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Hydrogenation of Propylene and Hydrogenolysis of Cyclopropane on Activated $Mo(CO)_6$/Alumina Catalysts

ROBERT G. BOWMAN AND ROBERT L. BURWELL, JR.[1]

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

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The hydrogenation of propylene and the hydrogenolysis of cyclopropane has been studied on $Mo(CO)_6/Al_2O_3$ activated in flowing He or H_2. The γ-alumina was either partially dehydroxylated in flowing He at 475°C (PDA) or nearly completely dehydroxylated at 950°C (DA). In a pulse reactor with hydrogen carrier, $Mo(CO)_3$/PDA converted propylene both to ethylene + 2-butene (metathesis) and to propane (hydrogenation). Activation in He or in H_2 to 300°C (average ON $\simeq +2$ and $+3$, respectively) greatly enhanced the activity of $Mo(CO)_3$/PDA for hydrogenation which had to be measured in a flow reactor at −46°C. $Mo(CO)_6$/DA activated to 300–500°C in He or in H_2 (average ON near zero) was an even more active catalyst and heating DA;He,300° in H_2 to 500°C led to a still more active catalyst. Hydrogenation was approximately zero order in propylene and first order in hydrogen. The same materials catalyzed the hydrogenolysis of cyclopropane at 0–100°C. DA;He,300° and PDA;He,300° were the most active catalysts. Both single and double hydrogenolysis occurred as initial reactions to form propane and methane + ethane, respectively. Double hydrogenolysis was favored by molybdenum in lower ON.

INTRODUCTION

Activated molybdenum hexacarbonyl on partially hydroxylated alumina ($Mo(CO)_6$/PDA) was one of the first catalysts to be discovered (*1*) in the class of (metal carbonyl)/Al_2O_3 (*2, 3*) and other (organometallic complex)/support (*3, 4*) which currently attract considerable attention. The metathesis of olefins was discovered on activated $Mo(CO)_6$/PDA (*1*) and subsequently various of the activated $Mo(CO)_6/Al_2O_3$'s have been found also to catalyze hydrogenation of CO (*5*), the hydrogenation of olefins (*6–8*), double bond migration in olefins (*9*), isotopic exchange between D_2 and alkanes (*8*), and the hydrogenolysis of alkanes (*10*).

A variety of materials with different compositions and catalytic activities can be obtained starting with $Mo(CO)_6/Al_2O_3$. The important variables affecting the results of activation are: (1) the gas flowing through the catalyst bed during activation, (2) the temperature of the catalyst during activation T_{act} and probably most important (*5, 11*), the degree of dehydroxylation of the alumina, that is, the degree to which the surface hydroxyl ions which cover the surface of the initial alumina have undergone condensation to evolve water and leave O^{2-} ions on the surface. In particular, catalysts starting as $Mo(CO)_6$/DA (DA is nearly completely dehydroxylated alumina) have provided the first examples of supported molybdenum catalysts in which the oxidation number of molybdenum is zero or nearly zero. These Mo(0)/DA catalysts exhibit remarkable catalytic activities (*5*) some of which are further elaborated in the present paper.

In retrospect, some earlier investigations on evaporated films of molybdenum or tungsten or on cleaned tungsten filaments had indicated that supported Mo(0) or W(0) catalysts might well be unusually active for some reactions. Thus, Kouskova *et al.* (*12*) reported that the hydrogenation of ethylene on molybdenum film was rapid at 0°C, Merta and Ponec (*13*), that the hydro-

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[1] To whom correspondence should be addressed.

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genolysis of cyclopropane was rapid on molybdenum film at 0°C, James and Moyes (*14*), that the hydrogenation of benzene and its isotopic exchange with deuterium were rapid on tungsten at 0°C, and Kelley *et al.* (*15*), that the hydrogenation of CO was rapid on tungsten filament.

Further, of course, considerable work has been done on MoO_3/Al_2O_3 catalysts after pretreatment in hydrogen at up to ~500°C. Here, the work of W. K. Hall and collaborators has been particularly extensive (*16, 17*). In general, reduction does not seem to go much below Mo(IV), catalytic activities for reactions not involving oxidation increase with increasing degree of reduction, and activities are lower than for the molybdenum catalysts of lower oxidation number prepared from $Mo(CO)_6/Al_2O_3$.

In this paper we report the results of our studies on the hydrogenation of propylene of which only a few items have been previously published (*5, 8, 18*) and studies on the hydrogenolysis of cyclopropane.

EXPERIMENTAL

Materials and Techniques

The support was PHF γ-Al_2O_3 of the American Cyanamid Company, 99.99% pure. It was used in three degrees of hydroxylation: HA, nearly fully hydroxylated; PDA, partially dehydroxylated by heating in flowing helium at 475°C; and DA, nearly fully dehydroxylated by heating at 950°C in flowing helium (5). DA appears to be a mixture of γ- and δ-alumina with little loss in texture from that of the initial alumina.

Catalysts were prepared by evaporation of pentane from a pentane solution of $Mo(CO)_6$ in a fluidized slurry of HA, PDA, or DA previously prepared in the reactor, a U-tube of fused silica (*11*). We employed 0.25 g of alumina (120–140 mesh) and from 2 to 45 μmol of $Mo(CO)_6$ dissolved in ~1.5 cc of pentane. The apparatus could be operated either as a pulse or a flow reactor. In the former case the loop volume was 1.019 cc so that at a pressure of 740 torr, a pulse contained about 40 μmol. Flow rates of hydrogen or helium in the pulse mode were normally 30 cc min^{-1} and the pulse width at the catalyst was about 15 sec. Since the catalysts employed are very air-sensitive, the content in oxygen was reduced to below 0.02 ppm by MnO traps (*19*).

