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The Hydrogenolysis of Propane on Mo/Al_2O_3 Catalysts

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Metallic molybdenum on dehydroxylated alumina (prepared by impregnating $Mo(CO)_6$ onto alumina which had been dehydroxylated in flowing helium at 950°C and then treating the $Mo(CO)_6/Al_2O_3$ by He,300–500°;H_2,650–950°) is one of the more active catalysts for the hydrogenolysis of propane. Its turnover frequency per surface Mo atom at 250°C is ~0.2 sec^{-1} at $P = 1$ atm and $C_3H_8/H_2 = 0.038$. Both single and double hydrogenolyses occur simultaneously, the latter having the larger apparent activation energy. Mo/Al_2O_3 catalysts with higher oxidation numbers of molybdenum are less active. $Mo(0)/Al_2O_3$ is easily poisoned for hydrogenolysis by O_2, CO, H_2O, and even to some extent by N_2. Initial activity is restored by H_2 at ~950°C. MoO_3/hydroxylated alumina is reduced by H_2 at 650°C to an average ON (oxidation number) of Mo of +2 and by 800–950°C to an ON of zero. The catalytic activities of these materials for the hydrogenolysis of propane at 200–300°C, the hydrogenation of propylene at −46°C, the metathesis of propylene at 65°C, and the hydrogenolysis of cyclopropane at 0–100°C are very nearly the same as those of Mo^{2+}/Al_2O_3 and $Mo(O)/Al_2O_3$ made from $Mo(CO)_6/Al_2O_3$. © 1985 Academic Press, Inc.

INTRODUCTION

Although the catalytic properties of reduced MoO_3/Al_2O_3 have been extensively studied, temperatures of reduction in hydrogen prior to catalytic runs have usually not exceeded about 500°C. At this temperature, the average oxidation number of Mo, ON, is about +4 (*1*). However, appropriate activation of $Mo(CO)_6/Al_2O_3$ (*2*) can generate materials with ON from 0 to nearly 6 (*3*). The average ON depends upon the degree of dehydroxylation of the alumina, whether the gas flowing during activation is H_2 or He, and upon the temperature of activation (for further details and references to earlier work, see Ref. (*4*)).

In our work with $Mo(CO)_6/Al_2O_3$, we have employed γ-Al_2O_3 at three levels of dehydroxylation: HA (nearly fully hydroxylated alumina), PDA (alumina partially dehydroxylated at ~475°C where the number of surface OH groups, σ-OH, is about 4 per nm^2), and DA (alumina dehydroxylated at 950°C where σ-OH amounts to about 0.12 per nm^2) (*4*).

In a flow of helium or hydrogen, the loss of CO begins at about 25°C and by 100°C the catalyst can be represented as $Mo(CO)_3/Al_2O_3$. Further loss of CO starts at ~150°C. With PDA in flowing helium, the molybdenum atoms are oxidized by σ-OH and by 300°C the overall reaction can be roughly represented by

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

However, 10% of the hydrogen is diverted into converting CO into $CH_4 + H_2O$. Activation above 300°C results in further oxidation of Mo^{2+}. Thus, using PDA as the support and helium as the activating gas the lowest ON in which Mo^{n+}/Al_2O_3 can be formed is +2.

We have measured the average ON of Mo (*3*) in these catalysts but we know little about the actual distribution of the ON. However, Mo in materials of ON = 0 and ON = 6 are presumably all in ON of 0 and 6, respectively.

