.

Three samples of ~0.9% Mo/DA, C1, C2, and C3, were prepared in the reactor from $Mo(CO)_6$/DA (*5*). They were not calcined before use.

Measurement of Chemisorption and Oxidation Number of Mo

Chemisorption of CO at −78 and 25°C was measured by (i) flowing CO over a catalyst for 5–10 min at −78°C and flushing with He, (ii) passing He over the catalyst and thence through a trap of Davison 62 silica gel at −196° while the temperature of the catalyst was raised to 25°C, and (iii) releasing a pulse of CO by warming the trap rapidly to 25°C, and repeating (ii) and (iii) to T_{des} = 350°C. With Mo/Al_2O_3, hydrogen flow was then started and the effluent from the catalyst was trapped by silica gel at −196°C as the temperature was raised to a new and higher T_{des}. CH_4 was collected in the bed, released as a pulse, and measured catharometrically.

Chemisorption of H_2 was measured by (a) exposure of the catalyst to H_2 at T_{ads} and flushing with Ar, (b) isolating the catalyst region by manipulating the Carle bypass valve and heating the catalyst rapidly to 500°C, and (c) reestablishing the flow of Ar and measuring the evolved pulse of H_2. Steps (b) and (c) were repeated to 850°C. Divergence between duplicate runs was usually ≤10%.

Fast and irreversible adsorption was often determined by measuring the loss from a pulse of adsorptive passed over the catalyst in carrier He or Ar. A pulse of H_2 in He was converted into one of H_2O by passage through a bed of CuO at 450°C. In measuring the O.N.s of reduced catalysts, loss from several pulses of O_2 (Matheson Zero Gas) at 500°C was first measured and then a pulse of O_2 in He was trapped in the catalyst region for 0.5 h and then released for measurement. In calculating O.N., oxidation of Mo to O.N. = +6 was assumed (*5*, *6*, *18*).

TABLE 2

Oxidation Numbers of Catalysts as a Function of Pretreatment Conditions

Pretreatment	Catalyst		
	0.89% Mo	4.8% Mo	7.4% Mo
H_2,650°;He,650°	4.08 3.64 3.50	2.56 2.64	1.90
H_2,650°;He,950°	5.50 5.74[a]	3.14	2.36
H_2,950°;He,650°	0.26	−0.04	−0.12
H_2,950°;He,950°	0.42 0.26	0.22	0.16

[a] After trapping O_2 at 500°C, O_2 was trapped at 600°C. No additional O_2 was consumed.

EXPERIMENTAL RESULTS

Reduction of Alumina

Samples of alumina remained white after He,950°;H_2,650°. However, a subsequent H_2,950°,4 min changed the color to gray. O_2,650°,1 effected no change in color, but O_2,800°,1 restored the color to white.

The gray color does not result from deposition of carbon as shown by experiments using Matheson Zero Gas oxygen reported to contain less than 0.5 ppm of carbon. A 0.25-g sample of PHF Al_2O_3 was exposed to 10 cycles of alternate oxidation (O_2,950°, 0.33;He,950°,1) and reduction (H_2,950°, 0.33;He,950°,1). The CO_2 collected decreased from 53.4 μmol in cycle 1 to 5.4 μmol in cycle 2 to 0.16 μmol in cycle 10, a value near that expected from carbon impurity in the O_2, but the color change remained identical. After cycle 10, several pulses of O_2 were passed over the gray Al_2O_3 at 950°C. The absorption of dioxygen at 950°C from several pulses of O_2 was 2.5 μmol g^{-1}. Loss of O_2 from a pulse of O_2 trapped for 0.5 h was 3.2 μmol g^{-1} for a total loss of 5.7 μmol g^{-1}. The alumina became white and no liberation of CO_2 was detected.

Oxidation Numbers of Reduced Catalysts

The additional O_2 consumed during trapping was ≤0.15 O/Mo after H_2,650° and 0.25 ± 0.05 after H_2,950°. Results appear in Table 2.

Samples of ~0.9% Mo/DA (catalysts C1, C2, and C3) were used for studies of the adsorption of CO and H_2, following which the catalysts were treated H_2,950°,1;He, 950°,1 and titrated with oxygen. The values of O.N. so found were catalyst C1, +0.06; catalyst C2, +0.22; and catalyst C3, +0.16.

Chemisorption of Oxygen

Since it might provide a way to measure percentage exposed, the adsorption of O_2 was measured at −78°C by the pulse technique (*5*). The temperature was then raised to 25°C and the additional adsorption from a pulse was measured. Results should be accurate since the exit pulses were sharp and devoid of tails.