TABLE 1

Activity of Alumina Alone

Reactant	Alumina	T°C	Conversion (%)	N_t per nm^2 (sec^{-1})
Pulse reactor, flowing hydrogen				
Propylene	PDA	100	4[a]	
Ethylene	PDA	150	10[a]	
Propylene	DA	100	9[a]	
Propylene	DA	125	19[a]	
Propylene	DA	150	35[a]	
Cyclopropane	PDA	150	1,[a] 0.5[b]	
Cyclopropane	DA	155	1.5[a] 1[b]	
Continuous flow reactor, H_2/propylene = 4.7				
Propylene	PDA	100	0.7[a]	3.8×10^{-4}
Propylene	PDA[c]	100	0.85[a]	4.6×10^{-4}
Propylene	DA	100	1.05[a]	5.6×10^{-4}

[a] Yield of alkane (%).

[b] Yield of propylene (%). No methane or ethane were noted.

[c] Dehydroxylated at 600°C.

Mixtures of propylene and hydrogen for use in the flow reactor mode were prepared by passage of hydrogen through a bed of Filtros saturated with liquid propylene and held at −78°C (*20*). Before distilling the propylene into the porous Filtros, the propylene was collected as a liquid, a first fraction was rejected, the middle fraction was distilled onto the Filtros, and the residue was rejected. The exit gas from the Filtros saturator contained 132 torr of propylene. The flow rate of hydrogen was normally 30 cc min^{-1}.

Activity of Alumina Alone

At 60°C, neither PDA nor DA alone exhibited significant activity for the metathesis or hydrogenation of propylene or for the hydrogenolysis of cyclopropane. Some activities at 100–150°C are shown in Table 1.

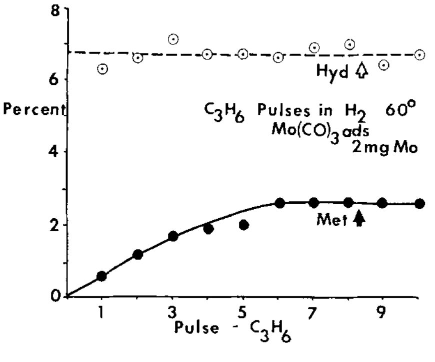


FIG. 1. Hydrogenation (Hyd) and metathesis (Met) in pulses of propylene in hydrogen carrier passing over $Mo(CO)_3$/PDA at 60°C (2.00 mg Mo/PDA; H_2,100°,1). Filled circles give the conversion per pulse into products of metathesis (ethylene and 2-butene) versus pulse number. Open circles give the conversion per pulse by hydrogenation to propane. The two reactions are concurrent.

Metathesis and Hydrogenation on $Mo(CO)_6$/PDA and $Mo(CO)_6$/HA Activated at 100°C

Activation to 100°C in helium gave the same results as in hydrogen, but this was not usually true for larger T_{act}. Figure 1 shows conversions for metathesis ($C_2 + C_4$, alkenes or alkanes) and hydrogenation to propane of pulses of propylene in flowing hydrogen at 60°C. In helium carrier, conversion in metathesis also rose with pulse number (*21*) but the maximum conversions for metathesis were 2.5 times larger in helium. At 0°C in hydrogen, traces of propane but no products of metathesis were detected. The activity for hydrogenation and the maximum activity for metathesis were linear in loading from 5 to 40 μmol Mo per 0.25 g of Al_2O_3.

Hydrogenation and Metathesis on $Mo(CO)_6$/PDA Activated above 100°C

Figure 2 shows conversions in the hydrogenation of propylene at −46°C and in metathesis in a pulse reactor in flowing helium at 60°C as a function of T_{act} with PDA;He, T_{act}. One sample of catalyst was employed for all hydrogenations, another for metatheses and after the measurement of conversion, the catalyst was activated in helium to the next higher temperature, a new measurement was made, etc.

To avoid a series of successive activations, activity for metathesis by PDA;He, 300°,1 was measured in helium as in Fig. 2. The catalyst was then retreated He,300°,1 and metathesis in helium at 60°C and then hydrogenation at −46°C were measured as in Fig. 2. The degree of metathesis was 98% of that after the first He,300° and absolute conversion in hydrogenation was 19%. Another sample of catalyst was examined in the same fashion, but the retreatment was He,400°,1. Metathesis was 1.5% of that after the original He,300° and the absolute conversion in hydrogenation was 15%. When the retreatment was He,500°,1, metathesis was zero and hydrogenation, 1%. The catalysts contained 6.6–9.0 μmol Mo but the figures given have been converted to a 6.6 μmol basis.

At 60°C, 21 μmol/PDA;H_2,175° hydrogenated 88% of the first pulse in carrier hydrogen. The conversion decreased to 81% in pulse 9 and then was constant to pulse 15. After activation in H_2 to much above 175°C, conversions in the pulse mode at 0°C were 100% even for loadings of 3 μmol of Mo. Figure 3 shows the activity for PDA;

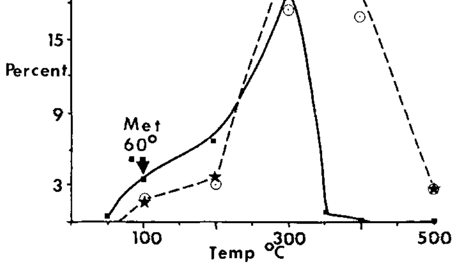


FIG. 2. Activity for the hydrogenation (Hyd) and metathesis (Met) of propylene as $f(T_{act})$ of PDA;He, T_{act}. Hydrogenation was measured in a flow reactor at −46°C on 0.82 mg Mo/PDA activated in sequence at increasing temperatures. Stars represent activity after 5 min on stream, circles, after 30 min. Metathesis, squares, was measured in a pulse reactor with helium carrier at 60°C on 1.21 mg Mo/PDA.