Activation in H_2 to 300°C leads to an ON

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of ~+3 because about one-half of the CO in $Mo(CO)_3$/PDA is reduced to CH_4 + H_2O and the H_2O further oxidizes the Mo^{2+} formed by the equation given above. However, in the activation of $Mo(CO)_3$/DA in helium, the few σ-OH present are consumed initially as in the equation. Following that, the remaining units of $Mo(CO)_6$/DA lose CO to form Mo(0)/DA. In a typical case of $Mo(CO)_6$/DA;He,300–500°, the average ON of Mo is ~0.3. After such pretreatment, the catalyst still contains carbon to the extent of C/Mo = 0.2–0.3. Flowing hydrogen begins to remove the carbon as CH_4 at ~400°C. At 650°C C/Mo is ~0.01 and at 950°C it is 0.00. After H_2, 650–950°; the catalyst consists of small particles of metallic molybdenum on alumina. We believe that these particles are clean, i.e., free of surface C and O, and ~3 nm in diameter (*3, 4*). After 950°C, the alumina has been converted to a mixture of γ- and δ-Al_2O_3. Catalysts activated at 650 and at 950°C are nearly indistinguishable in their catalytic activity. These were the first "clean" supported metallic molybdenum catalysts.

Some of the activated $Mo(CO)_6/Al_2O_3$ catalysts have outstanding catalytic activity for several reactions (*4*). The clean Mo(O)/DA is a particularly unusual catalyst. It is among the most active supported metallic catalysts for isotopic exchange between alkanes and deuterium. It is very active for the hydrogenation of propylene at −46°C (*4, 5*). It catalyzes the hydrogenolysis of cyclopropane at 50–100°C giving both single hydrogenolysis (to CH_4 + C_2H_6) and double hydrogenolysis (to $3CH_4$), but Mo^{2+}/PDA is a much more active catalyst for the metathesis of propylene at 60°C. Mo(O)/DA has high activity for the hydrogenation of CO and CO_2 at 300°C (*3, 6*).

Mo^{2+}/PDA is active for propylene hydrogenation at −46°C and for the isotopic exchange of alkanes at 20°C, although distinctly less active than Mo(0)/DA. It is about as active for the hydrogenolysis of cyclopropane as Mo(0)/DA and about 1/30 as active per surface Mo atom (Mo_s) as Mo(0)/DA for the hydrogenation of CO. Mo^{4+}/PDA is much less active for these reactions.

A preliminary communication (*7*) has reported that Mo(0)/DA ranks with the more active supported metal catalysts for the hydrogenolysis of propane. The present paper reports further details on that reaction and the following paper deals with the hydrogenolysis of higher alkanes. In addition the present paper provides details on the reduction of MoO_3/HA to Mo^{2+} by H_2 at 650°C and to Mo(0) at ~950°C which was reported in the preliminary communication (*7*).

EXPERIMENTAL PROCEDURES

Catalysts were prepared by the activation of molybdenum hexacarbonyl deposited on γ-alumina (AERO 1000 PHF extrudate of the American Cyanamid Co., 99.99% pure) by the method previously described (*3*). The alumina was first dehydroxylated in flowing helium at 475–500°C to give a partially dehydroxylated alumina (PDA) or at 950°C to give a nearly completely dehydroxylated alumina (DA). After slurrying the alumina with about 4 cm^3 of a pentane solution of the hexacarbonyl, the pentane was evaporated at 0°C in flowing helium and the $Mo(CO)_6/Al_2O_3$ was then activated to appropriate temperatures first in flowing helium and then in hydrogen. We tried to keep the contents in oxygen of both gases at the catalyst at less than 0.02 ppm (*3*). The evolved CO, CH_4, and H_2 were measured as previously described (*3*), expressed as CO/Mo, CH_4/Mo, and H/Mo, and used to calculate the average chemical composition of the resulting catalyst. The ratios are estimated to be accurate to within about 2%. The error occurs largely in the weighing of the small amounts of $Mo(CO)_6$ which the high activity of these catalysts required us to employ. Catalyst loadings are given as micromole of molybdenum on a specified amount of alumina.

