

Organometallic Complexes on Alumina¹

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Three aspects of the surface chemistry and catalytic activity of organometallic complexes on alumina are covered with particular attention to the effect of the surface concentration of OH⁻ present after various degrees of dehydroxylation. (1) The formation of Lewis acid–Lewis base pair sites during dehydroxylation of alumina. (2) The effect of the degree of dehydroxylation upon the course of the reaction of Mo(CO)₆ with the surface of alumina during heating in He and in H₂. Various activated Mo(CO)₆/Al₂O₃ are catalysts for the hydrogenation of propylene, the exchange of alkanes with D₂, the hydrogenolysis of alkanes, the hydrogenolysis of cyclopropane, the hydrogenation of CO, and the metathesis of olefins. Metallic Mo(0)/Al₂O₃ is among the most active catalysts known for the first three reactions. (3) Organoactinide complexes on alumina. The complexes (Cp')₂Th(CH₃)₂, (Cp')₂U(CH₃)₂, and (Cp')₂ThH₂ (where Cp' is pentamethylcyclopentadienyl) lead to very active catalysts for the hydrogenation of propylene at -63°C and the polymerization of ethylene at 25°C. The surface chemistry of the reactions of the complexes with the surface of alumina during activation has been partially elucidated. High catalytic activity is favored by nearly complete dehydroxylation of the alumina support.

INTRODUCTION

Three aspects of our work on organometallic complexes on alumina will be considered here: (1) the direct demonstration of the occurrence of Lewis acid–Lewis base pair sites on alumina, (2) the surface chemistry and catalytic activity of materials derived from Mo(CO)₆/Al₂O₃ with particular attention to metallic molybdenum on alumina, and (3) the surface chemistry and catalytic activity of organoactinide complexes on alumina. Two of these investigations involved collaboration with colleagues in the inorganic group at Northwestern University and that work required knowledge and techniques which my laboratory alone could not have provided. The research on Lewis acid–Lewis base sites was in collabo-

ration with Duward F. Shriver and that on organoactinides with Tobin J. Marks.

There has recently been considerable interest in organometallic complexes deposited upon oxide supports (1). The work may be classified in two categories (a) the complex is decomposed to form a supported metal or metal ion and (b) the initial complex or some derived complex is retained. Both types of materials appear in the work reported here. In some cases silica and alumina function in rather similar ways. In the present work, however, the use of alumina was either necessary or it led to much higher activities than silica gel.

Features of the surface chemistry of alumina (2) which are essential to the present purpose follow. The crystal lattice of γ -alumina resembles that of a spinel. It involves a cubic close-packed lattice of O²⁻ ions in which Al³⁺ ions are distributed among the octahedral and the tetrahedral holes. The texture of usual samples of γ -Al₂O₃ is rather like that of a loose, cemented gravel bed in

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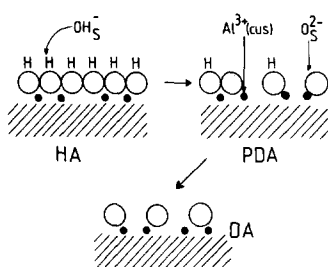


FIG. 1. Schematic representation of the partial and complete dehydroxylation of alumina, HA \rightarrow PDA \rightarrow DA. Bulk alumina is indicated by the cross-hatching. The representation is oversimplified because distinctions between tetrahedral and octahedral holes of the oxide ions are omitted. See Refs. (2, 3).

which the primary particles are crystalline γ -Al₂O₃ of a diameter of about 10 nm. The surface of a sample of γ -Al₂O₃ prepared by the usual wet methods is fully hydroxylated, that is, the surface is covered by OH⁻ ions to be designated σ -OH. Such a surface is represented schematically in Fig. 1. Upon heating hydroxylated alumina to above about 200°C, dehydroxylation begins. As shown in the figure, two σ -OH react to form water which desorbs and a surface oxide ion, to be represented σ -O⁻ (3). It also forms a surface vacancy in the oxygen-ion lattice which to some degree exposes an aluminum ion Al³⁺ (*cus*) where *cus* indicates that the ion is a "coordinatively unsaturated surface" species. As such, it should be a Lewis acid. The O_s²⁻ (or σ -O⁻) species is coordinated to fewer Al³⁺ than an oxide ion in bulk would be. σ -O⁻ should be a Lewis base. Dehydroxylation occurs to a degree which increases as the temperature of treatment increases. At about 475°C, a temperature we commonly employed, about 4 of the original 15 σ -OH per nm² remain. By about 950°C, the alumina has become nearly but not completely dehydroxylated; about 0.12 σ -OH remain per nm² (4). The alumina has also become partially converted to δ -alumina. The hydroxylated, partially dehydroxylated (at 475°C), and nearly completely dehydroxylated aluminas (at \sim 950°C) will be designated HA, PDA, and DA, respectively.

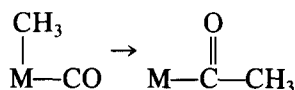
In the present work we usually employed a 99.99% pure γ -alumina of the American Cyanamid Company, designated PHF, $a_s = 160$ m² g⁻¹, pore volume = 0.6 cm³ g⁻¹, and average pore diameter = 12 nm (4). Equivalently pure materials, Catapal SB and transparent alumina foil used for infrared studies, appeared to exhibit the same behavior.

All of the organometallic complexes on alumina were very sensitive to oxygen. We avoided exposing our catalysts to vacuum and, instead, effected dehydroxylation, catalyst preparations, catalyst pretreatments and catalytic reactions in flowing helium or hydrogen in which the contents in oxygen were less than 0.03 ppm as measured at the catalyst (4). Such products of activation or reaction as CO, CH₄, and C₂H₆ were removed from flowing helium by adsorption upon silica gel at -196°C. Warming led to the release of a pulse of products suitable for gas chromatography. Hydrogen was adsorbed from helium on molecular sieve (5A) at -196°C and measured after conversion to water.