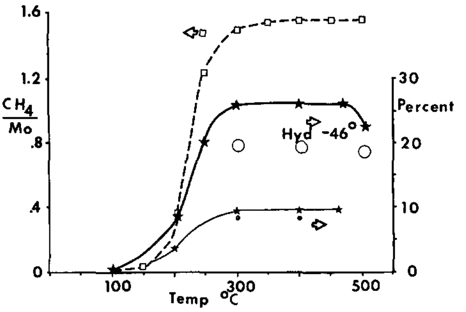


FIG. 3. Conversion of propylene to propane in a flow reactor at −46°C and CH_4/Mo during activation vs T_{act} for PDA;H_2,T_{act}. Large stars give the conversion after 5 min on stream for a catalyst with 0.60 mg Mo and the small stars, 0.33 mg Mo. Circles represent activity after 60 min. Squares represent the cumulative liberation of CH_4/Mo at increasing T_{act} for a 1.88 mg Mo sample.

H_2,T_{act} and the parallel evolutions of methane (formed by reduction of carbonyl ligands by H_2) expressed as CH_4/Mo.

At 25°C, H_2 + propylene, 10 μmol PDA; He,300°, flow reactor, the products of metathesis (ethane and butane) increased over one hour to reach ~2% for 10 μmol Mo. In another run which differed only in the carrier being helium, the yield in metathesis decreased with time, from 4.1% (for 10 μmol Mo) at 5 min to 2.8% at 60 min. The initial value of turnover frequency N_t was 0.014 sec^{-1} per Mo.

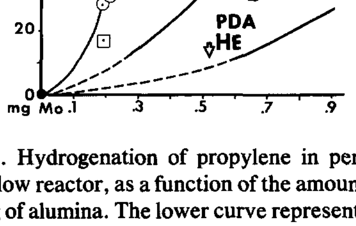


FIG. 4. Hydrogenation of propylene in percent at −46°C, flow reactor, as a function of the amount of Mo on 0.25 g of alumina. The lower curve represents PDA; He,300°,1; the middle curve, PDA;H_2;300°,1; the upper curve, DA;H_2,500°,1 (squares) and DA;He,300°,1 (circles). The filled diamond is DA;He,300°,1;H_2, 400°,1 and the star is DA;He,300°,1;H_2,400°,1;H_2, 500°,1.

Conversion in hydrogenation at −46°C as a function of loading is shown for PDA;He, 300° and PDA;H_2,300° in Fig. 4.

The activity for hydrogenation of PDA; He or H_2,300° at −46° generally declined during the first 30 min, typically by about 30%, but then declined negligibly in a further 60 min. H_2,300°,1 restored the initial activity and rate of decline of a catalyst originally activated H_2,300°,1, but H_2,30° or H_2,200° led to incomplete restoration of activity.

In duplicate experiments, a pulse, O_2/Mo = 1.0, was injected into the hydrogen stream passing at 60°C over PDA;H_2,100° after the activity for metathesis had maximized (see Fig. 1). The conversion in metathesis rose by a factor of 3.5, whereas that in hydrogenation was halved. Another pulse, O_2/Mo = 0.5, roughly halved both activities. Results of flow experiments at 25°C in which O_2 was injected are given in Table 2.

Injection of CO into the hydrogen-propylene flow at −46°C caused the activity for hydrogenation to drop nearly to zero. However, the activity recovered slowly to about 10% of the initial activity both for PDA;He, 300° and PDA;H_2,300°. In a flow experiment at 25°C with PDA;H_2,300°, a pulse of

TABLE 2

Poisoning of Catalysts on PDA by O_2[a]

Catalyst	O_2/Mo[b]	Metathesis (%)	Hydrogenation (%)
13.8 μmol/PDA;	0.00	0.0	100
H_2,300°	0.79	5.3	2.3
10.4 μmol/PDA;	0.00	1.7	87.4
He,300°	0.21	6.2	11.0
	0.42	6.6	1.0
	0.63	3.9	0.0
	1.05	3.9	0.0
	4.84	3.3	0.0

[a] Flow mode, propylene + H_2 at 25°C.
[b] Cumulative amount of O_2 injected.

TABLE 3

Isomerization of 1-Butene to 2-Butene on 32 μmol PDA/He,T_{act}, Pulse Reactor, 60°C

T_{act} (°C)	2-Butene[a] (%)	Metathesis, 5[b]
100	54	6
300	46	20
400	2.9	0.15

[a] Percent of 1-butene converted to *cis*- and *trans*-2-butene.

[b] Ethylene and propylene measured. It was assumed that amounts of 3-hexene equal to that of ethylene and of 2-pentene equal to that of propylene were formed.

CO, CO/Mo = 3 caused the hydrogenation to drop from 100 to 55%. In 10 min the hydrogenation returned to 100%. A further CO/Mo = 12.5 depressed the conversion to 3%, but it had returned to 100% in 30 min. PDA;He,300° and PDA;He,400° behaved similarly, but the recovery stopped at about 50% hydrogenation for He,300° and at 25% for He,400°.