The hydrogenolysis of propane on these catalysts was measured by a flow technique with C_3H_8/H_2 = 0.038 prepared by passing hydrogen through a thermostatted tube containing macroporous Filtros FS140, the pores of which were filled with liquid propane (*8*). The total pressure was 1 atm. Propane was degassed by several repeated distillations in the system. In pulse experiments the propane was injected as a gas at a measured pressure into hydrogen flowing over the catalyst. Weights of alumina (0.05–0.25 g) are expressed in terms of HA dried at 125°C.

EXPERIMENTAL RESULTS

Characterization of Catalysts

CO/Mo, CH_4/Mo, and H/Mo during the activation of $Mo(CO)_6/Al_2O_3$ were nearly the same as reported previously (*3*, *9*). The results of one experiment appear in Table 1. In other experiments the treatment H_2,950° liberated $CH_4/Mo \simeq 0.01$ when the previous treatments had been H_2,650 and 0.00 when the previous treatment had been H_2,800°.

The average oxidation numbers, ON, of molybdenum after activation were measured by titration with oxygen at 500°C assuming that this treatment converted all Mo to Mo(+6) (*3*). The catalysts were usually pretreated (activated) He,300°,1;H_2,300°,0.5;H_2,T_{act};He,T_{act},0.25. Here, He or H_2 indicates the flowing gas, 300° indicates a temperature in °C, and the third entry indicates the time in hours. A semicolon separates successive treatments. Four pulses of O_2 (41 μmol per pulse) in flowing helium were passed over the catalyst at 500°C. Loss of O_2 occurred only from pulses 1 and 2. Significant amounts of CO desorbed during these two pulses, but CO/Mo was only about 0.005 in pulse 3 and negligible in pulse 4. The cumulative liberation of CO_2 expressed as CO_2/Mo was less than 0.01. It was assumed that all carbon was present initially in ON +2 and all hydrogen in ON +1. Results of two such experiments are given in Table 2.

TABLE 1

Gas Liberation during Activation of 11.8 μmol $Mo(CO)_6$ on 0.10 g of DA

	Treatment[a]		
	He,650°,0.5[b]	H_2,650°,0.5	H_2,950°,0.5
H/Mo	0.29	—	—
CH_4	0.0203	0.256	0.261
CO/Mo	5.75	5.76	5.76
CO_2/Mo	0.0012	0.0012	0.0012
C/Mo[c]	0.25	0.006	(0.000)

[a] The treatments were successive and the values of H/Mo, CH_4/Mo, CO/Mo, and CO_2/Mo are cumulative.

[b] For all gases liberated up through this treatment.

[c] The value of residual C/Mo after the listed treatment. Since it is assumed that C/Mo = 0.000 after H_2, 950°, this value does not quite agree with a value calculated from the amounts of CH_4, CO, and CO_2 liberated, but it should be more accurate.

TABLE 2

Oxygen Titration at 500°C after Activation of $Mo(CO)_6$/PDA, 8.8 μmol on 0.10 g of PDA

Activation[a]	ON	C/Mo[b]	H/Mo[c]
H_2,650°,1	1.9–2.1	0.18	0.2
H_2,800°,0.5	−0.4–0	0.022	0.18

[a] The treatment was He,300°,1;H_2,300°,0.5, the activation listed in the table, followed by He for 0.25 hr at the temperature in the table and cooling to 500°C in He.

[b] Residual C/Mo before treatment with oxygen.

[c] H/Mo before treatment with oxygen calculated from evolution of H_2O. Some H_2O comes from dehydroxylation of the alumina support.