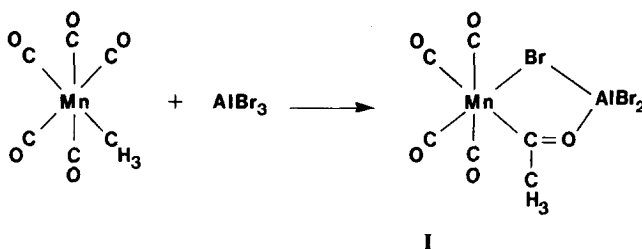
LEWIS ACID-LEWIS BASE PAIR SITES ON ALUMINA (*F. Correa, R. Nakamura, and R. E. Stimson*)

H. Pines appears to have been the first to propose the simultaneous presence of acidic and basic catalytic sites on alumina. The work described here aimed at establishing that the two sites could occur in immediately adjacent locations.

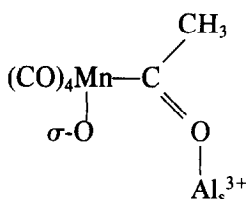
D. F. Shriver and co-workers had shown that the diphilic properties of such molecular acids as aluminum bromide led to strong promotion of the methyl migration reaction in certain complexes containing CH₃ and CO ligands (5).



Thus, the following reaction occurred rapidly in toluene solution at 25°C:



Structure I was confirmed by X-ray diffraction. Here, Al^{3+} serves as a Lewis acid and the Br^- as a base to provide an enormous acceleration in the rate of the migration of the CH_3 group. It occurred to us that the $\text{Al}^{3+}(\text{cus})$ ion of the surface of a dehydroxylated alumina might similarly serve as an acid in conjunction with a $\sigma\text{-O}^-$ serving as a base. Accordingly, a pentane solution of the manganese complex was injected onto a transparent alumina foil in an infrared cell past which a current of helium was flowing (6). There was an immediate change in color as the solution came in contact with the alumina, but there was no further change in color during the evaporation of the pentane. The infrared absorption spectrum of the sample was determined and found to be very close to that of compound I. Essentially identical results were obtained for PDA and for DA. Further, negligible liberation of methane or hydrogen accompanied the evaporation of the pentane solvent. Thus, the product of adsorption of the manganese complex is



and the surface of dehydroxylated alumina provides Lewis acid–Lewis base pair sites which are within a few tenths of a nanometer from each other. Further, protonolysis of M-CH_3 by $\sigma\text{-OH}$ on PDA to form methane is slow vs methyl migration. Similar reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CH}_3)(\text{CO})_2$ also occurred immediately upon injection of a

solution of that complex onto alumina foil (6).

In the work just described, an organometallic complex served to provide information about the nature of the surface of alumina. Such a reaction could not occur on the surface of pure silica since that surface is devoid of Lewis acid sites. The next two sections are more concerned with the catalytic properties of the products of depositing organometallic complexes on alumina.

MATERIALS STARTING AS $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$

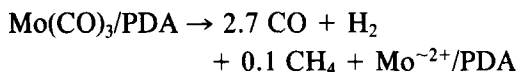
Catalysts prepared by activating $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ were first reported by Banks and Bailey in 1964 (7) and the olefin metathesis reaction was discovered on one of these catalysts (7, 8). These materials were among the first organometallic complexes supported on oxides to be used as catalysts. Whan and colleagues at Edinburgh investigated the catalytic activity of these materials for the metathesis of olefins and they correlated this activity with the results of ir, EPR, and XPS studies (see leading Ref. (9)). This work showed that activation to higher temperatures in an inert gas led the evolution of CO to accompany the development of catalytic activity, but the Edinburgh group did not analyze the gases liberated during activation and for a while they prepared the $\text{Mo}(\text{CO})_6/\text{PDA}$ in air. Such a preparation would appear to be quite reasonable since $\text{Mo}(\text{CO})_6$ itself is air stable. However, $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ turns out to be air sensitive even at 25°C . Our attention to these catalysts was attracted by the work of Whan and we started an investigation of these materials about 10 years ago with the doctoral research of A. Brenner (10), but

here I shall discuss the subsequent work done by R. G. Bowman, C. Defossé, R. Nakamura, M. Laniecki, and D. Pioch.

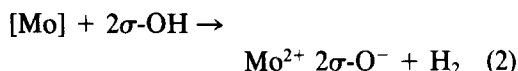
Surface Chemistry

For background it will be necessary to present some of the surface chemistry which accompanies the activation of $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$ in flowing hydrogen or helium (4).

Activating $\text{Mo}(\text{CO})_6/\text{PDA}$ in He or H_2 to 100°C leads to the formation of $\text{Mo}(\text{CO})_3/\text{PDA}$ in which surface ligands have replaced CO (11, 12). Elevation of the temperature in He to above 100°C leads to further liberation of CO starting at about 150°C . Carbon monoxide is accompanied by hydrogen and small amounts of methane. At 300°C , the products are roughly

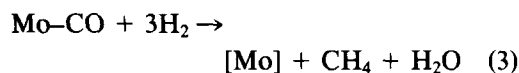


The surface reactions involved can be represented approximately by



Formation of H_2 and CH_4 , first observed with $\text{Mo}(\text{CO})_6/\text{PDA}$, has since been found to occur rather generally with metal carbonyls on alumina. Mo^{2+} represents only an average oxidation number and as shown by EPR even a little $\text{Mo}(\text{V})$ is formed. Heating above 300°C results in further liberation of H_2 and further oxidation of $\text{Mo}(\text{II})$ and by 500°C , the Mo is mostly $\text{Mo}(\text{VI})$.

