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The Reaction between Hydrogen and Carbon Monoxide on Catalysts Derived from $Mo(CO)_6/Al_2O_3$

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If $Mo(CO)_6$/(dehydroxylated alumina, γ- + δ-Al_2O_3) is activated in helium to 500°C, clusters of Mo about 4 nm in diameter are formed. They are contaminated with some retained carbon which is essentially completely removed as methane by hydrogen at 650°C. The average oxidation number of the molybdenum is about +0.3 and it is suggested that the clusters consist of Mo^{2+} plus Mo(0) in which the charge is delocalized and balanced by $Al\text{–}O^-$ groups at the surface. The clusters are not identical with metallic molybdenum since they do not chemisorb nitrogen. Materials so prepared exhibit a turnover frequency for formation of methane at 300°C of about 0.04 sec^{-1} per surface atom of molybdenum in flowing hydrogen plus carbon monoxide (mole ratio = 5). Smaller amounts of ethane and propane are also formed. Activation at 300–500°C in helium or hydrogen leads to similar turnover frequencies and selectivities.

Activation of $Mo(CO)_6$/(alumina dehydroxylated at 475°C) at 300°C in hydrogen or helium results in a material in which Mo is ionic and highly dispersed. Turnover frequencies for formation of methane at 300°C are about 0.001 sec^{-1} per atom of molybdenum and selectivities are about the same as for the catalyst on dehydroxylated alumina. Activation in hydrogen results in formation of about 1.4 molecules of methane per molecule of $Mo(CO)_6$ and the resulting water, in essence, further oxidizes the molybdenum beyond the Mo^{2+} formed initially by reaction of Mo(0) with surface hydroxyl groups, $Mo + 2Al\text{–}OH_8 \rightarrow Mo^{2+} + H_2 + 2Al\text{–}O_8{}^-$.

INTRODUCTION

The material made by activating molybdenum hexacarbonyl deposited on alumina can be considered to be the earliest example of the class of catalysts consisting of organometallic compounds deposited on such supports as alumina and silica. It was first reported by Banks and Bailey (*1*) as a catalyst for the metathesis of olefins. It was later investigated at Edinburgh (*2*). A subsequent examination of the chemistry of the process of activation in flowing helium disclosed that results depended upon the degree of dehydroxylation of the alumina (*3*, *4*). When the alumina had been partially dehydroxylated, loss of carbon monoxide at 100°C slowed with time and essentially stopped at $Mo(CO)_3$ads. Further heating to 300°C led to the loss of most of the residual carbonyl and the liberation of about one molecule of hydrogen per atom of molybdenum. The overall reaction can be represented,

$$2\sigma\text{-OH} + Mo(CO)_3\text{ads} \rightarrow 2\sigma\text{-O}^-Mo^{2+} + 3CO + H_2. \quad (1)$$

The number of elementary processes involved in this reaction is unknown. Heating in helium to 450–500°C led to further oxidation of the molybdenum. If molybdenum hexacarbonyl was deposited upon alumina which had been pretreated at 950°C so as largely to dehydroxylate it, reaction (1) was suppressed and the adsorbed molybdenum carbonyl decomposed mainly to yield Mo(0).

Materials on both types of alumina were found to be catalysts for the hydrogenation of propylene (*5*). In subsequent work (*6*), we have investigated the activation of $Mo(CO)_6/Al_2O_3$ in hydrogen and we have found that materials so activated as well as those activated in helium were active catalysts for the hydrogenolysis of propane and cyclopropane and that optimally activated catalysts were more active for the hydroge-

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nation of propylene at low temperatures than were supported platinum catalysts. Further, these materials catalyze isotopic exchange between deuterium and cyclopentane at room temperatures (*7*).

It had been noted previously that small amounts of methane were liberated when molybdenum hexacarbonyl on partially dehydroxylated alumina was heated in helium to 500°C (*3*). Upon heating in hydrogen to above 150°C, it was found that large amounts of methane were formed (*6*). Accordingly, we investigated the reaction between carbon monoxide and hydrogen on these materials. This paper reports the results of that investigation, some studies of adsorption on activated catalysts, and related studies of the chemistry of the activation process.

Formation of methane during the activation of carbonyl complexes of other elements in an inert atmosphere has been reported (*8, 9*).

EXPERIMENTAL METHODS

Materials

The γ-alumina used as the support was AERO 1000 extrudate of the American Cyanamid Company, lot 1951, reported to be about 99.99% pure. It was manually crushed and sieved to 120–140 mesh. The specific surface area was 160 $m^2\ g^{-1}$ as measured by adsorption of nitrogen. To remove fines and possibly contaminant ions, the alumina was washed successively several times with doubly distilled water, 0.1 *M* nitric acid, and water. It was heated in tank air (Matheson) and then in hydrogen at 600°C. It was then rehydroxylated as previously described (*3*).

Molybdenum hexacarbonyl was twice sublimed *in vacuo*. Pentane was twice distilled in a nitrogen atmosphere from liquid sodium–potassium alloy and stored under nitrogen. Helium was purified by permeation through fused silica (Electron Technology, Inc.); hydrogen, by passage through a Deoxo purifier, and carbon monoxide, by passage through a trap of MnO reported to remove oxygen to 1 part in 10^9 (*10*). All three gases were further passed through a trap of MnO just preceding the activated $Mo(CO)_6/Al_2O_3$.

Techniques

In each experiment, 0.25 g of alumina was placed in the reactor and heated in helium flowing at 30 $cm^3\ min^{-1}$ to 450°C (or 500°C if the material was subsequently to be heated to 500°C) to give partially dehydroxylated alumina (PDA) and to 950°C for dehydroxylated alumina (DA). As determined in a vacuum microbalance by heating in flowing helium, the alumina was 74% dehydroxylated after 1.25 hr at 470°C. If a monolayer of OH^- on γ-Al_2O_3 amounts to 15 $OH^-\ nm^{-2}$, the OH^- content of PDA was about 4 $OH^-\ nm^{-2}$. With PDA, the alumina was supported on a fritted disk in a Pyrex tube; with DA, on silica wool in a tube of fused silica. A degassed solution of molybdenum hexacarbonyl in pentane was added to the alumina at 0°C and the slurry was fluidized by passage of helium or hydrogen at 30 $cm^3\ min^{-1}$. Passage of the carrier gas was continued to evaporate the pentane which was collected downstream in a trap at −196°C together with any volatilized molybdenum hexacarbonyl. Evolved gases were trapped in a following trap of Davison Grade 62 silica gel at −196°C. Hydrogen, when present in helium carrier, passed this trap and was collected in a trap of 5A molecular sieve at −196°C. Pulses of the gases were released by warming the traps and analyzed by gas chromatographic techniques (*3*). The amount of volatilized molybdenum hexacarbonyl (~10%) was determined and subtracted from the amount added (*3*).

