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The Surface Chemistry of Molybdenum in States of Lower Oxidation on Alumina

ALAN BRENNER[1] AND ROBERT L. BURWELL, JR.

Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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The interaction of $Mo(CO)_6$ with γ-alumina has been studied in the temperature range of −17 to 1000°C. It is likely that most of the dominant surface species formed during the decomposition of the complex have been identified. Activation in flowing helium at 100°C of $Mo(CO)_6$ on partially hydroxylated alumina results in the formation of $Mo(CO)_3$ads which is 100% dispersed and probably *molecularly* dispersed. Above 200°C, the remaining CO of $Mo(CO)_3$ads is liberated but detectable amounts of $Mo(CO)_2$ads and Mo(CO)ads do not accumulate. It is likely that "$(\sigma\text{-}O^-)_2Mo$" is the dominant species after activation near 270°C. After heating to 500°C, the average oxidation number of the decarbonylated Mo is about 5.6. The oxidation of the originally zero-valent Mo occurs due to reaction with surface hydroxyl groups of the alumina. Mo(VI) also results from heating $Mo(CO)_2O_2$ads and "$Mo(CO)(O_2)_2$ads" [both formed by reaction of $Mo(CO)_3$ads with O_2] to 500°C. Alumina pretreated at 950°C behaves as a quite different support. Due to the absence of hydroxyl groups, heating $Mo(CO)_6$ on this material leads to the formation of molybdenum mostly in oxidation number zero. Since Mo(0) supported on alumina is difficult to prepare by other techniques, dehydroxylated alumina may provide a useful synthesis for this type of catalyst.

INTRODUCTION

Molybdenum trioxide (MoO_3) is an initial constituent of a number of important catalysts, in particular, of catalysts for hydrodesulfurization and for the metathesis of olefins. The chemistry of MoO_3/Al_2O_3 has recently been extensively studied (*1–5*). An important finding is that, while bulk MoO_3 may be readily reduced to metallic molybdenum by hydrogen at 500°C, similar treatment of MoO_3/Al_2O_3 does not readily give reduction below Mo(IV) (*2, 3, 5*). Thus, the lower oxidation states of molybdenum are not easily accessible by reduction of MoO_3 supported on alumina (or silica).

The interaction at temperatures below 100°C between alumina and molybdenum originally present in an oxidation number of zero as $Mo(CO)_6$ has previously been reported. It was shown that $Mo(CO)_6$ supported on alumina which had been calcined at 450°C quickly decomposes to yield quantitatively $Mo(CO)_3$ads when activated at 100°C in flowing helium. The identity of $Mo(CO)_3$ads is strongly supported by a large number of accurate, quantitative measurements of the amounts of CO evolved during catalyst activation at 100°C (*6*), as well as by recent temperature-programmed decomposition studies (*7*). The decomposition is reversible in integral steps. It has been possible to isolate each of the species, $Mo(CO)_4$ads, $Mo(CO)_5$ads, and $Mo(CO)_6(g)$, in greater than 90%

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[1] Present address: Department of Chemistry, Wayne State University, 247 Life Sciences Building, Detroit, Michigan 48202.

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yield (*8*). Using infrared spectroscopy, Howe (*9*) was unable to show the existence of a single, stable $Mo(CO)_3$ads species and challenged the above interpretation. However, as noted in the literature (*6–8*), his activation temperatures are inappropriate to obtaining a quantitative yield of any of the isolatable subcarbonyl species. Previous work by a group at Edinburgh reported two bands in the C–O stretching region for $Mo(CO_6)$/alumina activated at 100°C *in vacuo* when the catalyst was examined as a Nujol mull (*10*), but they found four bands when the sample was a pressed disk (*11*). A possible reason for the discrepancy may be a lowering of symmetry of the complexes when supported on a pressed disk (*11*). In both cases it appears that the $Mo(CO)_6$/alumina was exposed to air during sample preparation and it is possible that this may have further affected their results [Ref. (*6*); also see Results section of this paper] and made it difficult to identify $Mo(CO)_3$ads. These workers did claim that decomposition proceeded through a $Mo(CO)_5$ads species, as later verified by the isolation of this species (*8*).

It was also reported (*6*) that $Mo(CO)_3$ads is very air sensitive. It quantitatively reacts with a small pulse of oxygen (O_2/Mo $\simeq 1.3$) at 23°C according to the equation:

$$Mo(CO)_3ads + O_2 = Mo(CO)_2O_2ads + CO.$$

In this paper we further characterize these surface species and examine the interaction between aluminas of varying degrees of hydroxylation and $Mo(CO)_6$ at temperatures up to 1000°C. It will be shown that these are good starting systems for the preparation and characterization of molybdenum in lower oxidation numbers on alumina.

EXPERIMENTAL

The catalysts in this paper contain about 0.6% Mo. The details for preparing $Mo(CO)_6/Al_2O_3$ and for measuring the amounts of CO and hydrogen evolved during activation have been described (*6*, *12*). $Mo(CO)_6/Al_2O_3$ is prepared by impregnating 0.250 g of 60- to 80-mesh γ-alumina (Harshaw Chemical Co., No. AL3940, made from Catapal SB, a_s = 205 m^2 g^{-1}) with a pentane solution of $Mo(CO)_6$ and evaporating the pentane. In a few experiments the $Mo(CO)_6$ was sublimed directly onto alumina at 100°C in a flow of helium to test the effect of pentane solvent.