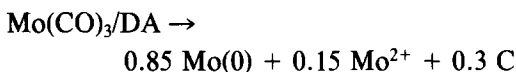
Heating in flowing H_2 results in the occurrence of reaction 1 accompanied by roughly an equal amount of reaction 3. $[\text{Mo}]$ presumably then reacts as in



reaction 2 and some of the H_2O from reaction 3 further oxidizes Mo^{2+} . By $\text{H}_2, 300^\circ$,

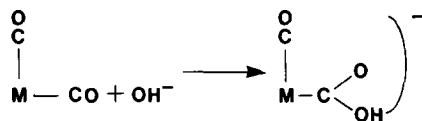
1 (which denotes heating in H_2 at 300°C for 1 hr), the oxidation number of Mo has an average value of about +3.

When $\text{Mo}(\text{CO})_6/\text{DA}$ is heated in helium, a reaction equivalent to 1 occurs, but the amount of $\sigma\text{-OH}$ present is insufficient to oxidize most of the $[\text{Mo}]$ formed. After $\text{DA};\text{He}, 300\text{--}500^\circ$ (which means that $\text{Mo}(\text{CO})_6/\text{DA}$ is heated in He to $300\text{--}500^\circ\text{C}$), the results can be represented in a typical case approximately by



If the sample is now heated in H_2 , methane liberation starts at about 400 and by 650°C , C/Mo on the catalyst has been reduced to 0.01 and by 950°C the catalyst consists of pure $\text{Mo}(0)$ supported on DA (4). This appears to have been the first preparation of a supported metallic molybdenum catalyst. Judging from the extent of CO chemisorption, the percentage exposed of Mo would be in the vicinity of 30%.

The first step in the preparation of all of these $\text{Mo}/\text{Al}_2\text{O}_3$ catalysts, the reaction of $\text{Mo}(\text{CO})_6$ with the surface of alumina, is a curious one. The usual substitution reactions of the carbonyl itself are very sluggish and temperatures above 100°C are needed for significant rates. Yet substitution of CO by surface ligands of alumina starts even at 25°C . The following reaction is known in



solution (11, 12). Formation of the COOH^- group labilizes a *cis*-CO and facilitates its substitution, for example, by phosphines. Probably, then $\sigma\text{-O}^-$ or $\sigma\text{-OH}$ functions in the same fashion and promotes the substitution of CO by other $\sigma\text{-O}^-$ or $\sigma\text{-OH}$ (11).

Catalytic Activity

Some of the activation procedures described above lead to materials of record or

TABLE 1
 Catalytic Activity of Various Activated Mo(CO)₆/Al₂O₃

	Metathesis of C ₃ H ₆ ^a	C ₃ H ₆ + H ₂ → C ₃ H ₈ ^b	Alkanes + H ₂ ^c	CO + H ₂ ^d	RH + D ₂ → RD + HD ^e	cyclo-C ₃ H ₆ ^f + H ₂
Mo(0)/DA ^g	?	++++	++++	+++	?	+++
Mo(0.3)/DA ^h	+	+++	+	+++	++++	+++
Mo(II)/PDA ⁱ	+++	++	0	++	++	+++
Mo(IV)/PDA ^j	0	+	0	?	0	++

^a Metathesis of propylene at ~60°C.

^b Hydrogenation of propylene at -46°C.

^c Hydrogenolysis of alkanes at ~250°C.

^d Hydrogenation of CO at 300°C.

^e Isotopic exchange between D₂ and cyclopentane at 20°C.

^f Hydrogenolysis of cyclopropane at 0–100°C.

^g DA;He,300°,1;H₂,650°,1, average oxidation number of Mo = 0.

^h DA;He,300–500°,1.

ⁱ PDA,He,300°,1.

^j PDA,He,400°,1.

near record highs for the catalytic activities in certain reactions. Table 1 gives a general overview of the catalytic activities of materials prepared by four particular pretreatments which were chosen to typify the general range of catalytic behaviors. A few specific comments on the details of each reaction follows.

Metathesis

The largest activity for metathesis results from sites which start as Mo²⁺(*cus*), *N_t* (turnover frequency per Mo) was 0.15 at 60°C. Only a small fraction of these sites become converted to sites active for metathesis (10). Presumably, precursor sites are converted to Mo=CHR species which effect metathesis by the Chauvin-Hérrison mechanism. The oxidation number of Mo in these sites is presumably higher than that in the precursor sites.

Hydrogenation of Propylene

(R. G. Bowman and M. Laniecki)

Many of the variously activated Mo(CO)₆/Al₂O₃ materials are catalysts for the hydrogenation of olefins (13, 14).

At 60°C in a pulse reactor using hydrogen carrier, Mo(CO)₃/PDA catalyzes simultaneously the metathesis and the hydrogenation of propylene. Increase in the pretreatment temperature in helium causes the rate of both reactions to increase, but that of hydrogenation increases much more rapidly than that of metathesis and conversions in hydrogenation become 100% even at 0°C. We, therefore, had to study hydrogenation at -46°C in a flowing mixture of propylene and hydrogen. Under these conditions, no products of metathesis were observed.