Catalytic activities were determined by either pulse or continuous-flow techniques. Pulses of 0.99 cm^3 of carbon monoxide were injected into hydrogen flowing over the catalyst at 30 $cm^3\ min^{-1}$. Reaction products were trapped in silica gel at −196°C and subsequently released for gas chromatographic analysis. In the continuous-flow techniques, mixtures of carbon monoxide and hydrogen were passed over the catalyst at 30–45 cm^3 min^{-1} and samples of effluent were periodically analyzed by gas chromatography.

The oxidation number of the molybdenum on various catalysts was assayed by oxygen titration. The catalyst was flushed with helium at 300°C, pulses of oxygen ($\leq$0.3 O/Mo) were injected into the helium, and consumption of oxygen was calculated from the amount which passed the catalyst. The catalyst was then heated to 500°C (no oxygen was released) and further pulses of oxygen were passed. Small additional consumption of oxygen was usually noted. The original oxidation number (O.N.) of the molybdenum could then be calculated from the total amount of oxygen consumed assuming that Mo(VI) is the final product. Residual carbon monoxide on molybdenum was displaced as carbon monoxide, not as carbon dioxide, during these treatments.

Amounts of adsorption of various gases were determined either by measuring the loss from several pulses (~0.3 gas/Mo) passed over the catalyst or by passage of a continuous flow of gas over the catalyst followed by flushing with helium. The catalyst was then heated in flowing helium, the evolved gas was trapped in silica gel at −196°C, and later released for measurement by catharometry.

Loadings in the adsorption experiments were 2–3 mg Mo/0.25 g of alumina or about 100 μmol/g. In catalytic experiments, loadings were 1–3 mg Mo/0.25 g of alumina.

EXPERIMENTAL RESULTS

A summary of the experimental results for the more carefully investigated catalysts is given in Table 1.

Heating $Mo(CO)_6/PDA$ and $Mo(CO)_6/DA$ in Hydrogen and in Helium

Heating in hydrogen or helium liberates the cumulative amounts of carbon monoxide, methane, and hydrogen shown in Table

TABLE 1

Characteristics of Some Activated $Mo(CO)_6/Al_2O_3$ Catalysts

	PDA,He,300°C	PDA,H_2,300°	DA,He,300°;H_2,650°	DA,He,500°
Composition[a]	Mo(II) + 0.3C	Mo(IV)	Mo(0) + Mo(II)	Mo(0) + Mo(II) + 0.3C
Color	sandy brown	brown	black	black
		Adsorption irreversible at listed temperature		
CO/Mo	0.66, −78°C	0.42, −78°C	0.17, 0°C	0.17, 0°C
H/Mo	0.03, −78°C	—	1.8, 25°C	1.1, 25°C
O/Mo	0.8, 25°C	—	0.5, 25°C	—
		Approx turnover frequencies per Mo (sec^{-1})		
CO + H_2,300°[b]	0.001	0.001	0.01	0.01
Propene + H_2,−46°C, flow[c]	0.09	0.24	1.9[f]	0.8
D_2 + C_5H_{10},19°, flow[d]	0.08	0.03	—	1.5
Propene, 60°, metathesis[e]	0.15	0.01	—	0.02

[a] Possible composition, see text.

[b] For formation of hydrocarbon in flow experiments, see text.

[c] Initial turnover frequency for hydrogenation, propylene/H_2 = 0.21. The steady state N_t values were $\frac{2}{3}$ to $\frac{1}{2}$ of listed values (*6*).

[d] Isotopic exchange between D_2 and cyclopentane (*7*).

[e] Pulse technique, propylene in helium, R. G. Bowman, unpublished.

[f] On DA,He,300°;H_2,500°.

TABLE 2

Chemical Results of Activating $Mo(CO)_6/Al_2O_3$

Alumina T_{act}	PDA 300°C	PDA 500°C	DA 300°C	DA 500°C
Activation in helium				
CO/Mo[a]	5.57 ± 0.09	5.80 ± 0.13	5.60 ± 0.17	5.78 ± 0.15
CH_4/Mo[a]	0.09 ± 0.02	0.17 ± 0.02	0.01 ± 0.01	0.02 ± 0.01
H/Mo[a]	2.0 ± 0.1	4.3 ± 0.2	0.4[d]	0.32 ± 0.2
C/Mo[b]	5.66 ± 0.09	5.94 ± 0.08	5.63 ± 0.15	5.81 ± 0.11
O.N.[c]	1.9 ± 0.1	5.7[d]	—	0.36 ± 0.06
Activation in hydrogen				
CO/Mo[a]	4.43 ± 0.08	4.45 ± 0.09	4.4 ± 0.2	4.4 ± 0.2
CH_4/Mo[a]	1.44 ± 0.07	1.58 ± 0.08	1.4 ± 0.2	1.6 ± 0.2
C/Mo[b]	5.85 ± 0.08	5.99 ± 0.08	5.77 ± 0.15	5.98 ± 0.09
O.N.[c]	3.1–3.8	3.0[d]	1.0 ± 0.5	—

[a] The cumulative yields per MO of CO, CH_4, and H (i.e., twice H_2/Mo) upon activating to the listed temperature.

[b] The cumulative total loss of carbon upon activating to the listed temperature.

[c] The apparent oxidation number as determined by oxygen titration.

[d] Single experiment.

2. The table also shows the total liberation of carbon. These data with a few indicated exceptions result from a number of experiments for each entry. The estimated errors come from errors in the loading of Mo and the cumulative errors of measuring the evolved gases. Heating $Mo(CO)_6$/PDA in hydrogen to 100–150°C gave $Mo(CO)_3$ads as was previously found for heating in helium; see Fig. 1.