The oxygen adsorption expressed as O/Mo on 0.89 and 7.4% Mo/Al_2O_3;H_2,950°; He,950° $\rightarrow$ −78° was 0.33–0.35 at −78°C and the cumulative adsorption at 25°C was 0.46–49. The same values of O/Mo were found on a sample of the 0.89% Mo catalyst which had been used for chemisorption measurements and then treated O_2,500°;H_2, 950°;He,950°. With the less investigated H_2,950°,He,650°, O/Mo was 0.45–0.50 at −78°C and 0.74 at 25°C. O/Mo on $Mo(CO)_6$/DA;He,500°;H_2,650° at 25°C was close to 0.52 (*5*).

Adsorption of Carbon Monoxide on Alumina

After H_2,650°;He,650°, the adsorption at 25°C was about 15 μmol g^{-1}; after H_2,950°; He,950°, 5 μmol g^{-1}; and after He,950°, about 2 μmol g^{-1}. The adsorptions at −78°C were about 60 μmol g^{-1} for the two pretreatments in H_2 but only about 16 μmol g^{-1} for He,950°.

Adsorption of Carbon Monoxide on Mo/Al_2O_3

Correction for adsorption on the free alumina surface introduced serious uncertainties in attempts to measure CO_{ads} on Mo at −78°C. With the 0.89% catalyst, the blank corrections even led to substantial negative values of adsorption. However, the uncertainty at 25°C is much smaller because of the smaller blank correction. Yields of methane presumably involve no blank correction and, indeed, the amounts of methane formed were nearly the same for initial adsorption at 25 and −78°C.

Tailing of the exit pulse prevented accurate measurement of CO/Mo at 25°C by the pulse method on the catalysts derived from MoO_3/HA, but the pulse method could be used on those derived from $Mo(CO)_6$/DA.

The data on the adsorption of CO on Mo/Al_2O_3 catalysts given in Table 3 result from experiments with two samples each of the 0.89 and the 7.4% catalysts. A sample was first pretreated H_2,650°;He,650° (to be called MoO_3/HA;H_2,650°) and chemisorption measured. It was then "repretreated" H_2,950°;He,650° (MoO_3/HA;H_2,950°) and chemisorption was measured. The amount of methane released above 650°C was less than 5% of total carbon. The amount of CO adsorbed at −78°C was measured similarly. In the terminology of Table 3, at −78°C for 7.4% MoO_3/HA;H_2,950°, CO/Mo off to 350°C was 0.063 (0.138) and for 7.4% MoO_3/HA;H_2,650°, 0.151 (0.238). With 4.8% MoO_3/HA, the helium and hydrogen effluents were passed through traps of silica gel at −196°C. The pulses released on warming the trap were analyzed chromatographically on a column of silica gel.

TABLE 3

Adsorption of Carbon Monoxide on Mo/Al_2O_3 as CO/Mo at 25°C

	MoO_3/HA;H_2, 650°;He,650°		MoO_3/HA;H_2, 950°;He,650°		
	0.89%	7.4%	0.89%	4.8%	7.4%
CO off to 350°	0.05 (0.22)[a]	0.058 (0.078)[a]	0.10 (0.15)[a]	0.18[b] 0.008[c] 0.006[d]	0.055 (0.061)[a]
CH_4 off to 500°C	0.03	0.015	0.24	0.039[e]	0.052
CH_4, 500–950°C	0.02	[g]	0.05	0.049[f]	0.059
Total C	0.10 (0.27)[a]	0.073 (0.093)[a]	0.39 (0.44)[a]	0.246 (0.30)[a]	0.166 (0.172)[a]

[a] Value without correction for blank. For 0.25 g of 7.4% Mo/H_2,950°, CO on Al_2O_3 alone = 0.25 × 0.926 × 5 = 1.2 μmol and Mo = $10^6 \times 0.25 \times 0.074/96$ = 193 μmol. Whence, the correction for CO adsorbed on the surface of Al_2O_3 expressed as CO/Mo is 1.2/193 = 0.006. Here, 0.926 is g of Al_2O_3 per g of catalyst and 5 is the μmol of CO adsorbed on 1 g of Al_2O_3.

[b] CO released 25–230°C in He, not corrected for blank. CO_2 was collected, CO_2/Mo = 0.018. No further CO_2 was collected at higher temperatures.

[c] CO released 230–500°C in He.

[d] CO released 500–950°C in H_2.

[e] CH_4 released by H_2,500°,1/6.

[f] CH_4 released by H_2,500–950°C.

[g] Not measured.

Adsorption of Hydrogen

There are multiple chemisorbed states of hydrogen on reduced MoO_3/Al_2O_3. Adsorption was measured on three samples each of the 0.89 and 7.4% catalysts. Two of the latter samples were about 0.14 g. A catalyst was first pretreated H_2,650°,1;Ar,650°,cool in Ar to the adsorption temperature, T_{ads}, and the chemisorption of H_2 was measured. Divergence between duplicate runs was usually ≤10%. A number of runs at various T_{ads} were made on a sample of catalyst after the H_2,650° pretreatment. This pretreatment was usually repeated after each adsorption run. The catalyst was then treated H_2,950°,1;Ar,650°,cool in Ar and adsorption measured at several T_{ads} with the treatment H_2,950°;Ar,650° repeated between runs.