Figure 2 shows conversion in hydrogenation at -46°C for catalysts with four different pretreatments vs loading of Mo. Conversions for PDA;He,300°,1 were readily measured. The catalyst, PDA,H₂,300°,1 provided more difficulty, since even with only 0.7 mg of Mo on 0.25 g of PDA, conversions were almost 100%. DA;He or H₂,300°,1 were still more difficult and more than 0.2 mg was too much. When 0.2 mg Mo on DA;He,300°,1 was further pretreated H₂,400°,1, the conversion rose from 30 to 60% and H₂,500°,1 led to 100% hydrogenation. Thus, we do not know how active DA,He,300°,1;H₂,

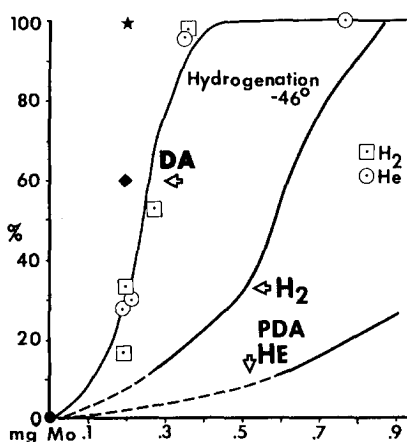


FIG. 2. Hydrogenation of propylene in percentage at -46°C , flow reactor, as a function of the amount of Mo on 0.25 g of alumina. The lower curve represents PDA;He, 300° , 1; the middle curve, PDA;H₂, 300° , 1; the upper curve, DA;H₂, 300° , 1 (squares) and DA;He, 300° , 1 (circles). The filled diamond is DA;He, 300° , 1; H₂, 400° , 1 and the star is DA;He, 300° , 1; H₂, 500° , 1.

650° , 1 (clean, metallic Mo/DA) would be. N_t per atom of Mo was greater than 1.7 sec^{-1} for DA;He, 300° , 1; H₂, 500° , 1 or, per Mo_s, N_t was greater than 5 sec^{-1} . For reference, under these conditions, N_t per Pt_s in Pt/SiO₂ would be about 0.3 sec^{-1} (15). The Mo/DA catalysts were so active that intrusion of mass and heat transfer effects may have led to some error in N_t 's.

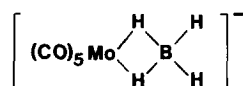
When propylene + D₂ was passed over the three catalysts of Fig. 2 at -46°C , the initial product of hydrogenation was predominantly C₃H₆D₂, but hydrogenation was accompanied by formation of exchanged propylene (14). Thus, at higher conversions, multiply exchanged propane appeared in the products. However, only very small amounts of propane with more than 5 atoms of deuterium were detected. Apparently, CD₂=CDCH₃ is for the most part the maximally exchanged propylene. We cannot be sure that the exchange of propylene did not occur at least in part on the alumina, since alumina alone is known to effect isotopic exchange between olefins and deuterium (16).

Isotopic Exchange between Deuterium and Cyclopentane (C. Defossé and M. Laniécki)

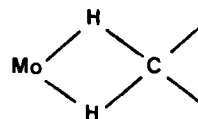
The catalysts activate cyclopentane rapidly at 20°C and are among the most active known supported catalysts for its isotopic exchange. Monodeuterocyclopentane constitutes 90% or more of the product. At 19°C , N_t per Mo was 0.5 sec^{-1} for DA;He, 300° , 1 or 1.5 sec^{-1} per Mo_s. N_t per Mo on PDA;He, 300° , 1 was 14% as large and for PDA;H₂, 300° , 1, 6%. Under these conditions, N_t per Pt_s in Pt/SiO₂ is about 0.001 sec^{-1} . Rhodium has about the same N_t as Mo/DA and that of tungsten is probably larger. Unfortunately, the activity of DA;He, 300° ; H₂, 650° has not been measured.

The rate of exchange of neopentane is less than 10% that of cyclopentane and that of methane is even slower.

The X-ray structure of the stable Mo(CO)₅(BH₄)⁻ is (17)



Methane is isoelectronic with BH₄⁻ and perhaps it is initially adsorbed in the same fashion. Because of the removal of one unit of overall negative charge, such a complex would be much less stable than the borohydride complex, but one does not seek a

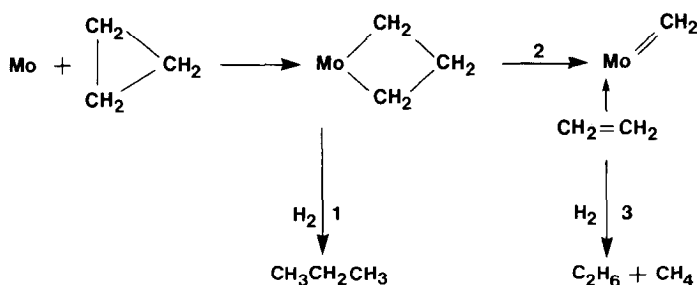
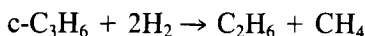
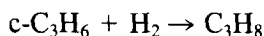


very stable intermediate for a reaction which is fast at 19°C . However, the intermediate must be stable enough to form to a substantial degree. The inductive effect of alkyl groups should make the complexes of higher alkanes more stable than that of methane, but the higher C-H bond energy in methane might also contribute to its slow reaction.

Hydrogenolysis of Cyclopropane

(R. G. Bowman)

Most of the pretreatment conditions lead to catalysts which are moderately active for the hydrogenolysis of cyclopropane. The catalysts belong to the class of Ni (18), Fe, Ru, Os (19) which give both single and double hydrogenolyses as concurrent reactions



One must assume that the reaction 2 + 3 is relatively most rapid vs. reaction 1 on the Mo(0) catalysts. Yet, these materials are not good metathesis catalysts. However, slow formation of a carbene intermediate from propylene might be the origin of slow metathesis on the Mo(0) materials.

Hydrogenation of Carbon Monoxide and Carbon Dioxide (R. G. Bowman)

Both DA and PDA and most pretreatments led to materials which converted H₂ + CO (5:1, P = 1 atm) to methane plus some ethane and propane at T ≈ 300°C (4). DA;He,300°,1 and DA;He,300°,1; H₂,650°,1 had the same activity, N_t (300°C) per Mo_s = 0.04 sec⁻¹. Such activity by supported metallic molybdenum is not surprising since a tungsten filament has been reported to be an active catalyst for methanation (20). Under equivalent conditions, N_t per Ni_s is 0.24 sec⁻¹ (21). Mo(II)/PDA (PDA;He,300°,1) and Mo(III)

Although rates vary rather little with alumina and pretreatment, the fraction of double in single plus double hydrogenolysis varies from 0.06 for Mo(III-IV) to 1 for catalysts on DA. For DA;He,500°, N_t per Mo_s was about 0.02 sec⁻¹ at 0°C. Pt_s in Pt/SiO₂ is 10 times more active, although it catalyzes only single hydrogenolysis (15).