Isomerization of 1-butene to 2-butene. This reaction was investigated in the pulse mode, helium carrier, 60°C, see Table 3.

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

Figure 4 shows activity for hydrogenation at −46°C as a function of loading for DA;He,300° and DA;H_2,500°, but all temperatures in the range of 300–500°C give rather similar activities for both gases.

Propylene was hydrogenated on 14.4 μmol/DA;He,500° at −78°C in a slurry reactor. After preparation and activation of the catalyst, 1 cc of propylene was condensed in the reactor (10-mm i.d.) at −78°C and hydrogen saturated with propylene at −78°C was passed through the reactor to fluidize the catalyst in the liquid propylene. After 5 min, the exit gas contained 2.5% propane and after 30 min, 4.4%.

Hydrogenolysis of Cyclopropane

The hydrogenolysis of cyclopropane on activated $Mo(CO)_6/Al_2O_3$ catalysts involves two concurrent reactions, a single hydrogenolysis with a rate r_I and a double hydrogenolysis with the rate r_{II}. The amounts of methane and ethane formed were equal within the experimental error. Results of pulse experiments are shown in Table 4. The ratio of moles of propane formed to that of one-half of ethane plus methane was taken as equal to r_I/r_{II}. Only short sequences of pulses were examined. Conversions were nearly constant to five pulses.

Pulses of cyclopropane were injected into helium flowing over some PDA;He, 300°,1 catalysts at 150°C. Catalysts containing 33.2, 26.0, and 20.3 μmol Mo led to 30, 15, and 8% conversion to olefins. In the first pulse about 30% of the product corresponded to metathesis of the propylene formed initially. Metathesis decreased with pulse number but total conversion was independent of pulse number. The 20 μmol catalyst was reactivated He,395°. It gave

TABLE 4

Hydrogenolysis of Cyclopropane in the Pulse Mode

Catalyst	Mo (μmol)	T_{rxn}[a] (°C)	Conversion (%)	r_I/r_{II}[b]
HA;H_2,300°	26.1	100	14	3.6
PDA;H_2,280°	15.6	100	60	23[e]
H_2,300°	26.6	25	1.3	18
	22.1	100	74	7.0[d]
H_2,500°	15.6[c]	100	80	~200
PDA;He,300°	33.2	65	51	5.8
	24.3	100	100	2.5
He,400°	31.4	100	25	18
DA;He,300°	17.0	100	100	1.7[f]
He,500°	14.4	0	3.5	1.2[f]
	32.8	0	8.6	1.0[f]
	33.5	0	6.6	0.63
	32.8[c]	55	80	0.75
	3.6	100	63	0.75
DA;H_2,300°	29.3	0	5.4	0.73
	12.6	100	100	0.41
	21.3	100	100	0.30
H_2,400°	21.3[c]	100	93	0.78
H_2,500°	17.4	100	68	1.2
DA;He,300° followed by				
H_2,300°	16.7	100	100	0.53[d]
H_2,650°	15.3	100	61	1.3

[a] Temperature of reaction.

[b] For the second or third pulse unless otherwise noted.

[c] The catalysts with the same loading in Mo previously pretreated in H_2 was treated with H_2 at the higher temperature.

[d] Fourth pulse.

[e] Fifth pulse.

[f] First pulse.

7% conversion to propylene but only traces of ethylene.

The order of decreasing activity for the activated $Mo(CO)_6/Al_2O_3$ catalysts was DA;He,500° ≃ DA;H_2,300° > PDA;He, 300° > DA;H_2,400–500° ≃ PDA;H_2,300° > PDA;He,400°.

Reactions on Activated $W(CO)_6/Al_2O_3$

A few experiments were run using activated $W(CO)_6/Al_2O_3$ as the catalyst; 2.9 μmol W/PDA;He,250°;H_2,100° gave 46% conversion of pulses of cyclopropane in hydrogen at 100°C with $r_I/r_{II} = 31$. Pulses of propylene were then injected at 100°C. Conversion to propane was 76% and to hydrogenated products of metathesis, 24%.

Conversion of pulses of cyclopropane at 100°C on 2.7 μmol $W(CO)_6$/DA;He,300°; H_2,650° gave 66% conversion, $r_I/r_{II} = 1.8$. Pulses of propylene at 100°C then gave 93% propane and 7% hydrogenated products of metathesis.

DISCUSSION

Reactions during Activation

Activation of $Mo(CO)_6$/PDA in flowing helium or hydrogen at 100°C results in the loss of 3.00 ± 0.01 CO and the formation of $Mo(CO)_3$/PDA in which surface ions, O^{2-} or OH^-, have entered the coordination sphere of the molybdenum atom (*3, 5*).

When $Mo(CO)_3/Al_2O_3$ is activated to higher temperatures, the ensuing reactions can be represented by the following somewhat simplified scheme (*5, 11*). Here, PDA is γ-Al_2O_3 dehydroxylated at 475°C. It contains about 4 residual surface OH groups (σ-OH) per nm^2. DA is dehydroxylated at 950°C and contains about 0.12 residual σ-OH nm^2. The listed reactions start at 150°C and are nearly complete by 300°C except for the further oxidation of Mo^{2+} in reaction (1).