Treatment of $Mo(CO)_6$/PDA, He,300°,1 (where the code indicates that the carrier gas was helium and that activation was at 300°C for 1 hr) and $Mo(CO)_6$/DA,He,300°,1 with hydrogen at 300°C liberated much of the residual carbonyl as methane. Liberation of carbon dioxide was detected only in $Mo(CO)_6$/PDA,He,500°,1 where it amounted to 0.02 CO_2/Mo.

In agreement with previous work, $Mo(CO)_6$/DA,He,100° did not lead to a reaction which stopped at $Mo(CO)_3$ads. The range of evolution of carbon monoxide was 3.4–3.8 CO/Mo. Similar results were obtained with hydrogen except that traces of methane, 0.02 CH_4/Mo, also appeared.

$Mo(CO)_6$/PDA,H_2 or He,100° was golden yellow, but $Mo(CO)_6$/DA,He,100° and $Mo(CO)_6$/DA,H_2,100° were dark golden brown. $Mo(CO)_6$/PDA,He was sandy brown at 300°C and gray at 500°C, whereas $Mo(CO)_6$/PDA,H_2,300–500°C was brown. All examples on DA activated at 300–500°C in either hydrogen or helium were black.

In general, all samples on PDA turned white upon exposure to air at 25°C. The maximum time required was about 1 hr. On the contrary, the black samples on DA were unchanged in appearance for 3 days and then gradually became dark gray. The white samples prepared by oxidizing black samples on DA at 300°C in oxygen became brown on heating in hydrogen at 500°C [Mo(VI) → Mo(IV)] and these turned white upon exposure to air at 25°C.

Samples of $Mo(CO)_6$/DA,He,300°,1; H_2,675°,1 were examined by X-ray diffraction in air as rapidly as possible after exposure to air. No diffraction peaks not present in DA itself could be detected. However, DA is a mixture of γ- and δ-Al_2O_3, it has a very large number of diffraction lines, and there are interferences with all of the stronger lines of molybdenum metal.

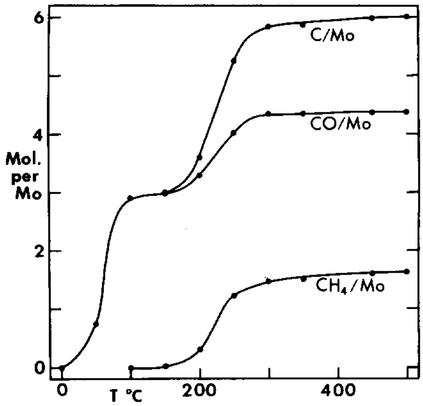

FIG. 1. The activation of $Mo(CO)_6$/PDA in hydrogen. After heating at a given temperature, the temperature of the catalyst was increased to a higher temperature at the rate of 5–10°C min^{-1} and held at the new temperature for 1 hr. The amounts of carbon monoxide and methane collected were measured while the catalyst was heated to the next higher temperature. The graph shows the cumulative amounts of carbon monoxide expressed as molecules per atom of molybdenum, the cumulative amounts of methane, and the sum of the two.

Adsorption on Activated $Mo(CO)_6/PDA$

Water. Water vapor reacted at 225°C with the Mo(II) sites on $Mo(CO)_6$/PDA,He,300°,1. About 1 H/Mo was liberated when such samples were exposed to a stream of helium containing 25 Torr of water vapor at a flow rate of 30 cm^3 min^{-1}. This would correspond to formation of Mo(III), but oxygen titration gave O.N. = +4. The origin of the discrepancy is not known, but this reaction was investigated only briefly. Elevation of the temperature to 300°C led to further evolution of a small amount of hydrogen, but raising the temperature to 500°C resulted in a cumulative liberation of 2.5 H and O.N. = 5.4–5.5 by oxygen titration.

Oxygen. In previous work (*3*), it had been found that $Mo(CO)_6$/PDA,He,300°,1 adsorbed about 0.6–0.8 O/Mo at 25°C. In the present work, catalysts on PDA were found to absorb 0.8–1.0 O/Mo after activation to 300°C in either hydrogen or helium. This exposure to oxygen at 25°C or exposure to oxygen at 300°C led to the liberation of much of the residual carbonyl as carbon monoxide.

Carbon monoxide. Carbon monoxide was passed over catalysts at 25°C and then at −78°C for 10 min each. The catalysts were then flushed with either hydrogen or helium for 3.5 hr at −78°C and warmed to various temperatures which never exceeded 10° below the temperature of activation. Evolved carbon monoxide was trapped and measured as previously described. The measured amount was corrected for the amount of carbon monoxide adsorbed on the alumina (PDA) base, 13.2 μmol g^{-1}. All of this was released by 0°C.

$Mo(CO)_6$/PDA,He,300°,1 adsorbed 0.66 CO/Mo as judged by the amount released by 290°C. Roughly 50% of this amount was released by 25°C and 80% by 100°C. Release of carbon monoxide by the starting material at 290°C was negligible. $Mo(CO)_6$/PDA,He,400°,1 released 0.33 CO/Mo by 390°C. Exposure to oxygen at 25°C expelled adsorbed carbon monoxide as such from the materials of both pretreatments.

$Mo(CO)_6$/PDA,H_2,300°,1, cooled in hydrogen, adsorbed 0.42 CO/Mo as judged by release of carbon monoxide between −78 and 290°C. Similar experiments but with H_2,475°,1 led to the release of 1.17 CO/Mo by 390°C.

Hydrogen. Only 0.034 H/Mo was irreversibly adsorbed on $Mo(CO)_6$/PDA,He, 300°,1 at −78°C as judged by the following experiment. The catalyst was exposed to hydrogen at 25°C, cooled to and maintained at −78°C for 1 hr, flushed with helium at −78°C for 15 hr, and heated to 290°C in helium.