Since these materials are believed to catalyze the metathesis of olefins by metallacyclobutane intermediates, it is tempting to think that single and double hydrogenolysis go by the following mechanism.

(PDA;H₂,300°,1) provided almost the same value of N_t, 0.001 sec⁻¹. The conditions of methanation expose a catalyst to CO, H₂O, and H₂ at 300°C. Presumably the Mo(II) and the Mo(III) catalysts come to some steady state oxidation number which is a balance between the simultaneous oxidation and reduction reactions which must be occurring. However, Mo(0) catalysts do not approach the same steady state level, at least during 1000 min which was our longest run. During this interval, rates are nearly constant. Apparently, the surface layer of the Mo(0) particles becomes converted to some steady state condition, but the metallic core remains unconverted. DA;He or H₂,300-500° are black and change to gray at 25°C in air only over several days. These catalysts remain black during methanation at 300°C.

Little carbon dioxide is formed during methanation, but H₂ + CO₂ gives the same products as H₂ + CO and at one-half the rate.

Hydrogenolysis of Alkanes (R. Nakamura and R. G. Bowman)

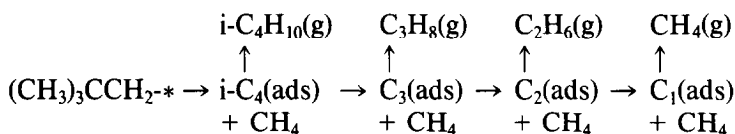
Mo(0)/DA ranks with the most active hydrogenolysis catalysts known (22). However, in contrast to methanation, only clean Mo(0)/DA is an active catalyst; in fact, as shown in Table 1, hydrogenolysis of alkanes is the extreme case of reactions for which Mo(0)/DA is the most active catalyst. Thus, with DA;He,300°,1;H₂,T_{act},1, trace activity for the hydrogenolysis of propane at 300°C appeared after T_{act} was 300°C and it increased steadily to T_{act} = 650°C. After T_{act} = 650–950°C, N_i(250°C) per Mo was 0.06 sec⁻¹ or per Mo_s, 0.2 sec⁻¹ (in a flow reactor with a large excess of hydrogen, H₂/C₃H₈ = 26). Both single and double hydrogenolysis were observed as concurrent reactions.



At 250°C, N_i per Mo for reaction 1 was

0.044 sec⁻¹ with E_a = 101 kJ mol⁻¹ and N_i for reaction 2 was 0.016 sec⁻¹ with E_a = 131 kJ mol⁻¹. The rate declined about 15% during the first hour on stream following which there was little decline for several hours. Carbonaceous deposits were formed during hydrogenolysis, since heating in H₂ to 950°C liberated CH₄ corresponding to C/Mo ≈ 0.05. This C/Mo is much smaller than would correspond to complete conversion to a molybdenum carbide.

Ethane, propane, and higher hydrocarbons were examined in a pulse reactor at 150–400°C. Except for ethane, single and double hydrogenolyses were observed and, for butane and higher, triple hydrogenolysis was also observed to give initial products. For example, on DA;H₂,650°,1 at 250°C, neopentane underwent 12% single, 46% double, 37% triple, and 5% quadruple hydrogenolysis. The last figure is subject to substantial error, but final cleavage of the adsorbed C₂ fragment was always found to be relatively slow. The surface reactions of neopentane can be represented

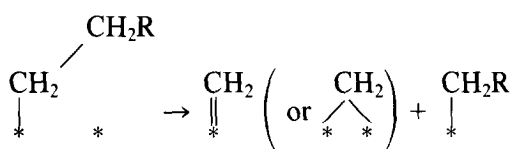


The last step is relatively slow.

Single hydrogenolysis of butane leads about equally to CH₄ + C₃H₈ and to 2C₂H₆. At 250°C, the relative rates of hydrogenolysis were propane 0.8, butane (1.00), pentane 1.4, neopentane 0.25, cyclopentane 0.9, and ethane 0.2. There was even less divergence in the rates at 300°C.

On ruthenium, N_i per Ru_s for the hydrogenolysis of ethane at 250°C may be calculated from the data of Sinfelt (23) to be 0.035 sec⁻¹. The experimental conditions were rather different from ours, but it appears likely that the hydrogenolytic activities of molybdenum and ruthenium are not far apart.

One may suspect that asking "what is the mechanism of hydrogenolysis?" is apt to be unrewarding. It is likely that a number of different mechanisms occur concurrently. A number of reactions are known in organometallic chemistry, the reverses of which should contribute to hydrogenolysis. These include, the formation and fragmentation of 1,3-diadsorbed alkane as at the end of the section on cyclopropane, the formation of 1,4-diadsorbed alkane and its decomposition into two molecules of adsorbed olefin (24), and a reaction like *CH₂CH₂* → 2CH₂=. In addition the retro-Fischer-Tropsch reaction should certainly have a finite rate (25).



Reduction of MoO₃/PDA to Mo(0)/DA
(R. Nakamura and D. Pioch)

Hydrogenolysis is very sensitive to poisoning. Pulses of O₂ and CO with O₂/Mo and CO/Mo not much in excess of unity almost completely eliminated hydrogenolysis. Even pulses of N₂ at 300°C gave substantial poisoning. In all cases the original activity was restored by H₂, 950°C, 0.5. Not many supported catalysts would survive such treatment. This resistance to loss of metal area is probably related to the very high lattice energy of molybdenum.