Experiments were performed on aluminas of three degrees of hydroxylation: standard, fully hydroxylated, and dehydroxylated. The standard alumina, which was prepared by calcination at 450°C in flowing oxygen, was used unless otherwise stated. Fully hydroxylated alumina was made by following the standard pretreatment with exposure of the alumina to a flow of helium containing 21 Torr of water vapor while the temperature was raised from 23 to 300°C, held at 300°C for 30 min, and then lowered to 100°C. The alumina was then evacuated for 10 min and purged with a flow of dry helium for 1 h at 100°C. This treatment leaves the alumina nearly 100% hydroxylated (*13*, *14*). Dehydroxylated alumina was made by heating the standard alumina for 2 h at 950°C in flowing helium. This procedure leaves the alumina less than 1% hydroxylated, does not result in the formation of θ-alumina, and causes less than a 20% loss in surface area (*13–15*).

The oxidation number of Mo was determined by exposing the catalysts at 500°C to small pulses of oxygen in a helium carrier flowing at 25 cm^3/min and measuring the amount of oxygen recovered. In a typical run, about 70% of the oxidation occurred in the first pulse, and a total of six pulses of oxygen were necessary to get 100% recovery of the last two pulses. To guard against incomplete oxidation, in most runs the catalyst was trapped with 11 Torr of oxygen at 500°C for at least 15 min, the reactor was purged with helium, and the amount of oxygen recovered was determined. This increased the amount of oxidation by about 8%. As an additional check that this treatment yields Mo(VI), ESCA was used to compare the Mo $3d5/2$ binding energy of an oxidized catalyst to that in MoO_3. The catalyst gave only a single doublet of normal appearance with Mo $3d5/2$ binding energy of 232.5 ± 0.2 eV, compared to 232.6 ± 0.2 eV found for MoO_3.

EPR measurements were taken at −196°C at 9.1 GHz with a 0.67 mW power level and 100 kHz modulation using a Varian E4 Spectrometer. A sample system was used which avoided exposure of the catalysts to air. Peak areas were obtained by graphical integration of the absorption peak obtained by an electronic integration of the first derivative spectra. Absolute spin densities (number of unpaired spins per Mo atom) were obtained by comparing the areas to the signal from a Varian standard (*16*). The spin densities were reproducible to ±5% and are accurate to ±30%. The alumina alone gave a weak, ill-defined spectrum with a spin density equivalent to about 0.004 spin/Mo at normal catalyst loadings. The reported spin densities have been corrected for this background.

RESULTS

Catalyst Loading

During catalyst activation some of the $Mo(CO)_6$ sublimes from the alumina. During activation for 1 h at 100°C in flowing helium, the amount of Mo which sublimed increased montonically from 8 to 69% as the final loading increased from 0.014 to 2.16% Mo. Extrapolation to 100% sublimation suggests that the capacity of the alumina is 2.2% Mo. Other runs in which the $Mo(CO)_6$ was sublimed onto the alumina at 100°C gave a maximum loading of 2.3% Mo. The amount of sublimation is sensitive to the exact technique of adding the $Mo(CO)_6$ to the alumina. Thus, using heptane as the solvent increased the sublimation to 70% at a final loading of only 0.07% Mo.

Nature of the Surface Subcarbonyl Species

(*i*) *Strength of the surface bond.* The strength of the surface bond to $Mo(CO)_3$ads was assessed by exposing it under a helium atmosphere to hot benzene and hot 1-octene in an attempt to desorb the tricarbonyl moiety into the liquid phase as a stable arene- or olefintricarbonyl complex. Infrared spectroscopic examination of the decanted liquid failed to reveal any carbonyl-containing species.

(*ii*) *Coordinative unsaturation.* It might be expected that, if $Mo(CO)_3$ads was coordinatively unsaturated due to the loss of CO ligands, olefins would be strongly adsorbed at the ligand vacancies. Coordinative unsaturation was therefore investigated by passing a 0.86 cm^3 STP pulse of propylene (propylene/Mo $\cong$ 3) in a helium carrier flowing at about 1 cm^3/sec over $Mo(CO)_3$ads at 53°C. No net adsorption (corrected for the adsorption on alumina as found in blank experiments) could be detected, the sensitivity being ≤ 0.01 propylene/Mo. Similar experiments using pulses of ethylene at −16°C also failed to reveal any irreversible formation of $(\text{olefin})_n Mo(CO)_3$ads.

(*iii*) *Reaction with oxygen.* Although crystalline $Mo(CO)_6$ is air stable, $Mo(CO)_6$/alumina is moderately air sensitive. Passing three small pulses of oxygen over $Mo(CO)_6$ads at 23°C resulted in the adsorption of 0.07 O_2/Mo. The ratio of (CO evolved)/(O_2 adsorbed) varied from 3.2 to 4.1. It is noteworthy that the value of this ratio is unity for the reaction given in the Introduction.