The adsorption of H_2 irreversible at 25°C on Al_2O_3;H_2,950°,1;He,950°,0.33 was negligible, ≤0.05 μmol g^{-1}, which is about the experimental error. No corrections have been made for adsorption on the support. Various studies with rather divergent results of the adsorption of H_2 on alumina have appeared (*19–22*) but comparison is complicated by varying pretreatment conditions and impurity contents. One TPD study has reported the presence of five forms of chemisorbed H_2 on pure γ-Al_2O_3 made from aluminum isopropoxide pretreated H_2,vac,650° and the occurrence of rapid H_2–D_2 equilibration at −75°C upon this material (*19*). The amount chemisorbed on Al_2O_3;vac,650° upon cooling in H_2 from $T \geq 350$°C would correspond to H/Mo on the 7.4% catalyst of 0.07. Like the adsorption of CO on alumina, the alumina surface of Mo/Al_2O_3 might well adsorb less than that of pure alumina. Except at 25°C and perhaps 150°C the exact interpretation of the data on chemisorption of H_2 on Mo/Al_2O_3 is open to some question and it may not be easy to decide in some cases just where H_2 is adsorbed.

As a test of the presence of contaminants, H/Mo at T_{ads} = 25°C was measured to T_{des} = 500°C on 0.25 g of 7.4% MoO_3/HA;H_2,950°. After 2 days in flowing argon at 25°C, H/Mo at T_{ads} = 25°C was then measured to be 0.163, whereas it was 0.165 when first measured.

Adsorption of Hydrogen on MoO_3/HA; H_2,650°;Ar,650°

Adsorption of hydrogen on MoO_3/HA; H_2,650°,Ar,650°,1 at $T \leq 25$°C was activated. Thus, on 7.4% MoO_3/HA;H_2,650° with desorption to 500°C, at T_{ads} = −130°C, H/Mo was 0.002; at −78°C, 0.006; and at 25°C, 0.029. Irreversible adsorption on the alumina surface was very small under these conditions. Using pulses of H_2 in helium carrier, at −196°C H/Mo was 0.146; at −78°C, 0.003; and at 25°C, 0.018. During desorption using helium carrier, the exit flow from the catalyst was passed through a trap of molecular sieve 5A at −196°C to collect evolved H_2 (*5*). Warming released the collected H_2 as a pulse for catharometric measurement.

At T_{ads} = 150°C, the H/Mo measured in the standard fashion by desorption in Ar depended critically upon the time of flush. For t_f = 5 min, H/Mo on 4.8% MoO_3/HA; H_2,650°;Ar,650° was 0.042; for t_f = 10 min, 0.016; and 15 min, 0.008. Thus, at this temperature, desorption is rather fast and H/Mo will depend critically upon t_f. Presumably, then, the adsorption at 250°C is a stronger form of adsorption too slow to be observed at 150°C.

Adsorption of Hydrogen on MoO_3/HA; H_2,950°;Ar,650°

Some data on the adsorption of hydrogen on the 0.89 and the 7.4% Mo catalysts appear in Table 4. The effects on the measured H/Mo of the time of exposure of the catalyst to hydrogen and of the flushing time in argon, t_f, were investigated on the 7.4% catalyst with T_{ads} = 25°C. H/Mo was independent of the exposure time between 5 and 60 min, but the effect of t_f was substantial. After exposing the catalyst to H_2

TABLE 4

H/Mo for the Adsorption of H_2 on MoO_3/HA;H_2, 950°;Ar,650°[a]

T_{ads} (°C)	0.89% Mo/DA		T_{des} (°C)	7.4% Mo/DA	
	500[a]	850[b]		500[a]	850[b]
−130			0.091		
−78	0.138		0.130		
25	0.162		0.100	0.102	
75	0.160[c]		0.080		
150	0.145	0.163	0.112	0.117	
250	0.210	0.253	0.101	0.108	
350	0.174	0.230	0.048	0.058	
450	0.054	0.124	0.010	0.109	

[a] In this column the catalyst was exposed to H_2 at T_{ads}, flushed with He at T_{ads}, and desorbed at 500°C. The measured pulse of H_2 which was evolved gave H/Mo in this column.

[b] After desorption to 500°C in the column to the left, the catalyst was heated to 850°C. The listed H/Mo is that resulting from desorption at 500°C plus that at 850°C.