The adsorption of nitrogen was measured on activated $Mo(CO)_6$/DA. In one experiment, during the overall activation He,500°,1;H_2,650 → 500°,1;He,500 → 300°, $CH_4/Mo = 0.30$ and $CO/Mo = 5.66$ were liberated from 15.1 μmol/0.25 g DA. Four 12.4-μmol pulses of N_2 were injected into flowing helium at 300°C. Adsorption was detected only from pulse 1 and N/Mo adsorbed was 0.078 ± 0.02. Helium continued to flow for 20 min and further pulses of N_2 were injected, but no additional adsorption was detected. The catalyst was then exposed to He,950°;H_2,950°,0.25 and the evolved gases were trapped on silica gel at −196°C and released for gas chromatographic analysis. N/Mo was 0.066 ± 0.01

and most of the liberated nitrogen was evolved during He,950°. A further series of nitrogen pulses in He at 300°C gave N/Mo = 0.065 on adsorption and 0.07 on desorption. In another experiment with 11.8 μmol Mo/0.10 g DA activated to 950° in H_2, N_2 was passed over the catalyst at 300°C for 0.5 hr and the catalyst was heated to 950°C in He, then H_2. N/Mo was 0.06 on desorption.

The adsorption of nitrogen at 25°C from 42-μmol pulses of N_2 in flowing He at 25°C onto 15.9 μmol $Mo(CO)_6$/0.20 g DA;H_2, 650–950° was measured by desorption to 950°C as described above. N/Mo was 0.017. Where the initial activation had been only to 650°C in H_2, desorption at 950°C led the evolved N_2 to be accompanied by small amounts of CO and CH_4 in amounts near those in Table 1.

Catalytic Runs

The dependence of the hydrogenolysis activity of propane as a function of catalyst preparation and pretreatment was first scanned by experiments using the pulse reactor. Better kinetic data were then obtained in flow experiments using catalysts selected on the basis of the scanning experiments. Poisoning by oxygen, carbon monoxide, water, and nitrogen was investigated in most cases with the pulse reactor.

The Hydrogenolysis of Propane in a Pulse Reactor

The scanning experiments with the pulse reactor used 0.25 g of alumina, about 35 μmol of Mo, a flow rate of hydrogen of 30 $cm^3\ min^{-1}$, and 40-μmol pulses of propane. The pulse width at the catalyst was about 15 sec. The results (see Table 3) established that Mo(0)/DA was a very active hydrogenolytic catalyst and they suggested that both single and double hydrogenolyses occurred during one period of adsorption since CH_4 considerably exceeded C_2H_6 in runs at low conversions. They also indicated that smaller amounts of catalyst and larger flow rates would be needed to study Mo(0)/DA catalysts at lower conversions.

Pulses of propane injected into helium flowing over 39 μmol Mo/DA;He,400°,1 at 400°C were 3.5% converted to propylene.

TABLE 3

The Hydrogenolysis of Propane in a Pulse Reactor[a]

Al_2O_3	Pretreatment	Average ON	T_{run} (°C)	Conversion (%)	CH_4/C_2H_6
PDA	H_2,300°,1	~3	300	Trace	
	He,300°,1;H_2,300°,1	~2	300	2.1	2.2
	He,300°,1;H_2,400°,1	?	400	4.9	2.4
	He,300°,1;H_2,650°,1	~2	400	69	3.1
	H_2,650°,1	~2	400	81	3.6
DA	He,300°,1;H_2,300°,1	0.3	300	56	2.4
	He,300°,1;H_2,650°,1	0	300	83	4.3
	H_2,650°,1	0	200	2.4	—
			300	91	8.1
	He,300°,1;H_2,1000°,1	0	100	Trace	1.0
			200	2.2	1.6
			250	34	2.5
			300	99	5.0
			400	100	∞

[a] 40-μmol pulse of propane, ~35 μmol Mo on 0.25 g Al_2O_3, H_2 flow of 30 $cm^3\ min^{-1}$.