$Mo(CO)_3$ads was exposed to six small pulses of oxygen (O_2/Mo = 0.4) at 23°C. After the sixth pulse a total of 1.2 O_2/Mo had been adsorbed and the rate of reaction was about one-tenth that in the first pulse, suggesting that a reaction similar to that given in the Introduction might proceed readily at a higher temperature. To test this, $Mo(CO)_2O_2$ads was made by reacting $Mo(CO)_3$ads with oxygen at 23°C and then this material was warmed to 85°C. The $Mo(CO)_2O_2$ads is slightly thermally unstable, losing about 0.1 CO/Mo before the rate of decomposition becomes very small. After allowing the catalyst to equilibrate, it was exposed to a pulse of oxygen at 85°C. The adsorption of oxygen was 0.79 ± 0.05 O_2/Mo and the ratio (CO evolved)/(O_2 adsorbed) was 1.00 ± 0.04 (three runs). Thus, the new catalyst stoichiometry was nearly "$Mo(CO)(O_2)_2$ads." $Mo(CO)_2O_2$ads and $Mo(CO)_3$ads had the same gold color, whereas the color of "$Mo(CO)(O_2)_2$ads" was somewhat lighter.

(*iv*) *EPR spectra.* The EPR spectra of $Mo(CO)_5$ads showed only a weak signal about 200 G wide centered at $g = 2.00$ and with a spin density of 0.007 spin/Mo. The EPR spectrum of $Mo(CO)_2O_2$ads showed a Mo^{5+} signal ($g = 1.938$) of intensity 0.005 spin/Mo and an O_2^- signal split by a hyperfine interaction with Al($I = \frac{1}{2}$) nuclei of intensity 0.033 spin/Mo. Conversion (75%) to "$Mo(CO)(O_2)_2$ads" did not affect the O_2^- signal, but the intensity of the Mo^{5+} signal increased to 0.015 spin/Mo. No signal of O_2^- appeared in a similar run with alumina only.

Decomposition of $Mo(CO)_6$/Alumina at Temperatures above 100°C.

(*i*) *Evolution of CO.* In 15 runs in which catalysts were heated in flowing helium for 1 h at 500°C, the recovery of CO was 5.76 ± 0.07/Mo (the recovery was nearly complete in 30 min). The catalysts were now light grey. Heating to 1000°C did not increase the recovery of CO nor were the results affected by using catalysts made by subliming the $Mo(CO)_6$ onto the alumina. In addition, heating at 500°C produced 0.024 ± 0.003 CO_2/Mo and, in one run using a fresh catalyst (not used for metathesis) made by sublimation, 0.20 CH_4/Mo (analysis was not made for CH_4 in the other runs). In this run the total recovery of carbon was 5.99 C/Mo, in agreement with the theoretical value of 6.00 within the experimental error of ±1%.

(*ii*) *Evolution of hydrogen.* Heating to about 270°C in flowing helium caused the rapid evolution of about 2 H/Mo and the slower loss of additional hydrogen. The catalysts were now sandy brown. At 500 and 730°C the evolution of hydrogen is complete in 1 h and nearly so in 30 min. Three measurements of the amount of hydrogen evolved at 500°C gave 4.02 ± 0.20 H/Mo, and three measurements after heating to 730°C gave 4.58 ± 0.04 H/Mo. No additional hydrogen is evolved upon heating to 1000°C. The amount of hydrogen evolved while heating at 500°C increases linearly with loading and it is zero in the absence of $Mo(CO)_6$. Runs using fresh catalysts in which the $Mo(CO)_6$ had been sublimed onto the support gave the same results indicating that the source of the hydrogen was surface hydroxyl groups on the alumina (not adsorbed hydrocarbons).

The more oxidized forms of the Mo liberated progressively less hydrogen upon heating. Thus, heating $Mo(CO)_2O_2$ads at 500°C for 1 h in flowing helium resulted in the evolution of 2.2 H/Mo (as well as 0.07 CO_2/Mo, a cumulative loss of 5.7 CO/Mo, and no molecular oxygen). Heating "$Mo(CO)(O_2)_2$ads" catalysts [actually composed of about 14% $Mo(CO)_2O_2$ads and 86% "$Mo(CO)(O_2)_2$ads"] at 500°C yielded only about 0.44 H/Mo (as well as about 0.32 CO_2/Mo, 0.04 O_2/Mo and a cumulative loss of 5.6 CO/Mo).