The regenerability of Mo(0)/DA poisoned by oxygen led us to test PDA; He, 300°, 1; H₂, 950°, 1, i.e., Mo(2+)/PDA; H₂, 950°. It gave the same activity for the hydrogenolysis of propane as Mo(0)/DA. This result then required us to test MoO₃/PDA; H₂, 950° (22). It gave essentially the same activity as Mo(0)/DA for the hydrogenolysis of propane and the hydrogenation of propylene. Titration of the samples to MoO₃/Al₂O₃ by O₂ at 500°C showed that H₂, 650°, 1 leads to Mo(II) and H₂, 800°, 1 gives Mo(0).

MoO₃/PDA; H₂, 900° has been examined by dark field electron microscopy by Professor M. J. Jacamán. He found the sample to consist of particles of metallic molybdenum, 1 to 4 nm in diameter supported on alumina. In the Department of Materials Science at Northwestern University, the material was examined by EXAFS by Messrs. S. Sunshine, D. Wilcox, and J. Watson supervised by Dr. P. Georgopoulos. After H₂, 900°, the material contained metallic molybdenum, but, after H₂, 650°, it was still oxidic. Reduction to Mo(0) has been confirmed by Peri using infrared absorption of adsorbed CO and NO as the test (26).

MoO₃/Al₂O₃ has been extensively exam-

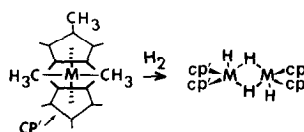
ined and with particular thoroughness by W. K. Hall (leading Refs. (27)). In general, previous literature reports that MoO₃/Al₂O₃ cannot be reduced below about Mo(IV), but this probably really means not below Mo(IV) in Pyrex apparatus. It would be interesting to determine the catalytic and surface chemical relationships among the Mo(CO)₆/Al₂O₃ catalysts, reduced MoO₃/PDA, variously treated Mo(π -allyl)₄/SiO₂, and Al₂O₃ (28–30) and Mo₂(π -allyl)₄/SiO₂ and Al₂O₃ (31). The last material has been reported to possess exceptional activity for the hydrogenation of olefins.

Activity of W(CO)₆/Al₂O₃

A few experiments have been run with W(CO)₆/Al₂O₃. The surface chemistry which occurs during activation appears to be very much like that with Mo(CO)₆/Al₂O₃. The catalytic activity is also similar for the hydrogenation of propylene and of carbon monoxide and for the hydrogenolysis of cyclopropane. It also has activity for the metathesis of olefins similar to that of Mo(CO)₆/Al₂O₃ (7, 13a).

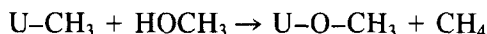
ORGANOACTINIDES ON ALUMINA (M.-Y. He, R. Nakamura, R. G. Bowman, and P. J. Fagan)

No history is needed here, because, insofar as we are aware, there has been no previous study of supported organoactinide complexes. Our attention was attracted to this area because the absence of such studies provided the possibility of discovering new chemistry which might result, in particular, from the large maximum coordination number of actinide atoms. We started with the U(CH₃)₂ complex shown below on alumina. The geometry of the complex is

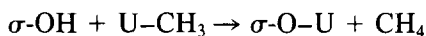


roughly tetrahedral and the use of the pentamethylcyclopentadienyl anion ligand (Cp, one methyl is shown above for emphasis)

gives a complex with only two dienyl ligands which is thermally stable yet coordinatively unsaturated. The complex reacts with hydrogen in solution to give the μ -bridged dimer shown in the insert above. It was thought that the steric bulk of the surface might inhibit dimer formation in adsorbed hydride. The complex reacts with alcohols by protolysis,



The σ -OH of alumina should react similarly to bind the complex to the surface



although, as it turned out, this last reaction is a disadvantage. The thorium complex behaves similarly.

We examined the catalytic activity of the hydride complexes in toluene solvent at 25°C. For the hydrogenation of 1-hexene at 25°C, $P_{\text{H}_2} = 1$ atm, uranium hydride complex, $N_t = 0.019 \text{ sec}^{-1}$; thorium hydride complex, $N_t = 0.00015 \text{ sec}^{-1}$. Both complexes exhibited only weak activity for the polymerization of ethylene at 25°C, 1 atm.

We then tested the hydrogenative catalytic activity of the $\text{U}(\text{CH}_3)_2$ complex which was deposited on alumina from a pentane solution by evaporating the pentane at 0°C. The sample was then pretreated at selected temperatures in helium and/or hydrogen and $\text{H}_2/\text{propylene} = 4.7$ was passed over the catalyst. The supported catalyst is extremely sensitive to traces of O_2 and H_2O , but even in our first experiments we had to lower the temperature of the catalyst to -47°C to keep the conversion under 100% (32). Improvements in technique soon led even -47°C to be too high a temperature as shown in Table 2. Although the flow rate was steadily increased during the series, we were fighting a losing battle against too rapid a reaction as may be seen from the course of the conversion. We had learned that activity increased with temperature of activation in hydrogen and that -47°C was too high a temperature for hydrogenation runs. We then lowered the temperature to

TABLE 2

Hydrogenation of Propylene on 13.2 μmol of $\text{U}(\text{CH}_3)_2$ on 0.25 g of DA at -47°C

Pretreatment ^a in H_2	0°,1	50°,1	100°,1	150°,1
Flow of C_3H_6 in $\text{cm}^3 \text{ min}^{-1}$	7.0	10.3	14.1	19.1
Conversion, %	96.5	99.7	99.9	100
N_t , sec^{-1}	>0.35	>0.53	>0.73	>1.03

^a After evaporating the pentane at 0°C, the catalyst was activated $\text{H}_2, 0^\circ, 1$ and a hydrogenation run made. The catalyst was then further activated $\text{H}_2, 50^\circ, 1$, a hydrogenation run made, etc.