Loss of CO and oxidation of Mo

(1) On PDA and DA in He and probably in H_2,

$$Mo(CO)_3 + 2\sigma\text{-}OH \rightarrow (\sigma\text{-}O^-)_2Mo^{2+} + 3CO + H_2$$

At higher temperatures with PDA in He, further oxidation of Mo^{2+} by σ-OH occurs.

(2) With PDA in helium carrier, about 10% of the H_2 from (1) is diverted to reduction of CO ligands to methane plus water.

Direct reduction of carbonyl by H_2

(3) In H_2 with PDA and DA.

$$3H_2 + [-CO] \rightarrow CH_4 + H_2O$$

Oxidation of Mo by H_2O

(4) Subsequent to (3) in H_2 and more extensively with PDA.

$$H_2O + Mo^{n+} \rightarrow Mo^{(n+2)+}\,O^{2-} + H_2$$

Formation of Mo(0) on DA in helium carrier

(5) After all σ-OH on DA has been removed by reaction (1),

$$Mo(CO)_3/DA \rightarrow Mo(0)/DA + 3CO$$

Residual C/Mo is about 0.3 after DA;He, 300°,1, a code which specifies that $Mo(CO)_6$/DA was heated in flowing helium for 1 h at 300°C. DA;He,500°,1 is a material of nearly the same composition because all σ-OH of DA will have reacted by 300°C. Heating materials with these pretreatments in H_2 results in the removal of C to form methane beginning at about 300°C. After H_2,650°,C/Mo = 0.01 and after H_2,950°, 0.5, C/Mo = 0.00 (*5, 11*).

The following pretreatments for one hour each which are those most employed in the present research led to the listed average oxidation numbers.

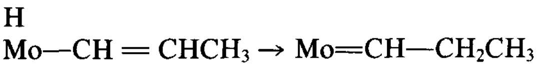
PDA;He,300°,	ON ≅ 2
PDA;He,400°,	ON ≅ 4
PDA;H_2,300–500°,	ON ≅ 3
PDA;He,500°,	ON ≅ 5.5
DA;He,300–500°,	ON ≅ 0.3
DA;He,300–500°; H_2,650–900°,	ON = 0.00

A few experiments were run on $Mo(CO)_6$ supported on a nearly fully hydroxylated alumina (HA), surface concentration of σ-OH, about 15 nm^{-2}.

Mo(CO)₃/PDA Activated at 100°C

We had previously examined the metathesis of propylene in *helium* carrier on PDA;*He*,100°,1 using a pulse reactor at 60°C (*21*). Figure 1 shows the results of passing pulses of propylene in *hydrogen* carrier over the catalyst PDA;H_2;100°,1. The metathesis of propylene to ethylene plus butylene develops during an activation period as was previously found using helium carrier. Presumably, surface Mo=CHR species are formed during pulses 1–5 and these are the operating sites in the Chauvin–Hérrison mechanism (*22, 21*). These sites are likely to be formed by

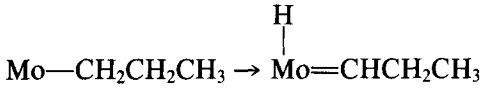
$$\text{Mo} + \text{CH}_2{=}\text{CHCH}_3 \rightarrow$$



$$\overset{\text{H}}{\text{Mo}}{-}\text{CH} = \text{CHCH}_3 \rightarrow \text{Mo}{=}\text{CH}{-}\text{CH}_2\text{CH}_3$$

or perhaps,

$$\text{Mo}{-}\text{H} + \text{CH}_2{=}\text{CHCH}_3 \rightarrow$$



$$\text{Mo}{-}\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \overset{\overset{\text{H}}{|}}{\text{Mo}}{=}\text{CHCH}_2\text{CH}_3$$

The conversion to products of metathesis in hydrogen carrier is only about 40% of that in helium carrier. Further, if after a steady state is reached with helium carrier, hydrogen is substituted for helium, conversion in metathesis falls and that in hydrogenation rises over 3 or 4 pulses to give a new steady state much like that of Fig. 1. It appears likely that the fraction of molybdenum atoms converted to Mo=CHR is not more than 1% (*21*). The results just given suggest that the concentration of hydrogenation sites is also small, that some Mo=CHR can be hydrogenolysed to form sites for hydrogenation, but that some Mo=CHR resist reaction with hydrogen. We do not know the detailed structures of the various sites.

Mo(CO)₃/PDA Activated above 100°C

As T_{act} in PDA;He,T_{act} was progressively increased above 100°C, there was a steady increase in the activity for metathesis and a much more rapid increase in the activity for hydrogenation such that conversions in the pulse reactor became 100% even at 0°C. Accordingly, the hydrogenation of propylene was studied in a flow reactor at −46°C. As shown in Fig. 2, the activity for metathesis measured at 60° in a pulse reactor, maximized at T_{act} = 300°C (average ON near 2) and became nearly zero by T_{act} = 400°C (average ON near 4). However, activity for hydrogenation was nearly the same after activating in helium either at 300°C or at 400°C and even 500°C gave a little activity. It appears likely that Mo^{2+} or possibly Mo^{3+} are the most active *cus* precursor sites for metathesis. If these were simply converted to Mo=CHR sites, the most active metathesis sites would be Mo(IV) or Mo(V) if one counts =CHR as −2. On the other hand, it is clear that a number of initial values of ON of Mo lead to sites active for hydrogenation: ON from 0 to +4 or +5.