(*iii*) *Characterization of species formed at high temperatures.* The ability to reverse decomposition beyond $Mo(CO)_3$ads was measured by passing an equimolar mixture of CO and hydrogen over a catalyst for 3 h at 100°C. The catalyst had initially lost

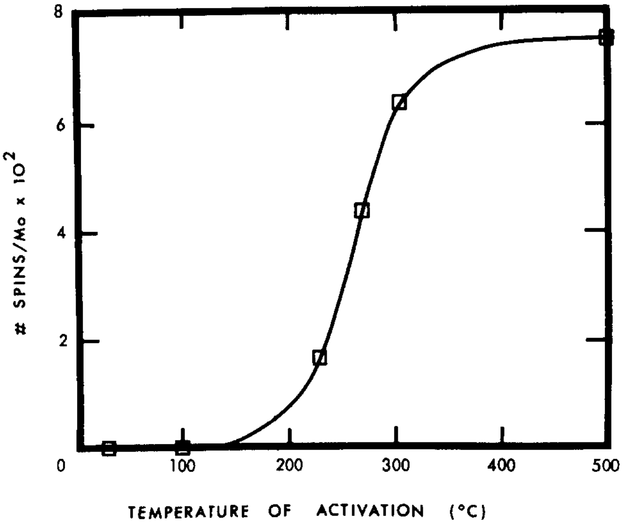


FIG. 1. The EPR signal of Mo^{5+} as a result of the activation of a 0.61% Mo catalyst. The catalyst was heated for approximately 30 min at each temperature.

5.6 CO/Mo and 2.3 H/Mo by activation at 280°C. The recovery of Mo [as $Mo(CO)_6$] was 8%.

Activation at high temperatures in flowing helium resulted in the appearance of the EPR signal of Mo(V) (Fig. 1) with a g value of 1.936 ± 0.002 ($g_{\parallel} = 1.915$, $g_{\perp} = 1.956$, peak to peak width of about 72 G). After heating $Mo(CO)_3$ads to 500°C for 1 h in flowing helium, the Mo had an average oxidation number of 5.6 ± 0.1, as determined by titration with oxygen.

Catalysts which have been decomposed beyond stoichiometric $Mo(CO)_3$ads adsorb less than one molecule of oxygen per atom of molybdenum from a pulse of oxygen at 23°C (see equation in Introduction). The amounts of CO released during this reaction are shown in Fig. 2 and suggest a linear decrease in the amount of $Mo(CO)_3$ads present.

Fully Hydroxylated and Dehydroxylated Supports

$Mo(CO)_6$/(dehydroxylated alumina) at 100°C loses CO with time as shown in Fig. 3. For comparative purposes, the evolution of CO for a catalyst made with a standard support is also shown. After a few minutes the dehydroxylated catalyst was dark gold and, after 2 h, very dark brown to black. $Mo(CO)_6$ on fully hydroxylated alumina behaved the same as on standard alumina with respect to the loss of $Mo(CO)_6$ during activation, the evolution of CO at 100°C, and the stoichiometry of the reaction of the resulting catalyst with oxygen. The color of the hydroxylated catalyst, however, was much lighter.

A catalyst which had been made by impregnation on dehydroxylated alumina and used for metathesis of propylene evolved 0.28 H/Mo while heated at 500°C for 80 min. The catalyst was now black and had an average oxidation number of 0.4.

DISCUSSION

Catalyst Loading

During catalyst preparation, $Mo(CO)_6$ physisorbed on alumina either reacts with the surface to evolve CO or it sublimes. The latter process is more extensive when a less volatile solvent is used, suggesting that the $Mo(CO)_6$ is not strongly bonded to the alumina until it decomposes. It is interesting that two unrelated methods of adding $Mo(CO)_6$ to alumina (impregnation and sublimation) yield the same maximum loading of about 2.2% Mo, corresponding to 0.7 site/nm^2. This may be the intrinsic capacity of the alumina. Davie *et al.* reported a value of only 0.3 site/nm^2 (*17*). Their lower value probably reflects their use of benzene as a solvent (their technique for determining the loading of the catalyst was also less accurate) and perhaps their different source of γ-alumina.

Physisorbed Mo(CO)₆

In contrast to an earlier claim that activation of $Mo(CO)_6/\gamma$-alumina at 20 or 100°C results in a Mo(V) spin density of about 0.02 spin/Mo (*18*), we detected no Mo(V) after activation at 23 or 100°C. The Mo(V) of the previous work probably resulted from the exposure of $Mo(CO)_6$/alumina to air during its preparation. As noted in the Experimental section, $Mo(CO)_6$/alumina is air sensitive at 23°C, the main reaction probably being

$$Mo(CO)_6ads + O_2 = Mo(CO)_2O_2ads + 4CO.$$

These changes in the stoichiometry of the catalyst are also consistent with the changes in activity of these catalysts for the metathesis of propylene (*19*).

Nature of the Subcarbonyl Species.