[c] At T_{ads} = 100°C, H/Mo was 0.085.

for 5 min at 25°C, with $t_f = 1.5$ min, H/Mo was 0.119; 3 min, 0.109; 5 min, 0.100; 20 min, 0.087; and 15 h, 0.066. Thus, at 25°C adsorption of H_2 is relatively fast, most H_2 is held rather strongly, but considerable H_2 is held rather weakly. The method of measuring H/Mo is not well suited to the situation at 25°C. Measurement of H/Mo vs P_{H_2} might provide more useful data.

In helium carrier and $T_{ads} = T_f = -196°C$, H/Mo was 0.144. When T_{ads} was −78 or 25°C, essentially all adsorbed hydrogen was liberated before 500°C but, as shown in Table 4, not when $T_{ads} \geq 150°C$. For $T_{ads} \leq 350°C$, H_2 liberated in the range 640–850°C was negligible, it was small for $T_{ads} = 450°C$, but it was substantial for $T_{ads} = 650°C$. Reproducibilities in H/Mo with 0.89% Mo at 25 and 150°C and for 7.4% at −130, −78, 25, 150, and 250°C were ±5%.

H/Mo was also measured by the pulse technique in helium carrier with an effective flushing time of 7 min (*6*). On 0.89% Mo, H/Mo was 0.142 at 25°C. On 7.4% Mo, H/Mo was 0.100 at 25°C and 0.115 at −78°C. These are in reasonable agreement with the data in Table 4 obtained from desorption.

H/Mo measured by desorption to 500°C in helium carrier on catalyst C2 (0.9% Mo, $Mo(CO)_6$/DA;He,400°,1;H_2,950°,1;He, 650°) was 0.111 at $T_{ads} = 25°C$ and 0.240 for $T_{ads} = 250°C$. However, $Mo(CO)_6$/DA;He, 400°,1 adsorbed no detectable amount of H_2 at 25°C.

Infrared Spectroscopy

Runs were made on $Mo(CO)_6$/transparent alumina film (*23*) treated He,500°;H_2, 650°;cool in H_2. There were no detectable bands due to adsorbed H_2. Exposure to CO at 25°C which is known to adsorb with displacement of H_2 (*5*) produced a substantial and rather wide band at 2025 cm^{-1} but no other bands.

Electron Microscopy

Dr. J. P. Zhang took transmission electron micrographs on a Hitachi-9000 high resolution instrument at a resolution of better than 1.9 Å and provided the interpretation (*24*). A sample of the 7.4% Mo catalyst was reduced in H_2 for 1.75 h at 950°C, cooled in H_2, and supported on a holey-carbon grid for examination in the electron microscope. The sample had to be exposed to air for about 15 min during these operations. The molybdenum particles on the average would have adsorbed O/Mo = ~0.7, but complete oxidation takes more than a day (*5*). One electron micrograph is shown in Fig. 1. A number of particles 3 to 5 nm in diameter are visible and the lattice grid is resolved in a number of them. Particles A and B are bcc metallic molybdenum oriented in the [001] direction. Particle C has not been securely identified. Particle D provides only one-dimensional information and cannot be identified. The image of some particles is blurred by surface contamination, probably oxide.

DISCUSSION

In general, as elaborated below, comparison of the results of the experiments on $Mo(0)/Al_2O_3$ prepared by reduction of MoO_3/HA at 950°C with $Mo(0)/Al_2O_3$ derived from $Mo(CO)_6$/DA indicates that the two are nearly equivalent materials. The preparation from MoO_3/HA is much simpler and can generate Mo/Al_2O_3 in a wide range of Mo contents. Preparation from $Mo(CO)_6$/DA is limited to about 2.3% Mo beyond which excess carbonyl sublimes from the alumina (*25*).

Oxidation Numbers of Molybdenum

As shown in Table 2, titration with oxygen at 500°C was used to measure the O.N. of Mo as a function of the conditions of pretreatment for two catalysts prepared by conventional impregnation with ammonium molybdate (0.89 and 7.4% Mo) and one by the "equilibrium method" (4.8% Mo).

Two reactions are important in determining O.N., reaction (2) and some form of reaction (1),