Adsorption on Activated $Mo(CO)_6/DA$

Hydrogen. $Mo(CO)_6$/DA,He,500°,1 exposed to hydrogen at 25°C liberated 1.0–1.2 H/Mo upon heating to 500°C in flowing helium. A sample, $Mo(CO)_6$/DA,He, 300°,1;H_2,650°,1 (where the semicolon separates successive treatments), was cooled in hydrogen to 0°C, flushed with helium for 16 hr at 0°C, and heated to 500°C in helium. The liberation of hydrogen was 1.8 H/Mo. Blank adsorptions of hydrogen on DA alone were negligible.

Carbon monoxide. Pulses of carbon monoxide (0.067 cm^3) were passed over activated samples at 0°C and loss of carbon monoxide was measured. The samples were then heated to high temperatures in hydrogen and the amounts of evolved carbon monoxide and methane were measured. Results are corrected for the blank on DA, 2.0 μmol CO g^{-1}.

Adsorption was 0.17 CO/Mo on what should be our cleanest sample, $Mo(CO)_6$/DA,He,500°,1;H_2,650°,17;He,500°,2, cooled in helium and exposed to pulses of carbon monoxide in flowing helium at 0°C. Heating in hydrogen to 650°C led to essentially complete recovery of adsorbed carbon monoxide, 60% as methane. Almost the same results were obtained when the last treatment in helium was omitted, the material was cooled in hydrogen, and pulses of carbon monoxide were injected into the flowing hydrogen. Subsequent heating from 650 to 950°C in hydrogen led to liberation of methane plus carbon monoxide, C/Mo equal about 0.005, and the adsorption of carbon monoxide after this treatment was normal. Almost the same adsorption of carbon monoxide was observed when the treatment with hydrogen at 650°C was only 1 rather than 17 hr. Further, adsorption was nearly the same on $Mo(CO)_6$/DA,He,300°,1;H_2,650°,1 cooled in hydrogen.

$Mo(CO)_6$/DA,He,500°,1, cooled in helium and with carbon monoxide injected into flowing helium, also gave adsorptions of about 0.17 CO/Mo and very nearly this amount of carbon monoxide was liberated during heating to 500°C in helium. However, upon subsequent heating in hydrogen at 500°C, a further evolution of 0.04 CO/Mo and 0.29 CH_4/Mo was observed. $Mo(CO)_6$/DA,H_2,500°,1, cooled in hydrogen, gave adsorptions of only about one-half of those described above. Heating in hydrogen to 515°C liberated amounts of carbon monoxide plus methane slightly in excess of the amounts of carbon monoxide adsorbed and subsequent heating to 650°C liberated about 0.1 CH_4/Mo. Thus, after He,500°,1, the sample appears to contain some form of carbon to an amount 0.3 C/Mo and after H_2,500°,1, 0.1 C/Mo. These numbers should be more accurate than those of Table 1.

Oxygen. The adsorption of oxygen was measured on two catalysts. First, 0.14 CO/Mo was adsorbed on $Mo(CO)_6$/DA, He,500°,1;H_2,650°,1 and then 0.067-cm^3 pulses of oxygen were injected into the flowing hydrogen. A total of 0.52 O/Mo was adsorbed and 0.13 CO/Mo was liberated. The catalyst was then treated H_2,650°,1 and oxygen adsorption remeasured, 0.51 O/Mo. Repetition gave 0.55 O/Mo. On another sample, $Mo(CO)_6$/DA,H_2,650°,1, 0.13 CO/Mo was adsorbed and pulses of oxygen were passed. Oxygen was adsorbed, 0.52 O/Mo, and carbon monoxide was liberated, 0.12 CO/Mo.

Nitrogen. Exposure of $Mo(CO)_6$/DA, He,500°,1;H_2,650°,1 to pulses of nitrogen at 25°C led to only trace adsorption as judged by release of nitrogen on subsequent heating to 1000°C in flowing helium. In addition no loss of nitrogen from the pulses could be detected. A pulse of nitrogen was trapped on the catalyst at −196°C, the catalyst was warmed to 100°C for 10 min, the temperature was lowered to 25°C, and after 1 hr the flow of helium through the catalyst was reestablished. On heating to 1000°C, 0.002 N/Mo was released. The catalyst was cooled to 25°C, exposed to nitrogen, flushed with helium, and the adsorption of carbon monoxide measured by loss of carbon monoxide from pulses injected ahead of the catalyst. The adsorption was normal.

Reaction of Carbon Monoxide and Hydrogen on Mo(CO)$_6$/PDA

Pulses of carbon monoxide (0.99 cm^3 STP min^{-1}) were injected into hydrogen flowing at 30 cm^3 min^{-1} over $Mo(CO)_6$/PDA which had been subjected to various activations. Results are shown in Fig. 2. When $Mo(CO)_6$/PDA,He,300°,1 was first exposed to hydrogen, most of the residual carbonyl was converted to methane as shown by the point at pulse 0 of curve I. The point at pulse 0 for curve II represents the amount of methane which had been liberated during the activation H_2,300°,1. Total methane for curve III is taken as zero at pulse 0. In addition to methane, ethane was formed, ~0.005 C_2H_6/Mo per pulse. The conversion per pulse for all three catalysts became nearly the same after pulse 3 as shown by curve IV. This conversion combined with the estimated width of the pulse at the catalyst, 15 sec, gives a crude turnover frequency, N_t, of 0.008 CH_4/Mo per sec. The relative conversions at 300, 400, and 500°C were 1.0 : 2.0 : 2.3.

Pulses of oxygen (0.13 cm^3 STP) were injected into hydrogen passing over fresh

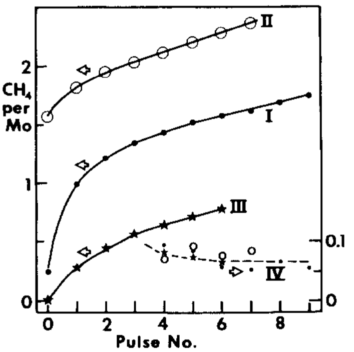

FIG. 2. Amounts of methane formed from injection of pulses of carbon monoxide into hydrogen flowing over activated $Mo(CO)_6/PDA$ at 300°C expressed as molecules of methane formed per atom of molybdenum. The amounts of molybdenum and the conditions of activation were: curve I, 0.00256 g, He,300°,1 and curve II, 0.00148, H_2,300°,1. Curve III represents an experiment after reactivating the catalyst of curve II by H_2,500°,1. Amounts of methane formed are cumulative in these curves. In curve I, CH_4/Mo at pulse 0 is the amount of methane formed upon replacing the flow of helium by one of hydrogen at 300°C. In curve II, CH_4/Mo at pulse 0 is CH_4/Mo formed during activation. CH_4/Mo for curve III is set equal to zero. Curve IV represents the incremental CH_4/Mo for pulses 4–9 in curves I, II, and III shown by smaller version of the symbols for I, II, and III.