The data in Ref. (*8*) establish that, at pressures of CO in the range of 50 to 760 Torr and at temperatures between 0 and 100°C, the relative thermodynamic sta-

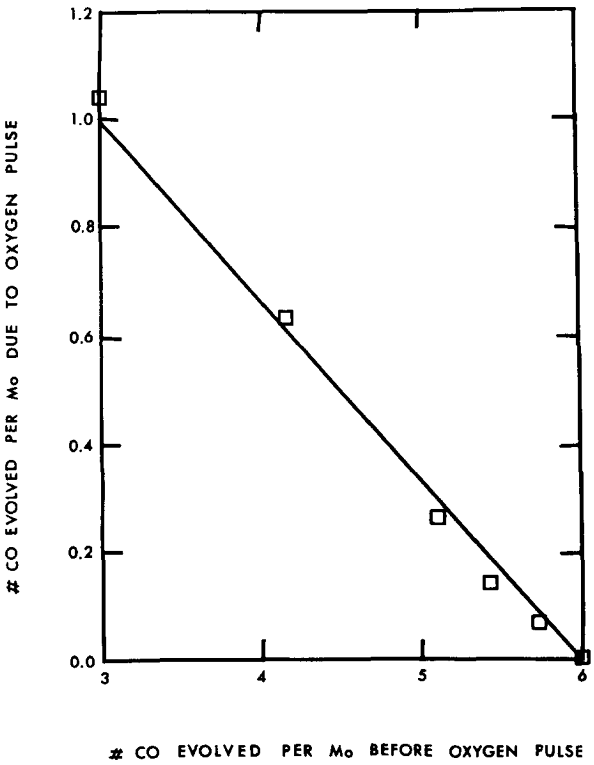


FIG. 2. The amount of carbon monoxide liberated by a pulse of oxygen at 23°C from catalysts activated at higher temperatures. The catalysts contained 0.54% Mo and the X axis represents the total number of molecules of carbon monoxide lost per atom of Mo during activation.

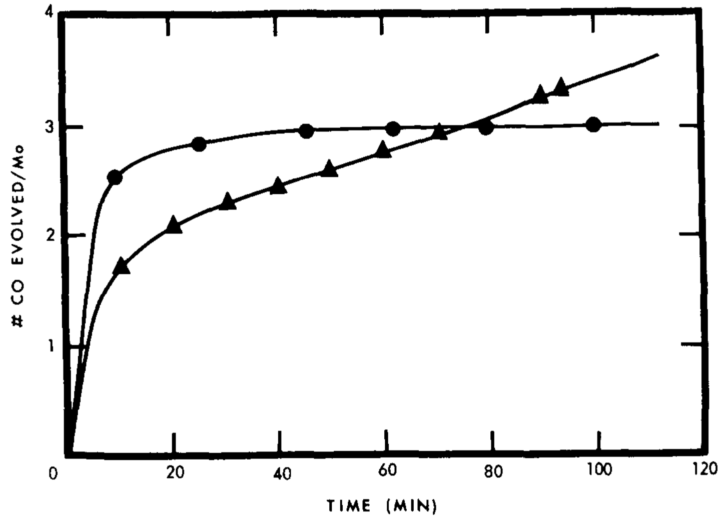


FIG. 3. The evolution with time of carbon monoxide from $Mo(CO)_6/Al_2O_3$ at 100°C. Circles are for a catalyst containing 0.7% Mo on standard alumina, and triangles indicate catalyst containing 1.27% Mo on dehydroxylated alumina.

bilities of the various carbonyl species are

$$Mo(CO)_5ads > Mo(CO)_6ads$$

and

$$Mo(CO)_5ads > Mo(CO)_4ads > Mo(CO)_3ads.$$

Since the Mo–CO bond dissociation energy for the first loss of CO from $Mo(CO)_6$ is at least 40 kcal/mole (*20*), it would appear necessary that the bond between $Mo(CO)_5$ and a surface ligand be at least this strong.

$Mo(CO)_3ads$ neither strongly adsorbs olefin nor is it extracted by warm benzene to form the stable compound $(C_6H_6)Mo(CO)_3$. In contrast, the coordinatively unsaturated species $Mo(CO)_5$, which can be formed in solution by the photolysis of $Mo(CO)_6$ (*21*), is a very strong electrophile which rapidly reacts with a weak donor, D, to form $Mo(CO)_5D$. It is therefore likely that $Mo(CO)_3ads$ has three bonds to the surface and is formally a coordinatively saturated species.

Adsorption of CO on coordinatively saturated $Mo(CO)_3ads$ presumably occurs by a ligand displacement adsorption mechanism (*22*). The rapid adsorption of CO at −17°C (*8*) indicates that all of the $Mo(CO)_3ads$ is readily accessible and is therefore 100% dispersed. The steric requirements of five CO ligands around each Mo in $Mo(CO)_5ads$ further suggest that the carbonyl species are *molecularly* isolated on the alumina surface, but we cannot rigorously exclude the presence of adsorbed species with bridging carbonyl groups.