-63°C and after activations in hydrogen at 0, 100, and 150°C , the values of N_t were 0.58, 0.89, and 0.92 sec^{-1} , respectively.

Rates of hydrogenation on $\text{Th}(\text{CH}_3)_2$ were nearly the same as on $\text{U}(\text{CH}_3)_2$. PDA gave rates which were only a few percent of those of DA and silica gel was an even less active support than PDA.

In certain experiments, after a hydrogenation run at -63°C , small pulses of CO were injected into flowing He or H_2 at 25°C and the amount of "irreversible" adsorption (that is, the amount of CO retained by the catalyst after a 7-min sweep by the carrier gas) was measured. Amounts of CO adsorbed were small; values of CO/M were only about 2% for both $\text{U}(\text{CH}_3)_2$ and $\text{Th}(\text{CH}_3)_2$, but rates of subsequent hydrogenation were drastically reduced. Where injection of CO was effected into carrier hydrogen, the low subsequent rate of hydrogenation at -63°C persisted for at least 2 hr, but for injection into carrier helium, the rate rose over 90 min to near its original value.

Thus, only about 2% of U and Th had become converted to active catalytic sites. Per active site, N_t would be in the vicinity of $30\text{--}50 \text{ sec}^{-1}$. These are very active hydrogenation catalysts. For comparison, we measured the rate of hydrogenation on a Rh/SiO₂ catalyst (percentage exposed of Rh = 60%) prepared by ion exchange with $\text{Rh}(\text{NH}_3)_5(\text{OH}_2)^{3+}$ and pretreated $\text{O}_2, 300^\circ, 0.5; \text{H}_2, 300^\circ, 1; \text{He}, 300^\circ, 1$, cool to -63°C in He. After this, N_t per Rh_s for hydrogenation at -63°C was 28 sec^{-1} . Thus,

TABLE 3

Fraction of One CH₄ Liberated during Pretreatment of M(CH₃)₂/Al₂O₃

Activation ^a	44 μmol U on DA	26 μmol U on PDA	47 μmol Th on DA
He, 0°, 1	0.24	1.31	0.15
He, 25°, 1	0.03	0.06	0.02
He, 100°, 1	0.23	0.17	0.09
H ₂ , 100°, 1	0.24	0.06	
Total	0.74	1.60	

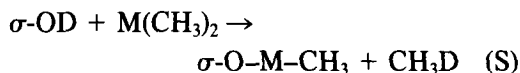
^a The activations were run in sequence on one batch of catalyst.

although the rates are so large that there may have been mass and heat transport problems, it is clear that U(CH₃)₂/DA and Th(CH₃)₂/DA rank among the most active hydrogenation catalysts known. However, they would be behind rhodium if activities were compared on the basis of total micromoles of metal.

Experiments were also run with M(CH₃)₂/Al₂O₃ to determine what gases were liberated during pretreatment and how much. Yields of methane are given in Table 3. No evolution of H₂ could be detected. Products of reaction of the Cp' ligand appeared in the gas phase only above 150°C.

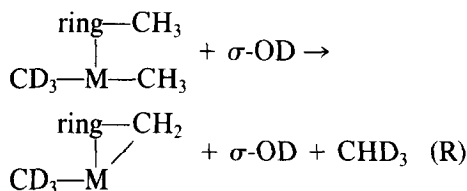
We have investigated a number of approaches to surface characterization. However, it is not easy to determine the identity of catalytic sites when they amount to only a few percents of the surface species. One approach involved deuterium isotopic labeling, σ-OH vs σ-OD and M(CH₃)₂ vs M(CD₃)₂ coupled with measurement of the isotopic yields of liberated methane, particularly CH₄ vs CH₃D and CHD₃ vs CD₄ (33).

Thus, formation of CH₃D from σ-OD and M(CH₃)₂ characterizes the protolysis mentioned in the introduction to this section.

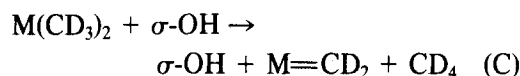


However, use of σ-OD and M(CD₃)₂ led to substantial amounts of CHD₃. We believe

that CHD₃ is formed by reaction between M-CD₃ and a CH₃ group of the pentamethylcyclopentadienyl ligand.



Finally, M(CD₃)₂ + σ-OH led to formation of some CD₄. This appears to result from



where the "carbene" M=CD₂ is probably stabilized by interaction with Al³⁺(*cus*)-O²⁻(*cus*) ion pairs of the surface in analogy to Group IVb carbenes stabilized by Al-X (34, 35). Results with U(CH₃)₂ are shown in Table 4. It is interesting that the yield of reaction C from U(CH₃)₂/DA, about 3% of total U, is close to that of the fraction of U atoms which become active catalytic sites. The product of reaction C is apparently not a conventional carbene since it is a very poor catalyst for the metathesis of propylene. Behavior with respect to yields via reactions S, R, and C from Th(CH₃)₂/DA is nearly the same as with U(CH₃)₂/DA.

TABLE 4

Surface Reactions with U(CH₃)₂/DA Determined by Isotopic Labeling

Surface Reaction (%)	Percentage of reaction via S, R, and C after ^a		
	He, 0°, 1	He, 25°, 1	He, 100°, 1
By S	45	25 ^b	19
By R	45	63 ^b	73
By C	7	12 ^b	11
Methane ^c	6	1 ^b	9.5

^a Deuteromethanes were collected after each successive pretreatment.