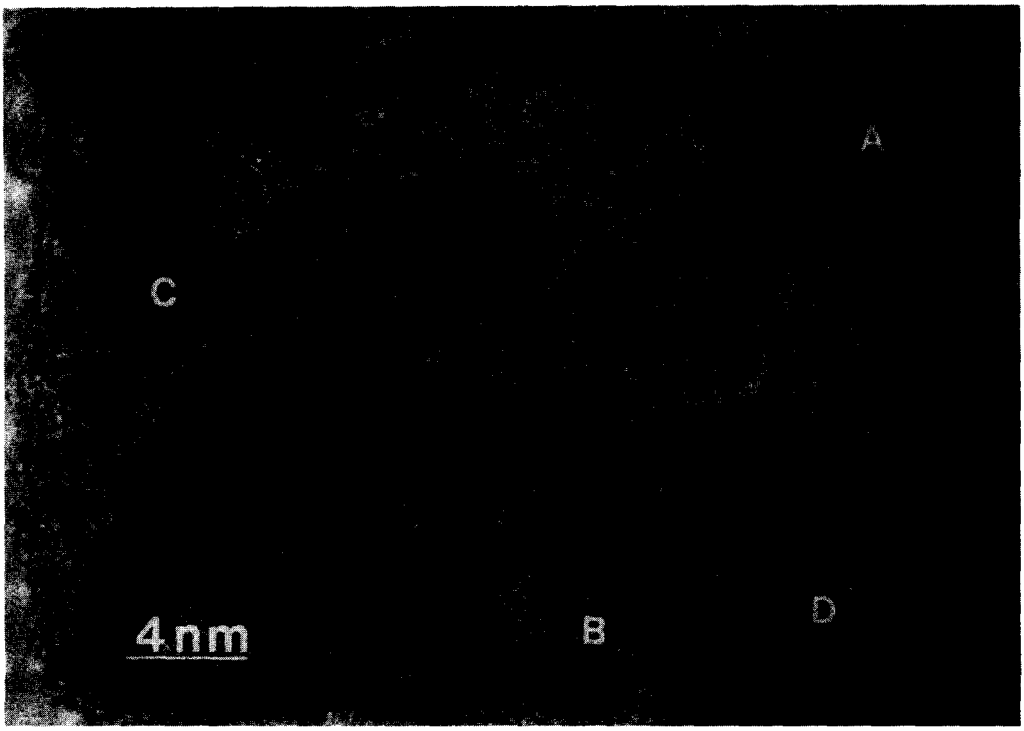

FIG. 1. Transmission electron micrograph of MoO_3/Al_2O_3 (7.4% Mo) heated in flowing hydrogen for 1.75 h at 950°C. Particles A and B are bcc metallic molybdenum oriented in the [001] direction.

$$\sigma\text{-}O^{2-} + Mo^{n+} + \tfrac{1}{2}H_2 \rightleftharpoons \sigma\text{-}OH^- + Mo^{(n-1)+} \quad (1)$$

$$2\sigma\text{-}OH^- \rightleftharpoons H_2O(g) + \sigma\text{-}O^{2-} \quad (2)$$

Therefore, other parameters held constant, values of O.N. nearest zero should be favored by higher temperatures of reduction in H_2 (because of Eqs. (1) and (2)) and by lower temperatures of flushing with He (Eq. (2) i.e. (Eq. (-1)). The data in Table 2 accord with these expectations. H_2,650° leads to larger O.N.s than H_2,950°, but He, 650° leads to smaller O.N. than He,950°. Further, the ratio σ-OH/Mo being larger, the effect of Eq. (-1) should be larger on lower loading catalysts, an effect clearly shown in Table 2 for the runs with H_2,650°. H_2,950°;cool to 650°;He,650° should give the lowest values of O.N. as is, indeed, observed. In addition, except on highly dehydroxylated surfaces, the intrusion of reaction (-1) will prevent the exclusive existence of highly reduced species on hydroxylated supports of any but the least oxidizable metals (*5*, *26*).

Holl *et al.* (*12*) have recently reported a study by XPS of the reduction of MoO_3/HA by H_2 at high temperatures. In fair agreement with work at this laboratory, they concluded that after H_2,950° the molybdenum was very close to the metallic state, that the Mo was aggregated to large particles, and that O_2, 550° reoxidized the Mo(0). The discussion of these interesting data was somewhat handicapped by their belief (since they had overlooked Refs. (*6*, *8*, *10*, and *11*)) that "Up to now, no one has studied the high-temperature reduction (between 550 and 950°C) of alumina-supported MoO_3 catalysts."

Since $Mo(CO)_6$/DA starts highly dehydroxylated, reaction (2) is not important and it makes little difference whether flushing with He is at 650 or 950°C. As reported under Experimental O.N. is zero within the experimental error after H_2,950°;He,950° (see also Ref. (*5*)) as is true for MoO_3/HA; H_2,950°;He,650°.

Reduction of Alumina

Samples of $Mo(CO)_6$/DA heated to 300–500°C in He became black and retained carbon and oxygen with C/Mo and O/Mo $\approx$ 0.3. Exposure to air led to no visible change for about 3 days following which the sample gradually became gray. Exposure to oxygen at 300°C changed the color to white (*6*). MoO_3/HA;H_2,950° behaved somewhat differently. These catalysts were very dark brown (0.89%) or black (7.4%). They became gray after O_2,500° and white only after exposure to O_2 at $T > 800$°C.