CO is rapidly lost from $Mo(CO)_6$ adsorbed on *hydroxylated* alumina at 100°C until the species $Mo(CO)_3ads$ is reached. By analogy with $(diglyme)Mo(CO)_3$ (*23*), the stable species on hydroxylated alumina is very probably $(\sigma\text{-OH})_3Mo(CO)_3$. On dehydroxylated alumina, CO is also lost from adsorbed $Mo(CO)_6$ but, as shown in Fig. 3, $Mo(CO)_3ads$, although presumably formed, is less stable and at 100°C it decomposes further. Presumably, σ-OH as a ligand conveys some stability to $Mo(CO)_3ads$. On the standard alumina $Mo(CO)_3ads$ is relatively stable against further loss of CO and its formula might be $(\sigma\text{-OH})_3Mo(CO)_3$ (*6*) or $(\sigma\text{-O}^-)(\sigma\text{-OH})_2Mo(CO)_3$. The standard alumina is about 36% hydroxylated (*14*). Thus, at the maximum loading (2.2% Mo) the ratio σ-OH/Mo = 6.5, but not all of the σ-OH are present in triads suitable to forming $(\sigma\text{-OH})_3\text{Mo(CO)}_3$. Figure 4 of Ref. (*24*) suggests that, at the maximum loading, the amount of σ-OH available in triads is about 2.8 σ-OH/Mo, quite close to the stoichiometric requirement of 3.0 σ-OH/Mo if $(\sigma\text{-OH})_3\text{Mo(CO)}_3$ is formed. Adjacent σ-OH are separated by about 0.28 nm on the surface of alumina (*24*), a distance which is nearly the same as the separation of the carbon atoms of the CO ligands in Mo(CO)_6 (*25*). Interaction of a transition metal with multiple σ-OH has also been reported by Chien (*26*), who found that VCl_4 reacts with an average of 2.4 σ-OH on γ-alumina at 150°C, and by Candlin and Thomas (*27*) who reported that Zr(benzyl)_4 can react with 2σ-OH of alumina.

Oxidized Species.

The exact structures of $\text{Mo(CO)}_2\text{O}_2\text{ads}$ and "$\text{Mo(CO)(O}_2)_2\text{ads}$" have not been elucidated. In "$\text{Mo(CO)(O}_2)_2\text{ads}$" all of the oxygen cannot be in the form of oxide ions if Mo is restricted to a maximum oxidation number of +6. It is likely that O_2 is present primarily as a peroxo ligand since formation of carbonyls usually requires Mo of low oxidation number. Small amounts of Mo(V) and O_2^- are detected by EPR and are presumably formed by a minor side reaction. These species were previously reported by Howe and Leith (*18*).

Nature of Catalysts Activated above 100°C.

(*i*) *Absence of subcarbonyl species.* The reaction of a catalyst activated above 100°C with a pulse of oxygen at 23°C provides a possible method for titrating $\text{Mo(CO)}_3\text{ads}$: One CO is displaced from each $\text{Mo(CO)}_3\text{ads}$ (see equation in Introduction). $\text{Mo(CO)}_2\text{ads}$ and Mo(CO)ads apparently do not interfere since Fig. 2 indicates either that these species are present in small amounts or that they do not release CO under the reaction conditions. In either case, the ordinate of Fig. 2 provides the fraction of the Mo which is in the form $\text{Mo(CO)}_3\text{ads}$. Let θ_n be the fraction of the Mo(CO)_6 which has thermally lost *n* CO/Mo, and let *N* be the measured average number of CO evolved per Mo during thermal activation. Then, for catalysts activated above 100°C, $N = 3\theta_3 + 4\theta_4 + 5\theta_5 + 6\theta_6$ (θ_0, θ_1, and θ_2 are zero; see Introduction). At $N = 3$ it has been shown that $\theta_3 = 1.00$ (see Introduction), and at $N = 6$ it is necessary that $\theta_6 = 1.00$. The linear relationship of Fig. 2 suggests that $\theta_4 = \theta_5 = 0$ throughout. This assumption can be tested by setting the ordinate of Fig. 2 equal to θ_3, letting $\theta_6 = 1 - \theta_3$, and then computing $N_{\text{calcd}} = 3\theta_3 + 6(1 - \theta_3)$. The good agreement with the experimentally determined value for *N* (Table 1) indicates the surprising result that neither $\text{Mo(CO)}_2\text{ads}$ nor Mo(CO)ads accumulates to a significant degree during decomposition of $\text{Mo(CO)}_3\text{ads}$ above about 200°C.

TABLE 1

The Values of *N* Calculated by Assuming that $\theta_4 = \theta_5 = 0$

θ_3[a]	$\theta_6 = 1 - \theta_3$	$N_{\text{calcd}} = 3\theta_3 + 6\theta_6$	N_{expt}[b]	Error
1.00	0.00	3.00	3.00	0.0
0.63	0.37	4.11	4.18	−1.7
0.27	0.73	5.19	5.07	+2.3
0.14	0.86	5.58	5.44	+2.5
0.09	0.91	5.73	5.76	−0.5
0.00	1.00	6.00	6.00	0.0

[a] θ_3 is equal to the ordinate of Fig. 2.

[b] Average number of CO evolved per Mo. (thermally).