$Mo(CO)_6/PDA,H_2$,300°,1 at 300°C. The loss of oxygen was 92% per pulse, presumably to form water, and this conversion persisted beyond amounts of oxygen more than sufficient to convert all molybdenum to Mo(VI).

A continuous flow of carbon monoxide and hydrogen, mole ratio 0.2, was passed over the catalysts at 300°C at flow rates of 30–45 $cm^3\ min^{-1}$. For $Mo(CO)_6/PDA,H_2$, 300°,1, turnover frequencies were 0.0013 sec^{-1} at 5 min, 0.0011 sec^{-1} at 60 min, and 0.0010 sec^{-1} at 1020 min. After 300 min on stream, hydrogen was passed over the catalyst for 1 hr. Pulses of carbon monoxide injected into the hydrogen gave conversions of 0.05 CH_4/Mo.

Reaction of Carbon Monoxide and Hydrogen on $Mo(CO)_6/DA$

As shown in Fig. 3, conversions of pulses on $Mo(CO)_6/DA$ of several different activations were about 10 times greater than those on activated $Mo(CO)_6/PDA$, 0.6 vs 0.06 CH_4/Mo. A catalyst containing 1.67 mg of molybdenum and pretreated H_2,500°,1 and one containing 1.53 mg of molybdenum and pretreated H_2,300°,1 gave results close to those of curve B (H_2,525°,1). After the run with the H_2,300° catalyst, it was treated H_2,500°,1 and exposed to pulses of carbon monoxide. It gave results indistinguishable from those of curve D.

Curve E in Fig. 3 shows that catalysts on DA of all pretreatments level out to nearly the same conversion, 0.5 CH_4/Mo per pulse. Further, a catalyst containing 2.7 mg Mo, treated H_2,650°,1 and exposed at 25°C

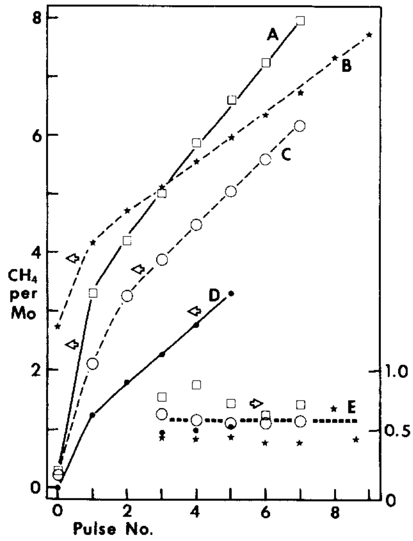

FIG. 3. Amounts of methane formed from injection of pulses of carbon monoxide into hydrogen flowing over activated $Mo(CO)_6/DA$ at 300°C expressed as molecules of methane formed per atom of molybdenum. The amounts of molybdenum and the conditions of activation were: curve A, 0.00125 g, He,300°,1; curve B, 0.00121 g, H_2,525°,1; curve C, 0.00198 g, He,500°,1. Curve D represents an experiment after reactivating the catalyst of curve C by H_2,500°,1. Amounts of methane formed are cumulative in these curves. In curves A and C, CH_4/Mo at pulse 0 is methane formed upon replacing the flow of helium by one of hydrogen at 300°C. In curve B, CH_4/Mo at pulse 0 is CH_4/Mo during activation. CH_4/Mo for curve D is set equal to zero. Curve E represents the values of CH_4/Mo per pulse for these experiments.

to carbon monoxide and then oxygen (see section on the adsorption of oxygen) was heated to 650°C in hydrogen. A pulse sequence was then run at 300°C. In pulse 5, CH_4/Mo was 0.45. A catalyst, 2.3 mg Mo,He,300°,1;H_2,650°,1, gave CH_4/Mo = 0.49 in pulse 5. The catalyst-activated He,300°,1 (curve A) appears to have been somewhat more active than the other catalysts. Yields of methane, ethane, and propane obtained during this experiment are given in Fig. 4. At pulse 7, conversions per pulse were 0.7 CH_4/Mo, 0.06 C_2H_5/Mo, and 0.03 C_3H_8/Mo. In flow experiments, traces of propylene, butane, and carbon dioxide were also observed.

In pulse runs, relative conversions at 300, 400, and 500°C were 1.0:2.8:3.6. At 300°C, the average value of N_t at steady state was 0.08 CH_4/Mo sec^{-1}, i.e., CH_4/total Mo.

In several flow experiments at 300°C, N_t for formation of methane was 0.013–0.035 at 5 min, 0.009–0.011 at 60 min, and, in one experiment, 0.012 at 1200 min. In one run, after 300 min on stream, the catalyst was flushed with hydrogen and exposed to pulses of carbon monoxide. Conversions were 0.5 CH_4/Mo.

Activated $Mo(CO)_6$/PDA and $Mo(CO)_6$/DA were exposed to hydrogen sulfide. One pulse (0.99 cm^3 STP) was injected into the usual feed stream during a continuous-flow experiment. The activity for formation of methane for PDA dropped by a factor of 5 and that for DA, by a factor of 10. The catalysts were then treated with hydrogen at 650°C for 1 hr. The PDA catalyst regained 80% of its original activity; that on DA, 40%.

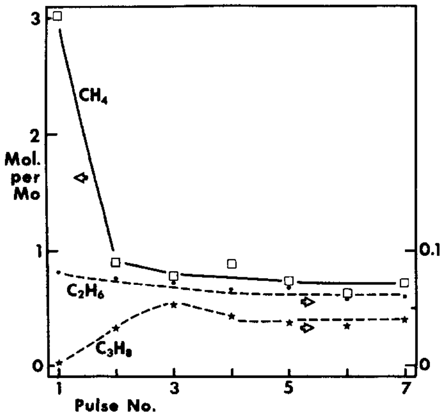

FIG. 4. Yields of methane, ethane, and propane per pulse in the experiment of curve A in Fig. 3 expressed as mole ratios to the molybdenum on the catalyst.