These data led to study of the treatment of γ-alumina by hydrogen and oxygen at higher temperatures. It was previously known that heating the PHF Al_2O_3 at 950°C for about 1 h led to considerable conversion of the γ-alumina to δ-alumina with relatively little loss in texture (*6*). In the present experiments, the Al_2O_3 remained white after He,950° and H_2,650°, but H_2,950°,4 min changed the Al_2O_3 from white to gray. O_2,650° was without effect on the color, but O_2,800° returned the color to white. It was shown that the gray color was not caused by carbon deposited on the catalyst, but involved the alumina itself. The amount of O_2 consumed in the reoxidation at 950°C was 5.7 μmol g^{-1}. If H_2,950° forms Al^{2+}, then the resulting Al^{2+}/Al^{3+} is about 0.0012.

It was reported some years ago by Teichner and colleagues that a particular amorphous alumina became black upon evacuation at 500°C apparently consequent to the release of oxygen, $2O^{2-} \rightarrow O_2 + 4e$ (*27*). Evacuation of this material at 800°C led to the evaporation of aluminum which condensed as metal on colder parts of the apparatus. The black alumina became white upon O_2,500°. As measured by oxidimetry, the black alumina was $Al_2O_{2.96}$. The alumina employed in this research never became gray upon heating in helium even at 950°C, nor have we observed any formation of an aluminum deposit. Treatment in flowing He should be equivalent to evacuation. Thus, the reducibility of PHF alumina is much less facile than that of the amorphous alumina studied in Ref. (*27*).

Adsorption of Carbon Monoxide

The adsorption of CO on Mo appears to be the same on materials derived from MoO_3/HA and from $Mo(CO)_6/Al_2O_3$. Subject to some uncertainly, irreversible adsorption of CO at 0–25°C appears to be a measure of the percentage exposed of Mo(0).

At −78°C, adsorption on the alumina surface of MoO_3/HA;H_2,950° seriously interferes with measurement of the adsorption on the Mo surface. Possible error is much smaller for T_{ads} = 25°C and the corrected and uncorrected values for desorption of CO upon heating from 25 to 350°C should bracket the true value. Further, not surprisingly, there appears to be some differences among the alumina surfaces of Al_2O_3;H_2, 650 or 950°, of MoO_3/Al_2O_3;H_2,650° or 950°, and of $Mo(CO)_6$/DA;He,400°;H_2,950°. Thus, the adsorption of CO at −78°C on Al_2O_3 is larger than that on the 0.89% Mo catalyst. CO pulses in He at 25° on the reduced MoO_3/HA tail rather badly presumably because of slowly reversible adsorption on the alumina surface. However, tailing is negligible on the catalysts derived from $Mo(CO)_6$/DA.

A. About 30% of CO adsorbed at 25°C on MoO_3/HA;H_2,950°;He,650° is liberated as CO in the interval 25–350°C. The remainder appears as CH_4 between 350 and 650°C except for about 5% which is liberated between 650 and 950°C (see Table 3). A small amount of CO_2 desorbs at $T \leq 230$°C but none at higher temperatures. All *C is fully converted to methane by H_2,950° and presumably all *O is converted to H_2O since H_2,950° fully regenerates catalysts exposed to CO or O_2 (*6*).

B. CO/Mo for catalyst C2 at 25°C was 0.21 after H_2,950°;He,650° and for catalyst C3 after He,400°,1 CO/Mo was 0.16. CO/Mo had previously been reported to be 0.17 on both $Mo(CO)_6$/DA;H_2,650° and $Mo(CO)_6$/DA;He,500° (*5*).

C. Unlike the case with the first material, He,500° liberated almost all adsorbed CO from $Mo(CO)_6$/DA;He,500° (*5*). A pulse of O_2 displaced all CO from the Mo(0) catalyst without formation of CO_2.

D. CO adsorbed at 25°C on $Mo(CO)_6$/DA;He,400°;H_2,650° exhibits one infrared absorption band at 2025 cm^{-1}. The intensity is substantial but data to quantitate the amount of *CO are lacking.

Two questions arise. How many Mo_s does adsorbed CO occupy? Is the CO adsorbed molecularly or dissociatively, i.e., as *CO or as *C + *O?

On single crystals of molybdenum, CO is generally considered to adsorb dissociatively (*28*), but the conditions of adsorption in surface chemical physics are very different from those in the present work.

The liberation of much of the adsorbed CO as CH_4 upon heating in H_2 above 350°C (item A) could be taken as indicating that much or all of adsorbed CO was adsorbed dissociatively. However, the CO might be *CO at 25°C and *C + *O might be formed on heating. Further, it has been proposed that the carbon in dissociatively adsorbed CO occupies an immediately subsurface position (*29*). Thus at saturation, CO/Mo_s might be unity even though the adsorption was dissociative.