Heating $Mo(CO)_3$/PDA in flowing hydrogen liberates about one-half of the carbonyl as CO, the other half as methane, reaction (3). After activation to 300°C, C(liberated)/Mo was 5.8 and to 500°C, 6.0. As shown in Fig. 3, the development of catalytic activity for the hydrogenation of propylene at −46°C roughly paralleled the liberation of CH_4 and CO. Unlike the case of PDA,He,T_{act}, the catalytic activity of PDA,H_2,T_{act} changed little as T_{act} was increased from 300 to 500°C. Since almost all CO had been removed by 300°C, there was little further liberation of H_2O which could further oxidize Mo by reaction (4) and the presence of hydrogen reversed more extensive oxidation of Mo by σ-OH.

When T_{act} was greater than 175°C in PDA;He or H_2,T_{act}, the only detectable product of the reaction between propylene and hydrogen at −46°C was propane. In the flow reactor at 25°C on PDA;He,300° the propane was accompanied by ethane plus butane which increased over the course of an hour to reach about 2% of the product. No products of metathesis were detectable using PDA;H_2,300° under the same conditions. No olefins remained in the effluent stream from either type of run at 25°C. Thus, metathesis competes better with hydrogenation on PDA;He,300° than on PDA; H_2,300°. Also, as shown in Fig. 4, PDA;H_2, 300° has a higher turnover frequency for hydrogenation than PDA;He,300°.

The kinetic order of the hydrogenation of propylene was determined at −46°C and a total pressure of 1 atm by varying the proportions in the reactant mixture by changing the temperature of the propylene saturator and by adding helium. Both PDA;He, 300° and PDA,H_2,300° gave kinetic orders of near zero for propylene and near unity for hydrogen.

No metathesis was observed on 41 μmol/HA;He,280° in helium carrier at 60°C, but it completely hydrogenated propylene in hydrogen at 0°C. Similar experiments had been run with HA;He or H_2,100°,1 (i.e., $Mo(CO)_3$/HA). There, too, activity for metathesis was zero but that for hydrogenation, about equal that for PDA;He or H_2, 100°,1. Perhaps the higher coverage of HA by surface oxygen species prevents formation of adsorbed species of high enough coordinative unsaturation, but perhaps σ-O^- or Al^{3+}(cus) of PDA are involved in the actual catalytic site for metathesis.

Treatment with Oxygen and Carbon Monoxide, Catalyst Deactivation

As shown in Table 2, injection of O_2 such that $O_2/Mo \cong 0.5$ promoted metathesis and nearly eliminated hydrogenation. This is particularly striking for PDA;H_2,300° where no metathesis was evident before exposure to oxygen. The effect of oxygen in promoting metathesis with PDA;He,300° has been noted before (*21*). Since an injection of $O_2/Mo = 0.21$ eliminates about 80% of the activity for hydrogenation of PDA; He,300°, it is clear that no more than one-fourth of the atoms of molybdenum on the surface have become "active" active sites for hydrogenation. These results demonstrate how easily these molybdenum/alumina catalysts can be poisoned and the need to work with carrier gases of high purity.

Carbon monoxide is a less severe poison than oxygen. At −46°C, flow, an injection of CO ($CO/Mo > 1$) almost completely eliminated hydrogenation, but activity returned slowly. At 25°C, flow, the degree of poisoning was less and the rate of return of activity was higher, particularly for PDA, H_2,300°. Sites active for hydrogenation hold carbon monoxide much more weakly than oxygen.

Even in the absence of oxygen, catalytic activity for hydrogenation declined slowly for about 0.5 h in flow experiments at −46°C and then changed little for a subsequent 60 min. H_2,300°,1 restored the initial activity and rate of decline for catalysts originally pretreated He or H_2,300°; H_2,30° or H_2,200° led to partial restoration.

Isomerization of 1-Butene

The isomerization of 1- to 2-butene was examined by Davie et al. (*9*) but the results were variable probably because of uncontrolled exposure to oxygen. The experiments of Table 3 were run to get some idea of the pattern of isomerization activity vs temperature of activation in helium. The isomerization appears to occur on sites some of which are converted to Mo═CHR sites for metathesis, that is the pattern of activity vs T_{act} for isomerization resembles that for metathesis much more closely than that for hydrogenation.

Hydrogenation of Propylene on Activated $Mo(CO)_6$/DA

In general, catalysts on DA were more active for hydrogenation and less active for metathesis than materials with the same pretreatment on PDA.

This is true even for activation at 100°C. Thus, three catalysts, 30 μmol DA;He or H_2,100°,1 all led to 100% hydrogenation of pulses of propylene in hydrogen carrier at 60°C and to no products of metathesis. An equivalent catalyst on PDA would have given 5% metathesis and 16% hydrogenation. The higher activity of $Mo(CO)_6$/DA activated at 100°C is probably related to the fact that $Mo(CO)_6$/DA does not stop so sharply at $Mo(CO)_3$(ads) as does $Mo(CO)_6$/PDA (*5, 11*).

Unlike the case for $Mo(CO)_6$/PDA, the hydrogenation activities of $Mo(CO)_6$/DA, activated He or H_2,300–500° are all roughly the same. The small content in σ-OH of DA is removed early in the activation procedure and little can happen as the temperature rises from 300 to 500°C. As shown in Fig. 4, catalysts on DA activated at 300–500°C are more active than the PDA counterparts. These measurements were difficult. We had to work with only 2 μmol (0.2 mg) of Mo in order to get less than 100% conversion. Matters became worse when we exposed 2 μmol DA;He,300°,1 to a subsequent treatment in hydrogen to remove residual carbon. The DA;He,300° was cooled to 0°C in helium, hydrogen was substituted for helium and reaction was then effected at −46°C. The degree of hydrogenation was 25%. The catalyst was then treated H_2,400°,1, cooled in hydrogen to −46°C to give a conversion of 70%. The treatment H_2,500°,1 then led to 100% conversion. DA;He,300°,1;H_2,650°,1 must be more active but we do not know how much more active.