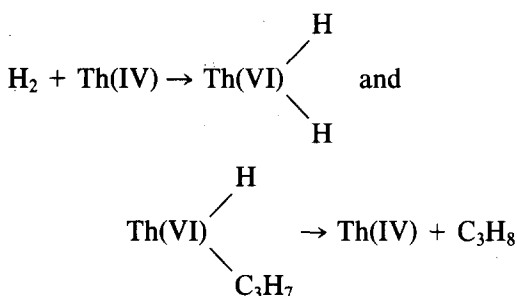
^b Low accuracy because of very small amounts of methane.

^c Yield of methane as percentage of total methyl groups in U(CH₃)₂.

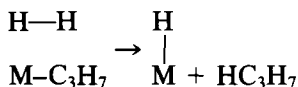
Not surprisingly, use of PDA led to a much larger yield of methane by reaction S (protolysis). Reaction S appears to be a dead-end reaction which leads to the loss of potential sites.

Thus, activated $U(CH_3)_2/DA$ and $Th(CH_3)_2/DA$ are very active hydrogenation catalysts. Further, we have found that the thorium hydride dimer shown at the beginning of this section deposited on DA has nearly as high an activity as these two, but the amount of CO adsorption needed to poison hydrogenation is larger, about 9% of Th. However, not all actinide complexes have high activity; the corresponding $(Cp')_2U(CH_3)Cl$ complex supported on DA had an activity of only 2–3% of the others.

Thorium is effectively confined to oxidation number +4. Therefore, all intermediates in the catalytic cycle with Th and presumably with U complexes have O.N. = 4. This information is important mechanistically since it eliminates the possibility of reaction via oxidative addition or reductive elimination, for example,



We suspect that the final step of the hydrogenation will be rather



However, these M–C and M–H bonds must have some special feature, perhaps interaction with $Al^{3+}-O^{2-}$, because most of the M– CH_3 bonds on the catalyst react only slowly with hydrogen (Table 3) and we do not yet understand why. Considerable further work will be needed to establish a reasonably secure mechanism.

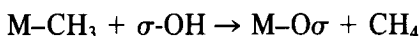
Polymerization of Ethylene

$U(CH_3)_2/DA$ and $Th(CH_3)_2/DA$ are also active catalysts for the polymerization of ethylene at 25°C, 1 atm. In these experiments we passed a series of pulses, $C_2H_4/M \approx 1$, over the catalyst and measured the amount of ethylene in the effluent. For the first pulses, adsorption was 100%. In some cases, the pulse sequence was continued until the moles of ethylene lost was 40–50 times as large as the moles of U or Th on the catalyst. At the termination of the sequence, the fraction of each pulse adsorbed was still 50–75%. The thorium hydride on DA was less active; at 25°C after He, 100°, 1, 50% of the first pulse of ethylene was adsorbed and the adsorption of ethylene became zero at the fourteenth pulse by which time C_2H_4/Th had reached 3.6. The $U(CH_3)Cl$ complex on DA had only a low activity for ethylene polymerization.

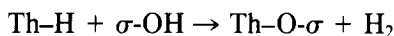
CONCLUDING REMARKS

Experiments with $Mn(CO)_5CH_3$ and $CpFe(CH_3)(CO)_2$ demonstrate the presence of adjacent $Al^{3+}(cus)$ (Lewis acid) and O^{2-} (Lewis base) sites on PDA and DA. Pure silica lacks both types of sites. Clusters of platinum atoms 1.2–8 nm in diameter interact little with the surfaces of silica or PDA and the catalytic activities of Pt/SiO_2 and $Pt/pure Al_2O_3$ differ little (36). However, $Mo(CO)_6/PDA$ and $Mo(CO)_6/pure silica$ behave quite differently. $Mo(CO)_6/PDA; He, 300^\circ$ and $Mo(CO)_6/DA; He, 300^\circ$ give active catalysts and little $Mo(CO)_6$ volatilizes from the alumina during evaporation of the solvent and subsequent heating in flowing helium. However, most of the $Mo(CO)_6$ volatilizes during similar treatment of $Mo(CO)_6/SiO_2$. Silica has no basic groups which can stabilize $Mo(CO)_6$ via formation of $(CO)_5Mo(COB)$.

The concentration of $\sigma-OH$ on alumina has a profound effect in suitable cases via protolysis and via oxidation of metal atoms. Thus, protolysis occurs with $U(CH_3)_2$ and $Th(CH_3)_2$ on alumina,



On PDA, protolysis is so extensive that little of the complex is available to form active sites for hydrogenation. On DA, however, where the concentration of $\sigma-OH$ is small, very active hydrogenation catalysts result. Similarly, protolysis occurs with the thorium hydride,



Such protolytic reactions of $\sigma-OH$ are old particularly in connection with the liberation of propylene from $M(\text{allyl})_n$ on silica or alumina.

In the oxidative reaction of $\sigma-OH$, the metal atom or ion is oxidized. In the case of $Mo(CO)_6$, Mo reacts after loss of CO



and some of the hydrogen is diverted to reduction of $Mo-CO$ to CH_4 . Thus, metallic molybdenum does not result from heating $Mo(CO)_6/PDA$ in helium to 300–500°C. Rather, surface $Mo^{2+}-Mo^{6+}$ are formed in an average oxidation number which varies from about +2 near 280°C to almost +6 at 500°C. With DA, these reactions are largely suppressed and metallic molybdenum results.

Finally, if Mo^{2+}/PDA or MoO_3/HA is heated in hydrogen to about 950°C, dehydroxylation of the alumina and reduction of the Mo^{n+} both occur to produce metallic molybdenum supported on DA.

ACKNOWLEDGMENTS

Without the skills and knowledge of my colleagues, T. J. Marks and D. F. Shriver, much of this work would have been impossible. This work was supported in large measure by the Ipatieff Fund of Northwestern University and also by the Department of Energy, the Petroleum Research Fund of the American Chemical Society, NATO, and the National Science Foundation.

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