The near identity in the amount of adsorbed CO on oxycarbide and on the Mo(0)/DA derived from it (item B) and the complete desorption of CO as such from the oxycarbide (item C) could be taken as indicating that CO adsorbed on Mo(0) was molecular. Ko and Madix have noted that *C and *O on Mo(100) inhibit the dissociative adsorption of CO (*30*).

It has also been reported that adsorbed CO at low temperature is molecular on Mo(110) (*31*) and W(110) (*32*), that at high coverages dissociation of *CO is inhibited by adjacent *CO, and that dissociation can require preceding desorption of molecular CO. Thus, the conditions of adsorption in the present work might give CO/Mo_s near unity.

The infrared data establish that a substantial amount of adsorbed CO is *CO (item D). The frequency of the adsorption band is the same as that reported by Peri (*10*) for CO on metallic Mo(0) and it establishes that the *CO visible in the IR is linear rather than bridged.

Percentage Exposed from CO Chemisorption

Since the question of the number of sites occupied by one molecule of CO is not entirely clear, we shall assume that each CO occupies 1.5 Mo_s. If CO/Mo_s is in fact unity, our values of percentage exposed should be multiplied by 1.33. However, the values should be relatively correct. The value for the 7.4% accords with the TEM results, but these experiments were aimed at the question of metallic state and gave only rough values of particle size. Taking CO/Mo_s as 1.5, the percentage exposed is 58% for the 0.89% catalyst, 37% for the 4.8% catalyst, 25% for the 7.4% catalyst, and 31% for catalyst C2.

Adsorption of CO at −78 and 25°C on MoO_3/HA;H_2,650° is reminiscent of that on Cr_2O_3 (*33*).

Adsorption of Hydrogen

The chemisorption of hydrogen on $Mo(0)/Al_2O_3$ is complicated (Table 4). There is weak chemisorption of H_2 at −196°C and an adsorbed state into which chemisorption is rather fast at −78°C and from which desorption occurs at a significant rate at 25°C. This chemisorbed state is unlikely to contribute much to the adsorption measured at 150°C. Hydrogen adsorbed below 150°C is essentially completely desorbed by 500°C, but at $T_{ads} \geq$

250°C, substantial desorption occurs above 500°C.

Except at 25°C, at which temperature irreversible adsorption of H_2 on alumina is negligible, and perhaps at 150°C, the exact interpretation of the data on chemisorption of H_2 on $Mo(0)/Al_2O_3$ is open to question and it may not be easy to decide in some cases just where H_2 is adsorbed by adsorption data alone. It is conceivable that some of the high temperature desorption involves the reverse of reaction (1) from σ-OH put on the surface during H_2,950° and not removed by condensation.

H_2 adsorbed at 78 K on Mo(100) is released by TPD to give three higher temperature peaks at 285 to ~430 K (*34, 35*). H_2 adsorbed and evacuated at 25°C would give $H/Mo_s = 1.0$ to 1.5, probably closer to 1.0. H_2 adsorbs on Mo(110) much more strongly and gives two peaks at 510 and 620 K and $H/Mo_s = 1.0$ (*36*). Although these results suggest that $H/Mo_s = 1$ is plausible for $T_{ads} = 25°C$ on a 3-nm molybdenum particle, one cannot securely extrapolate from single crystal surfaces to 3-nm particles. Considering the long time of flushing in the experiments with the supported catalysts vs rapid temperature ramps in TPD, the slow liberation of H_2 by the supported catalyst at 25°C is probably reasonable. Unfortunately, the surface chemical physics experiments involved only $T_{ads} = 78$ K. It would be interesting to know whether the higher temperature activated adsorptions observed on Mo/Al_2O_3 would occur on single crystal faces of Mo.

With 0.9% $Mo(CO)_6$/DA;He,400°,1;H_2,950°,1;He,650°,1 (catalyst C2) and $T_{des} = 500°C$, H/Mo was 0.111 for $T_{ads} = 25°C$ and 0.240 for $T_{ads} = 250°C$. These values accord reasonably well with Table 4. $Mo(CO)_6$/DA;He,400° adsorbed no detectable H_2 at 25°C.

Since $Mo(CO)_6$/DA;He,300–500° in which C/Mo is ~0.3 is an active hydrogenation catalyst even at −43°C, presumably H_2 does adsorb at Mo, but chemisorption of H_2 in a form reversible at lower temperatures would not be detected by our techniques. Mo_2C is reported not to adsorb hydrogen, but to adsorb CO (*37*). In contrast to the other measurements in this paper, the data for the adsorption of H_2 on catalysts derived from $Mo(CO)_6$/DA did not reproduce our earlier ones. Previously (*5*), the reported adsorption of H_2 on $Mo(CO)_6$/DA;He,300°1;H_2,650°,1 was much larger than found in the present work and substantial adsorption of H_2 was reported for $Mo(CO)_6$/DA;He,500°. We believe that some experimental artifact led to the previous results which were only a few in number.