Nitrogen pulses were passed over a catalyst ($Mo(CO)_6$/DA,He,500°,1;H_2,650°,1) after six pulses of carbon monoxide had been injected. Conversions of carbon monoxide in pulses passed subsequently were unchanged.

Pulses of carbon dioxide were injected into hydrogen flowing over a catalyst of this pretreatment at 300°C. Yields of methane were about 0.5 those obtained with pulses of carbon monoxide. Subsequent pulses of carbon monoxide led to normal yields of methane.

The catalysts on DA remained black during all of the experiments described in this section.

DISCUSSION

The Nature of Activated $Mo(CO)_6/Al_2O_3$ Catalysts

The amounts of hydrogen and methane liberated during activation in helium at 500°C require that alumina partially dehydroxylated at 475°C (PDA) contain at least 2.8 surface hydroxyl groups/nm^2 and dehydroxylated alumina (DA), 0.14. As measured by weight loss, the hydroxyl content of PDA was about 4/nm^2. By X-ray diffraction, DA was a mixture of γ- and δ-Al_2O_3 with negligible α-Al_2O_3. The specific surface area of DA was only a little smaller than that of PDA.

In preparing activated $Mo(CO)_6/Al_2O_3$ catalysts, $Mo(CO)_6$ is first physisorbed onto the alumina. In this state, $Mo(CO)_6$ should be mobile on the surface of alumina in view of the substantial volatility of $Mo(CO)_6$. The volatilization of ~10% of the added $Mo(CO)_6$ during activation to 100°C indicates that the carbonyl is also mobile via desorption–readsorption. A similar situation occurs during reaction of $Ni(CO)_4$ with alumina (*11*). During heating to 100°C, molecules of $Mo(CO)_6$ react with the surface of alumina losing carbon monoxide and forming surface complexes which are immobile or of greatly reduced mobility.

According to the conditions, a number of different catalysts can be formed by activating $Mo(CO)_6/Al_2O_3$. The identity of the sweep gas (helium or hydrogen), the surface content in hydroxyl groups (PDA vs DA), and the temperature of activation all influence the identity of the activated material. The various chemical reactions which can occur during activation are given in a simplified and schematic form below.

(A) $Mo(CO)_6\text{ads} \rightarrow Mo(CO)_{6-x}\text{ads} + x\text{CO}$

(B) $Mo(CO)_y\text{ads} \rightarrow Mo(0) + y\text{CO}$

(C) $Mo(0)\text{ads} + 2HO\text{-}\sigma \rightarrow Mo(II)\text{ads} + H_2 + 2\sigma\text{-}O^-$

(D) $Mo(II)\text{ads} + n HO\text{-}\sigma \rightarrow Mo(II + n)\text{ads} + 0.5nH_2 + n\sigma\text{-}O^-$

(E) $Mo(CO)\text{ads} + 6HO\text{-}\sigma \rightarrow Mo(VI)\text{ads} + CH_4 + H_2O + 6\sigma\text{-}O^-$

(F) $Mo(CO)\text{ads} + 3H_2 \rightarrow Mo(0)\text{ads} + H_2O + CH_4 \rightarrow MoO + H_2 + CH_4$

(G) $Mo(II)\text{ads} + CO + 2H_2 \rightarrow Mo(IV)O + CH_4.$

Reaction during activation of $Mo(CO)_6/DA$. Heating $Mo(CO)_6/DA$ in either flowing hydrogen or flowing helium at 100°C gave losses of 3.4–3.8 CO/Mo in contrast to the behavior of $Mo(CO)_6/PDA$ where loss stops sharply at 3.00 Co/Mo. Traces of methane were also observed during heating in hydrogen.

Upon activating to 300°C, the divergence in behavior between $Mo(CO)_6/DA$ and $Mo(CO)_6/PDA$ becomes more extreme. The low surface concentration of σ-OH on DA does not permit reaction (C) to dominate as it does on PDA (*3*). Thus, the average oxidation number, O.N., is about +0.3 after activating $Mo(CO)_6/DA$ by He,300–500° as against +2 after activating $Mo(CO)_6/PDA$ by He,300° and nearly +6 after He,500°. One could consider the activated catalyst on DA to consist of 15% Mo(II) and 85% Mo(0). The catalyst still contains residual carbonyl which is essentially completely removed as methane by H_2,650°,1. Thus, treatment of $Mo(CO)_6/DA$ by He,500°,1;H_2,650°,1 leads to nearly clean product.

Although the catalyst just described may somewhat resemble a supported metal catalyst, it does not appear to consist of Mo^{2+} plus separate particles of metallic molybdenum. Clean metallic molybdenum rapidly and strongly chemisorbs nitrogen at 25°C (*12, 13*) whereas 25°C $Mo(CO)_6/DA$,He, 500°;H_2,650° does not adsorb nitrogen. We suggest that Mo^{2+} is first formed on the surface of the alumina by reaction of residual σ-OH,

$$Mo(0) + 2\sigma\text{-}OH \rightarrow Mo^{2+} + 2\sigma\text{-}O^- + H_2$$

and that Mo(0) collects on the top of the Mo^{2+} to form clusters of molybdenum in which the charge is delocalized throughout the clusters and is balanced by adjacent σ-O^- ions. Such clusters would constitute altered particles of metallic molybdenum with properties somewhat different from those of pure metallic molybdenum. In particular, the clusters do not adsorb nitrogen. All products of activating $Mo(CO)_6/DA$ at $T \geq 300$°C are black which we take to be characteristic of the rather highly dispersed particles of "metal-like" molybdenum.

Yermakov (*14*) has proposed that atoms of platinum form clusters around ions of Mo^{2+} on silica in the case of certain catalysts which he has prepared. Such clusters may have some resemblance to those on activated $Mo(CO)_6/DA$. Similar charged clusters are likely to result when carbonyls of other nonnoble metals are decomposed on silica or alumina; for example, $Co_2(CO)_8$ on alumina which is active as a Fischer–

Tropsch catalyst (*15*) and $Ni(CO)_4$ on alumina (*11*).