(*ii*) *Oxidation of Mo by σ-OH.* The ready evolution of about 2 H/Mo when a catalyst is activated near 270°C suggests that the reaction,

$$\text{Mo(CO)}_3\text{ads} + 2\ \sigma\text{-OH} = \text{“}(\sigma\text{-O}^-)_2\text{Mo”} + 3\text{CO} + \text{H}_2,$$

may be important in this temperature region. Since the amount of hydrogen evolved is measured directly and θ_6 (completely decarbonylated Mo) can be determined by titration with oxygen (vide supra), the ratio θ_6/N_H, where N_H is the number of hydrogen atoms evolved per Mo atom, can be computed. After heating for 3.3 h at 260°C, $\theta_6/N_H = 0.43$. Since, by the previous equation, the ratio would be 0.50 for formation of only "$(\sigma\text{-O}^-)_2$Mo," about 17% of the decarbonylated Mo has reacted with more than two σ-OH. At lower temperatures the reaction,

$$\text{Mo(CO)}_3\text{ads} \rightarrow \text{Mo(0)} + 3\text{CO},$$

might be imagined to occur. For this reaction, θ_6/N_H is infinite. At the lowest temperature investigated, 240°C, θ_6 was 0.56, and θ_6/N_H was 0.48, consistent with the penultimate equation. Thus, complete decarbonylation of Mo(CO)_3ads is accompanied by the oxidation of the molybdenum. It is clear that there is not a sharp break in the rate of oxidation and more than one oxidized species is being formed. However, the data suggest that near 270°C about 70% of the Mo is "Mo(II)." It appears, then, that Mo(0) is not stable in contact with the σ-OH of alumina at temperatures above 200°C or so. This correlates with the difficulty in making Mo(0) by reducing $\text{MoO}_3/\text{Al}_2\text{O}_3$ with hydrogen. The reverse of the reductive adsorption of hydrogen,

$$\text{"}(\sigma\text{-O}^-)_2\text{Mo(II)"} + \text{H}_2 \rightarrow \text{Mo(0)} + 2\ \sigma\text{-OH},$$

is actually favored.

All catalysts prepared on standard alumina appear to approach Mo(VI) upon heating at 500°C for 1 h in flowing helium. Since the evolutions of hydrogen were the same for catalysts made by direct sublimation the source of hydrogen must be σ-OH groups and not residual pentane. Thus, by 500°C, "Mo(II)" has been further oxidized by σ-OH groups (the cumulative evolution of molecular hydrogen now being 4 H/Mo). A small amount of the hydrogen evolved goes to form methane. Thus, a sample of Mo(CO)_3ads heated at 500°C liberated 4.12 H and 0.20 CH_4 per Mo. From this, one calculates that the oxidation number of residual Mo was +5.3, in reasonable agreement with the value of 5.6 found by titration with pulses of oxygen.

Heating $\text{Mo(CO)}_2\text{O}_2$ads at 500°C results in the liberation of only 2 H/Mo, presumably by the following reaction:

$$\text{Mo(CO)}_2\text{O}_2\text{ads} + 2\ \sigma\text{-OH} \rightarrow (\sigma\text{-O}^-)_2\text{MoO}_2 + \text{H}_2 + 2\text{CO},$$

where the metal is now Mo(VI). Heating a "$\text{Mo(CO)(O}_2)_2$ads" catalyst which contained 3.67 O/Mo at 500°C resulted in the liberation of 0.01 O/Mo as dioxygen and 0.64 O/Mo as CO_2. The residue, then, contained 3.02 O/Mo, again indicating the formation of Mo(VI). The small evolution of hydrogen which occurred was presumably due to residual $\text{Mo(CO)}_2\text{O}_2$ads.

The scheme below summarizes the principal reaction of Mo(CO)_6 with standard (partially hydroxylated) alumina.

$$\text{Mo(CO)}_6\text{(g)} \rightleftarrows \text{Mo(CO)}_6\text{ads} \rightleftarrows \text{Mo(CO)}_5\text{ads} + \text{CO} \rightleftarrows$$

$$\text{Mo(CO)}_4\text{ads} + \text{CO} \overset{100^\circ\text{C}}{\rightleftarrows} \text{Mo(CO)}_3\text{ads} + \text{CO}$$

$$\text{Mo(CO)}_3\text{ads} \xrightarrow{270^\circ\text{C}} \text{"}(\sigma\text{-O}^-)_2\text{Mo"} + 3\text{CO} + \text{H}_2 \xrightarrow{500^\circ\text{C}} (\sigma\text{-O}^-)_2\text{MoO}_2 + \text{H}_2$$

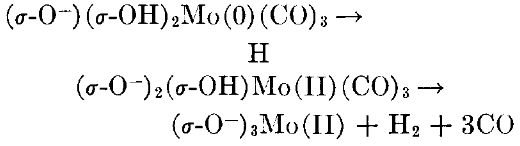
$$\text{O}_2 \downarrow 23^\circ\text{C}$$

$$\text{Mo(CO)}_2\text{O}_2\text{ads} + \text{CO} \xrightarrow{500^\circ\text{C}} (\sigma\text{-O}^-)_2\text{MoO}_2 + \text{H}_2 + 2\text{CO}$$

$$\text{O}_2 \downarrow 85^\circ\text{C}$$

$$\text{"Mo(CO)(O}_2)_2\text{ads"} + \text{CO} \xrightarrow{500^\circ\text{C}} (\sigma\text{-O}^-)_2\text{MoO}_2 + (\text{CO} + \text{CO}_2)$$