Three different forms of activated adsorption of H_2 were found on MoO_3/HA; H_2,650°;Ar,650°, at ~25, ~250, and ~450°C. There is also a weak chemisorption of hydrogen at −196°C which might be molecular (*38*). This situation is reminiscent of the adsorption of hydrogen on amorphous Cr_2O_3 activated at about 400°C *in vacuo* (*33*).

Constitution of MoO_3/Al_2O_3;H_2,950°

MoO_3/Al_2O_3;H_2,950° and $Mo(CO)_6$/DA;He,300–500°;H_2,650–950° are essentially equivalent in so far as O.N., adsorption of CO, and adsorption of H_2 are concerned. There appears to be some differences in the surfaces of the alumina in the two materials.

We believe that MoO_3/Al_2O_3;H_2,950° is $Mo(0)/Al_2O_3$ rather than a supported molybdenum carbide on alumina formed from adventitious impurities.

(i) Mo_2C would consume 4 atoms of oxygen per Mo during oxidation at 500°C rather than the measured 3 ± 0.2. We conclude that no more than 25% of the Mo could be present as Mo_2C.

(ii) The substantial degree of adsorption of hydrogen indicates that the material is not a carbide (*37*).

(iii) It appears that H_2,950°,1 would remove all or almost all of the carbon from a molybdenum carbide (*37*). This matter is discussed further in the following paper. Thus, any formation of carbide would have to follow the H_2,950° step. The likelihood of this seems small.

(iv) Most of the experiments with the 7.4% Mo catalyst employed about 50 μmol of Mo_s and gas flows of about 0.05 mol h^{-1} or 50,000 μmol h^{-1}. Thus, formation of a monolayer of Mo_2C in 1 h would require the presence in the H_2 or He of 25 parts of carbon in 50,000 or 0.05 mol%. Such a concentration seems unlikely.

Previous examination of $Mo(0)/Al_2O_3$ by dark field electron microscopy by M. J. Yacamàn had indicated that the Mo was present as bcc metallic Mo (*39*). The present paper reports that examination by a different electron microscopic procedure detected the presence of some particles of bcc metallic Mo. Considering that the catalyst had to be exposed to the air for 15 min during which time it should have acquired an average value of O/Mo of 0.7, the observation of particles of bcc Mo is indicative that all or most of the particles were originally bcc metal.

EXAFS analysis in an apparatus based on a rotating anode X-ray tube indicated the presence of a material in which the nearest-neighbor distance was the same as that of metallic Mo (*39, 40*). In the work by S. Sunshine, J. Watson, and D. Willcox, supervised by Dr. P. Georgopoulus, on a 2.2 wt% Mo catalyst prepared by impregnation with heptamolybdate and pretreated H_2,950°, the observed Mo–Mo distance was 2.74 ± 0.03 Å vs the bulk value of 2.726 Å.

A number of intermetallic compounds of Mo and Al are known, Mo_3Al_8, $MoAl_4$, $MoAl_5$, $MoAl_6$, and $MoAl_{12}$ (*41*). One could imagine the reaction

$$Mo + xAl_2O_3 + 3xH_2 \rightarrow MoAl_{2x} + 3xH_2O \quad (3)$$

to lead to the formation of particles of such alloys. However, the oxygen titration data of Table 2 exclude formation of bulk $MoAl_{2x}$ or of a monolayer of "aluminide," since this would lead to an apparent oxidation number of Mo of much greater than +6. However decoration of the Mo particles by small amounts of Al(0) or of some suboxide of Al cannot be excluded although the apparent regeneration by H_2,950° of the original surface of a catalyst after chemisorption of CO or of some continued catalytic reactions argues against this. One might expect further decoration to occur during H_2,950°.

CONCLUSIONS

Reduction by H_2 at 950°C of MoO_3 on high purity γ-alumina generates a material which consists primarily of small (3–5 nm) particles of metallic molybdenum supported on alumina. The catalyst is very refractory and can withstand repeated exposure to H_2,950° and He,950°.

H_2,950° changes the support to a mixture of γ- and δ-Al_2O_3. The alumina becomes slightly reduced, by about 0.0012 e^- per Al and acquires a gray color. O_2,550° oxidizes the Mo(0) particles to MoO_3 but leaves the alumina gray. Reoxidation of the aluminas requires $T > 800$°C.

Under adequately aseptic conditions, the product of MoO_3/HA;H_2,950° is devoid of carbide. Its chemisorptive behavior for CO and for H_2 at lower temperatures resembles bulk Mo, but some small degree of decoration of the surface by Al_xMo alloys cannot be excluded.

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