Reactant purity required close attention in these experiments which employed less than 1 μmol of Mo_s and hydrogen plus propylene flows of about 10^5 μmol h^{-1}. Activities usually decreased slightly in the runs of Fig. 4, but became constant after 0.5 h. Activity loss was reversed by heating in hydrogen to 300°C. Since removal of oxygen requires higher temperatures, the activity losses during hydrogenation on DA and PDA probably result from formation of small amounts of polymer or other slowly reacting carbonaceous deposits.

There is a question of temperature and concentration gradients in the catalyst pores. The nonlinearity of the lines in Fig. 4 might originate from temperature rises in the catalyst granules. If the percentage exposed of the molybdenum of the catalysts on DA is 30% (*5*), then the calculated turnover frequency of hydrogenation per surface atom of Mo on DA,He,300°,1 is 1.8 sec^{-1} at −46°C and on DA;He,300°,1;H_2, 500°,1 it is larger than 5.6 sec^{-1}. The latter value may well derive from a temperature somewhat higher than −46°C. For reference, N_t per surface atom of Pt on Pt/SiO_2 is 0.2–0.3 sec^{-1} at −46°C (*23*).

In a slurry reactor at −78°C, N_t for the hydrogenation of propylene on DA;He,500° was about 0.012 sec^{-1} per atom of Mo or 0.04 per Mo_s.

Hydrogenolysis of Cyclopropane

As shown in Table 4, two concurrent reactions occur during passage of cyclopropane in hydrogen gas (pulse reactor) over the activated $Mo(CO)_6/Al_2O_3$ catalysts of this paper. They are single hydrogenolysis and double hydrogenolysis.

$$C_3H_6 + H_2 \rightarrow C_3H_8 \qquad \text{at } r_I$$

$$C_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \qquad \text{at } r_{II}$$

The ratio CH_4/C_2H_6 was unity and no butane was observed.

Double hydrogenolysis of cyclopropane was originally discovered on nickel (*24*) and later found on iron, ruthenium, and osmium (*25*). It has not been previously reported on ionic sites like Mo(II). Platinum (*26, 27*) and palladium give only single hydrogenolysis.

At 0–100°C, the rate of hydrogenolysis of propane is too slow for double hydrogenolysis to occur by preliminary formation and subsequent hydrogenolysis of propane (*10*). The hydrogenolysis of cyclopropane has a negligible rate on PDA or DA alone at 100°C (Table 1). Further, in helium carrier, isomerization of cyclopropane to propylene was slow on Mo(II) and Mo(IV). Thus the sequence, isomerization of cyclopropane to propylene at acidic sites, hydrogenation of propylene, did not contribute significantly to the hydrogenolyses of Table 4. Double hydrogenolysis could not, of course, involve this sequence.

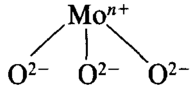
Metallic Mo/DA (average ON near zero) are the most active catalysts, but PDA;He, 300° is nearly as active (ON $\cong$ 2). These catalysts also exhibited the highest proportion of double hydrogenolysis. PDA;H_2, 300° (av ON $\cong$ 3) was less active and PDA, He,400° (av ON $\cong$ 4) was the least active. These materials gave much less multiple hydrogenolysis. If one assumes that hydrogenolysis is near zero order in cyclopropane, one can calculate a crude turnover frequency from loss in cyclopropane and pulse width. For DA;He,500°, N_t's per Mo_s were roughly 0.02 sec^{-1} at 0°C, 0.08 at 55°C, and 1.5 at 100°C. For reference, N_t per Pt_s in Pt/SiO_2 at 0°C is about 0.2 sec^{-1} (*23*).

Hall and co-workers (*28, 29*) previously studied the hydrogenolysis of cyclopropane on reduced MoO_3/Al_2O_3 in the same temperature range as in the present paper. Rates of hydrogenolysis were roughly similar. However, in Hall's experiments, no double hydrogenolysis was observed and down to an av ON of +4.3, the hydrogenolysis appeared to proceed by acid catalyzed isomerization to propylene as the first step. At an av ON of +5, some ethane and butane appeared in the products consequent to metathesis of propylene before its hydrogenation. However, at +4.3, the only product was propane. In sum, the mechanism of the hydrogenolysis of cyclopropane on reduced MoO_3/Al_2O_3 appears to differ from that in our case. Of course, the surface sites of reduced MoO_3/Al_2O_3 and those on activated $Mo(CO)_6$/PDA may well differ in the nature of their coordinative unsaturation.