Measurement of amounts of chemisorption should provide some information as to the percentage exposed of the clusters on activated $Mo(CO)_6$/DA. At 25°C, adsorptions on "clean" molybdenum were 1.0–1.2 H/Mo, 0.5 O/Mo, and 0.17 CO/Mo. It appears likely that H/Mo_s (where Mo_s designates a surface atom) is greater than unity in our experiments. Further reaction with oxygen occurs slowly at room temperature. Retention of the black color of activated $Mo(CO)_6$/DA upon rather long exposure to oxygen could hardly be compatible with large percentages exposed. Probably more than a monolayer results from exposure of the catalyst to oxygen at 25°C but extensive oxidation requires days. Films of molybdenum metal of a percentage exposed of 12–14% saturate upon exposure to low pressures of oxygen at O/Mo = 1.27 (*16*) and on the (100) plane of molybdenum (*17*), at 1.5. However, an analogy between our clusters and metallic molybdenum may not be a good one. The data for adsorption of carbon monoxide probably provide the best information on percentage exposed. On metallic molybdenum, carbon monoxide is largely dissociated (*18*) and each molecule occupies two sites, but we do not know whether dissociation occurs at 25°C on the clusters on DA. Thus, the percentage exposed is probably between 0.17 and 0.34 and the particle size is probably somewhere near 4 nm (*19*).

Heating $Mo(CO)_6$/DA,He,300–500° in hydrogen to 300°C removes considerable carbon from the surface but heating to 650°C is needed to remove almost all. H_2, 650°,1 also removes (O)ads, since if oxygen is adsorbed to the level 0.5 O/Mo, H_2,650°,1 restores the original adsorptive capacity for oxygen. Adsorption of carbon monoxide is stronger than that of hydrogen since the extent of adsorption of carbon monoxide is the same on clean and on hydrogen-covered catalysts. Exposure to oxygen at 25°C displaces adsorbed carbon monoxide without formation of carbon dioxide. At 300°C, treatment with oxygen displaces a substantial amount of carbon monoxide from $Mo(CO)_6$/DA,He,300–500° and again without formation of carbon dioxide.

Activation of $Mo(CO)_6$/DA in hydrogen at 300–500°C led to the formation of substantial amounts of methane. The yield in methane, CH_4/Mo, was rather variable. It was 1.4 ± 0.2 for H_2,300°,1. Decarbonylation was more extensive for heating in hydrogen than for that in helium. Residual carbon, C/Mo, was 0.1 after H_2,500°,1 as judged by release of methane upon heating in hydrogen to 650°C. Despite the large formation of water which accompanies reaction (F), the degree of oxidation of Mo(0) was much smaller than expected from the second step of reaction (F). Agglomeration of Mo(0) appears to be generally fast on DA and the resulting metal-like particles are not readily oxidized by water. After H_2,300°,1, the samples appear to consist of clusters of Mo(0) containing a rather large proportion of more oxidized species than after He,300°,1. However, as the temperature of treatment in hydrogen is increased, these oxidized species should be reduced and after H_2,650° the catalysts should be nearly the same whether they had been activated in hydrogen directly or activated in hydrogen after He,300–500°.

Activation of $Mo(CO)_6$*/PDA in helium.* The data of Tables 1 and 2 indicate that preparation of PDA,He,300° leads primarily to the formation of $Mo^{2+} + 2\sigma\text{-}O^-$ via reactions (B) and (C) accompanied by small contributions from reaction (E) leading to methane. The product would appear to be nonuniform since 0.3 CO/Mo remains on the catalyst. Further activation in helium to 500°C results in reaction (D) and further (E) to eliminate most residual carbonyl and to produce a material which is largely Mo(VI)/Al_2O_3. After activation to 400°C, the average O.N. of Mo is near +4.

Activation of $Mo(CO)_6$*/PDA in hydrogen.* Above 150°C, activation in hydrogen produces materials different from those obtained by activation in helium. PDA,H_2,300° is more oxidized than PDA,He,300° and PDA,H_2,500° is less oxidized than PDA,He,500°. The higher level of oxidation of Mo in PDA,H_2,300° can be considered to result from reaction with water formed in reaction (F), but whether water is actually formed as a desorbed intermediate is unknown. However, water vapor oxidized Mo(II)/PDA at 225°C and substantial further oxidation occurred at 500°C.

The oxidation state of Mo in PDA,H_2,300° and PDA,H_2,500° is subject to some uncertainty since one cannot directly determine the extent of reaction (C). Further, oxygen titration cannot distinguish between Mo^{2+}ads and $MoH(OH)^{2+}$ads although O.N. = +2 for the first species and +4 for the second if O.N. for H is taken as −1 as is conventional. Additional problems would arise if species resulting from the heterolytic dissociative adsorption of hydrogen on O_s^{2-} and Mo^{n+} were present. Thus, oxygen titration of OH_s + Mo(III)H would consume 1.25 O_2/Mo and give an apparent O.N. = +1 for Mo. Probably, PDA,H_2,300° is best interpreted as mostly Mo(IV) plus some Mo(II) or Mo(IV)H(OH). The last species is analogous to some advanced by Hall and Lo Jacono (*20*) as resulting from reduction of MoO_3/PDA. Indeed, PDA,H_2,300° and PDA,H_2,500° may be rather similar to reduced MoO_3/Al_2O_3. The presence of Mo(III) cannot be excluded.

Chemisorption on catalysts on PDA. Exposure of $Mo(CO)_6$/PDA,He,300° to carbon monoxide at 25°C and then at −78°C resulted in CO/Mo = 0.66, irreversible at −78°C. This corresponds to adsorption of carbon monoxide on a large fraction of Mo which had lost all carbonyl (Table 1). The ratio CO/Mo was 0.42 for H_2,300°,1 and 1.17 for H_2,475°,1. Clearly a number of different surface species of Mo adsorb carbon monoxide. Further, the surface sites are nonuniform in the strength of binding of carbon monoxide; in particular, 50% of the carbon monoxide adsorbed on PDA,He,300°,1 was released upon warming to 25°C, but at 100°C only 80% had been released. These data indicate that catalysts on PDA must have been highly dispersed, but we have no data which indicate whether or not small clusters of Mo ions were present or not.