In addition to the species shown, significant quantities of Mo(V)ads accompany the more oxidized species in the scheme. [It is likely that not all of the Mo(V) exhibits an EPR signal (*3*).] The exact details of the structures of the adsorbed species have not been established. It may be suggested, however, that decomposition of Mo(CO)_3ads proceeds thus:[2]



$$(\sigma\text{-O}^-)(\sigma\text{-OH})_2\text{Mo(0)(CO)}_3 \rightarrow (\sigma\text{-O}^-)_2(\sigma\text{-OH})\overset{\text{H}}{\text{Mo}}\text{(II)(CO)}_3 \rightarrow (\sigma\text{-O}^-)_3\text{Mo(II)} + \text{H}_2 + 3\text{CO}$$

The second reaction would presumably involve more than one step. Loss of hydrogen from the seven-coordinate molybdenum hydride is equivalent to the reverse of heterolytic dissociative adsorption.

Hall and LoJacono have recently reported that reductive adsorption occurs when MoO_3/γ-alumina is exposed to hydrogen at 500°C (*3*). It is believed that this hydrogen is retained in the form of hydroxyl groups bonded to Mo(V). This process may be closely related to the reverse of the reaction in which σ-OH reacts with Mo(CO)_3ads and hydrogen is evolved. In our system, however, the hydroxyl groups must originate on the alumina and not on the Mo.

(*iii*) *Irreversibility.* The catalyst which had lost 5.6 CO/Mo by activation at 280°C should have $\theta_3 = 0.13$ and $\theta_6 = 0.87$ by the formula given earlier. The recovery of 8% of the Mo as Mo(CO)_6 when the catalyst was exposed to a flow of CO and hydrogen suggests that $\theta_3 = 0.08$, since Mo(CO)_3ads has been shown to be reversibly formed (*8*). The two values for θ_3 are in reasonable agreement indicating that decomposition beyond Mo(CO)_3ads is irreversible.

Dehydroxylated Alumina

Mo(CO)_6 adsorbed on dehydroxylated alumina behaves very differently on heating since its surface is nearly devoid of σ-OH groups. It has already been noted that Mo(CO)_3ads is not readily isolated on this support. Activating Mo(CO)_6 on dehydroxylated alumina to 500°C resulted in the liberation of only 0.28 H/Mo. The result of the oxygen titration, O.N. = + 0.4, is reasonably consistent with this yield of hydrogen. The stoichiometry for the reaction of Zr(benzyl)_4 with σ-OH groups has also been reported to depend upon the degree of hydroxylation of alumina (*27*). Since Mo(0) cannot be made by either reducing $\text{MoO}_3/\text{Al}_2\text{O}_3$ or decomposing Mo(CO)_6/standard alumina, the use of a dehydroxylated support may have applications for preparing supported Mo(0).

SUMMARY

In conjunction with previous work, a fairly complete description has been obtained of the surface reactions which occur when Mo(CO)_6/alumina catalysts are activated under a wide variety of conditions. The identities of the various surface complexes largely rest on accurate quantitative measurements of the stoichiometrics of surface reactions. While such experiments usually lead to unambiguous interpretations, relatively little information has been obtained on the details of bonding and structure of the surface species. The salient features of the system are the following.

(i) At temperatures below 100°C, the subcarbonyl species, Mo(CO)_6ads, Mo(CO)_5ads, Mo(CO)_4ads, and Mo(CO)_3ads, are formed. Each step in the decomposition of Mo(CO)_6 is reversible, and Mo(CO)_3ads is fairly stable to further decomposition at 100°C. It is also likely that each of these species is *molecularly* isolated on the surface.

(ii) Further decomposition readily occurs

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[2] $\text{Mo(CO)}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)$, reacts with acid to form the seven-coordinate species, $\text{HMo(CO)}_4(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)^+$, in which Mo is formally in oxidation number II (*28*).

above 200°C and is not reversible. It is notable that there is not a significant accumulation of either $Mo(CO)_2ads$ or $Mo(CO)ads$.

(iii) Due to reaction with σ-OH, complete decarbonylation of $Mo(CO)_6$ does not yield the expected Mo(0). Rather, after activation near 270°C a moderately oxidized species, probably "$(\sigma\text{-O}^-)_2Mo$", is the dominant species and, after activation at 500°C, Mo(VI) is the dominant species. These surface reactions may partially explain the difficulty of fully reducing MoO_3/alumina.

(iv) The surface species formed are very sensitive to the exact pretreatment of the alumina. In particular, on a highly dehydroxylated alumina $Mo(CO)_3ads$ is not readily isolated and, after heating to 500°C, Mo(0) is the main product. The use of dehydroxylated alumina, then, affords a synthesis of Mo(0)/alumina.

(v) By appropriate choice of activation conditions, it is possible to prepare the Mo in a wide variety of reasonably well-defined forms and in oxidation states ranging from 0 to 6. This is not possible with MoO_3/alumina, which is essentially restricted to the oxidation states of 4 through 6.

Thus, $Mo(CO)_6$/alumina has afforded a unique opportunity for studying supported Mo catalysts. In an accompanying paper, the activity for the metathesis of propylene is investigated for each form of the catalyst (*19*).

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