Mechanistics Considerations

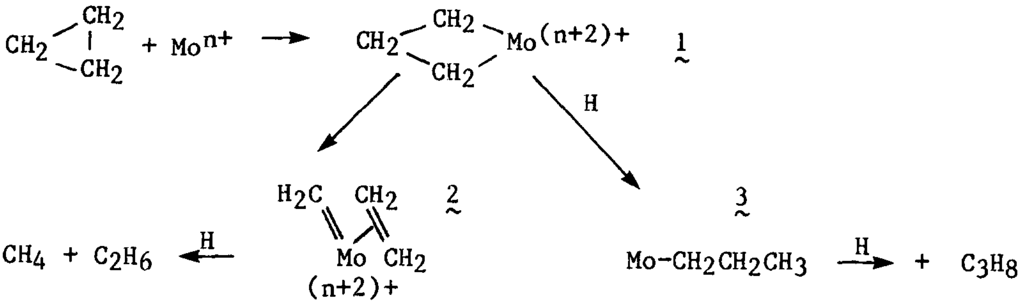
Sites. Sites of several different oxidation numbers appear to be active for hydrogenation of propylene and for hydrogenolysis of cyclopropane. Although we know only average oxidation numbers, it appears clear that *direct* single hydrogenolysis of cyclopropane is catalyzed by Mo with ON of 0 and 2–4, although ON = +4 must be distinctly less active. N_t for double hydrogenolysis decreases as av ON increases and ON = 3 and 4 are much less active for double hydrogenolysis than are the lower ON. Clean Mo(0) seems to be less active than the Mo(0.3) which results from DA;He, 300–500°. The reverse is true for hydrogenation (Fig. 4), but otherwise the relative activities for hydrogenation of av ON = 0–4 are rather like those for single hydrogenolysis. The range of ON leading to activity for hydrogenation may extend to ON = 5 since Hall and co-workers (*30, 31*) found that slightly reduced MoO_3/Al_2O_3 had some activity for the hydrogenation of ethylene. However, reduction to ON = 4.3 led to a much higher activity.

The catalytic sites must be substantially coordinatively unsaturated surface species. They are poisoned by exposure to carbon monoxide. For Mo^{n+}/PDA, active catalytic sites may resemble



This discussion is in terms of monomeric Mo^{n+}, but we do not really know what fraction, if any, is present in dimeric or polymeric species. Supported dimeric species have been reported to be very active hydrogenation catalysts (*32*).

Mechanism. Let us first consider reactions on Mo^{n+}/PDA. Since no hydrogenolysis accompanies hydrogenation of propylene at less than about 125°C, Mo-C_3H_7 presumably does not react to form CH_4 and C_2H_6 at lower temperatures. Thus, oxidative addition of cyclopropane to Mo^{n+},



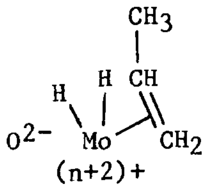
is an attractive intermediate, since both single and double hydrogenolysis could result as shown.

Cleavage of the metallacyclobutane **1** to form **2** is the same process as appears to be involved in olefin metathesis. The nature of the activation of hydrogen is less clear. Oxidative addition of hydrogen to **1** would require a species which was initially Mo$\square_4^{n+}$ and would form $Mo^{(n+4)+}$. Heterolytic dissociative adsorption of hydrogen which can be formally represented

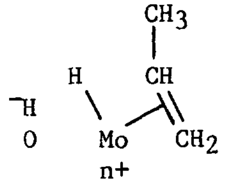
$$Mo^{n+}O^{2-} + H_2 \rightarrow Mo^{n+}H^-OH^-$$

does not change the ON of Mo^{n+} and requires initially only Mo$\square_3^{n+}$.

Similar problems of oxidative vs heterolytic adsorption appear in the hydrogenation of propylene. Two possible intermediates are



4 and



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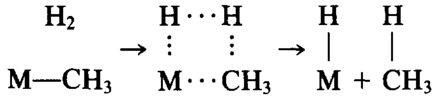
Successive additions of the two hydrogen atoms would then occur with negligible reversal of the two steps since $CH_2DCHDCH_3$ is the initial product of the hydrogenation of propylene with D_2. The reaction rate would presumably be that of the adsorption of hydrogen since rates are approximately first order in hydrogen and zero order in propylene. Hydrogenation via **4** is a variant of the Horiuti–Polanyi mechanism for hydrogenation and this variant is commonly employed for homogeneous hydrogenations. Formation of **4** requires Mo$\square_3^{n+}$ as the initial species, but **5** needs only Mo$\square_2^{n+}$. Most oxidative additions of hydrogen have involved d^8 species, but this may be primarily because oxidation of square planar M^+ to octahedral M^{3+} automatically provides the needed additional ligand positions. Several oxidative addition reactions have been reported for the transient species $(Cp)_2Mo$ and Cp_2W (Cp is cyclopentadienyl) including that of benzene to form $Cp_2MH(Ph)$ (*33*). Cp_2W also adds olefin to form a π-complex. However, Cp_2MoH_2 is a hydrogenation catalyst only at high temperatures and pressures of hydrogen (180°C, 160 atm) (*34*), but this sluggishness may result from the absence of an open ligancy position.

Hydrogenations of ethylene and propylene on rare earth (III) oxides (*35*) and some alumina-supported complexes of thorium (IV) (*36*) are rapid, but oxidative additions are unlikely since higher oxidation states of the metals are unknown. In homogeneous reactions involving certain complexes of early transition elements, of lanthanides and of actinides, concerted reactions like



$$\begin{array}{ccccc} H_2 & & H\cdots H & & H \quad H \\ & \rightarrow & \vdots \qquad \vdots & \rightarrow & | \qquad | \\ M{-}CH_3 & & M\cdots CH_3 & & M + CH_3 \end{array}$$

are probably involved (*37*).

Similar considerations probably apply to reaction on metallic molybdenum except that all hydrogen and hydrocarbon adsorbates may not need to be adsorbed upon one atom of Mo and distinctions between oxidative and heterolytic dissociative adsorption may lose their meaning.

Overall, however, further specification of the details of the reaction mechanisms is likely to require considerable further research.

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