All catalysts on PDA activated to 300°C were yellow to brown and, in contrast to catalysts on DA, they reacted in air at 25°C within 1 hr to form colorless materials, presumably Mo(VI)ads.

Reaction between carbon monoxide and hydrogen. Catalytic activity for the hydrogenation of carbon monoxide on catalysts derived from $Mo(CO)_6$/DA is nearly independent of the nature of the activation of the catalyst: hydrogen or helium, 300 or 500°. This is perhaps not surprising since the reaction must proceed on clusters covered with adsorbed carbon monoxide, its decomposition products, and perhaps hydroxide in unknown proportions. One might expect catalysts of differing degrees of initial surface cleanliness to come to the same steady state. If a catalyst used for methanation at 300°C is swept with hydrogen at 500°C, returned to 300°C, and pulses of carbon monoxide passed, initial activity is larger but it declines to the usual range of 0.5–0.7 CH_4/Mo per pulse by the third pulse. This observation plus the usual augmented yields of methane for pulses 1 and 2 (see Fig. 3) suggests that the surface of the clusters at steady state is more oxidized than as initially prepared. Presumably, the surface comes to a steady state with respect to reactions equivalent to

$$Mo + CO + 2H_2 \rightarrow MoO + CH_4$$

$$MoO + H_2 \rightleftharpoons Mo + H_2O$$

and, in fact, injection of pulses of oxygen has no more than a transient effect on the conversion of carbon monoxide or, therefore, on the oxidation level of the surface.

In flow experiments at 300°C, the activity was unchanged after the first few minutes for at least 6 hr. In these experiments, the turnover frequency, N_t, was about 0.04 sec^{-1} assuming that the percentage exposed of the molybdenum was 0.3. In pulse experiments, the relative degree of conversion at 300, 400, and 500°C was 1.0 : 2.8 : 3.6.

For metallic nickel at 300°C, N_t is about 0.24 under similar conditions (*21*). About the same N_t has been reported for reaction on a filament of tungsten at this temperature (*22*). However, this reaction was run with UHV techniques at 4×10^{-7} Torr. Extrapolation to 760 Torr poses some uncertainty.

Reaction on activated $Mo(CO)_6$/DA primarily gives methane but ethane and propane are also formed. In pulse experiments at 300°C, the mole proportions were $CH_4 : C_2H_6 : C_3H_8 = 1.0 : 0.12 : 0.04$. No liberation of carbon dioxide was detected in these experiments.

It is generally considered that adsorption of carbon monoxide on clean, metallic molybdenum is dissociative (*18*). This might be taken to favor a mechanism for methanation as proceeding by hydrogenation of surface carbide (*23*). If indeed the reaction proceeds

$$CO \rightarrow C* + O* \xrightarrow{H_2} CH_4,$$

then O* must react with hydrogen to form water at 300°C. However, there is no independent evidence that the catalytically active sites on activated $Mo(CO)_6$/DA under reaction conditions do not involve the hydrogenation of undissociated, adsorbed carbon monoxide. The data reported in this paper provide little information as to mechanism.

Catalysts prepared by the activation of $Mo(CO)_6$/PDA are also active for methanation but turnover frequencies are lower. After a few pulses, the activations He,300°,1, H_2,300°,1, and H_2,500°,1, all lead to about the same conversions, about 0.1 of the conversions on Mo/DA at similar loadings of molybdenum. In flow experiments at 300°C, N_t was about 0.001 sec^{-1}/atom of molybdenum. The ratio C_2H_6/CH_4 was 0.1, about the same as on Mo/DA. In flow experiments, catalytic activity appeared to be nearly constant from 5 to 100 min. Relative activities at 300, 400, and 500°C were 1.0 : 2.0 : 2.3.

The catalysts derived from $Mo(CO)_6$/PDA are probably related to catalysts derived from $MoO_3 \cdot Al_2O_3$ and $MoO_3/SiO_3–Al_2O_3$ which were prepared by Schultz, Kam, and Anderson (*24*). The activities of these catalysts were also rather low—they were studied at 400°C.

As with Mo/DA, the catalysts on PDA must come to some steady state with respect to the distribution of oxidation numbers of molybdenum. The water formed should convert the Mo(II) of He,300°,1 to Mo(IV) under reaction conditions. As judged by the lack of reduction of Mo(IV) by hydrogen at 300°C (*20*) one might expect that the active species was primarily Mo(IV) for catalysts on PDA. Since pulses of oxygen in hydrogen carrier are converted to water at 300°C on $Mo(CO)_6$/PDA, H_2,300°,1, it is reasonable to assume that species more oxidized than Mo(IV) would be reduced under reaction conditions. Our data provide little information as to mechanism on catalysts derived from $Mo(CO)_6$/PDA but a mechanism involving dissociative adsorption of carbon monoxide might appear less likely than on Mo/DA.

Catalysts derived from DA are black throughout a methanation experiment whereas those on PDA are brownish and rapidly become white upon exposure to air. It is perhaps curious that two such different forms of Mo/Al_2O_3 are both methanation catalysts.

Both types of catalysts are partially poisoned by hydrogen sulfide, but activity is at least partly regenerated in both cases by treatment with hydrogen at 650°C.

ACTIVATED $W(CO)_6/Al_2O_3$

The chemical reactions which occurred when $W(CO)_6/Al_2O_3$ was heated in flowing helium resembled those of $Mo(CO)_6/Al_2O_3$

(5). Formation of methane was observed when pulses of carbon monoxide were injected into hydrogen flowing at 300°C over $W(CO)_6$/DA,He,300°,1;H_2,300°,1. However conversions fell steadily with pulse number. Steady-state conversion was observed at 500°C at $CH_4/W = 0.4$. CH_4/Mo on $Mo(CO)_6$/DA similarly activated was about 4.5 times larger. At 550°C, CH_4/W was 0.55 on $W(CO)_6$/DA,He,535°,1;H_2, 550°,1.

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