TABLE 4

The Hydrogenolysis of Propane in a Flow Reactor

Catalyst	Mo (μmol)	Al_2O_3 (g)	Pretreatment[a]	N_t's at 250°C		$E_a(1)$[b]	$E_a(2)$[b]
				$N_t(1)$ (sec^{-1})	$N_t(2)$ (sec^{-1})	(kJ mol^{-1})	
F2, Mo/DA	5.0	0.05	H_2,950°	0.040	0.014	103	142
F3, Mo/DA	2.0	0.20	H_2,650°	0.044	0.016	101	131
F4, Mo/PDA	3.4	0.05	H_2,650°	0.0022	0.0005	(100)[c]	(127)[c]
			H_2,800°[d]	0.048	0.013	73	98
			H_2,950°[d]	0.038	0.010	76	96
F5, Mo/PDA	4.0	0.05	H_2,800°	0.062	0.016	88	117
F6, MoO_3/HA	7.2	0.09	H_2,800°	0.043	0.013	104	138

[a] H_2,650° was He,500°,1;He,650°,0.1;H_2,650°,1 in F3. In F4 it was He,300°,1;H_2,300°,0.5;H_2,650°,1 so as to start with Mo(II). Catalyst F2 was like F3 but with an additional H_2,950°,0.25. In catalyst F5 the pretreatment was He,300°,1;H_2,300°,0.5;H_2,800°,0.5. Catalyst F6 was heated directly to 800°C in hydrogen from 25°C.

[b] The estimated accuracy is ±6 kJ in experiment F3 and ±8 kJ in the other experiments.

[c] Because of the low conversion, these values are of low accuracy.

[d] The previous catalyst was treated with hydrogen as shown.

The Hydrogenolysis of Propane in a Flow Reactor

Table 4 lists some of the catalysts and pretreatment conditions employed in the flow experiments. These are identified by F (for flow). In view of the high hydrogenolytic activity of M(0)/DA found in the preliminary experiments, the catalysts studied were all Mo(0)/Al_2O_3 except for catalyst F4 after H_2,650° which had an av ON of +2.

Figure 1 shows the results of the hydrogenolysis of propane (experiment F3) on 2.0 μmol Mo/0.20 g DA;He,500°,1;He,650°, 1;H_2,650°,1. Two simultaneous reactions occurred.

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \quad (1)$$

$$C_3H_8 + 2H_2 \rightarrow 3CH_4 \quad (2)$$

$N_t(1)$ represents the turnover frequency for reaction (1) as molecules of propane converted per second per atom of Mo and $N_t(2)$ is that for reaction (2). Flow rates of H_2 varied between 33 cm^3 min^{-1} at 225°C (total conversion 4.3%) to 74 cm^3 min^{-1} at 249°C (5.6% conversion) to 176 cm^3 min^{-1} at 283.5°C (11.3% conversion). The conversion at 249°C dropped from 6.46 to 5.58% during the interval 5 to 60 min on stream. Deactivation during the subsequent 120 min was slight. Activation energies for reactions (1) and (2) are listed in Table 4. The hydrogenolysis of ethane is slow vs that of propane as shown in the following paper. Thus, negligible hydrogenolysis of ethane would have followed its desorption in these

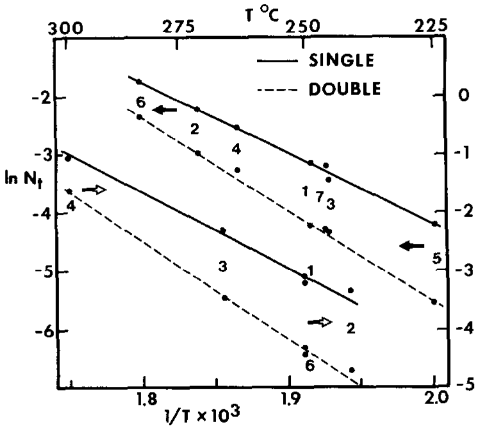

FIG. 1. Values of ln $N_t(1)$ (solid line) and ln $N_t(2)$ (dashed line) vs $1/T$ for catalysts F3 (y-axis on the left) and F6 (y-axis on the right). Catalyst F3 is 2.0 μmol Mo/0.20 g DA;He,500°,1;He,650°,0.1;H_2,650°,0.5 and catalyst F6 is 7.2 μmol MoO_3/0.09 g HA;H_2,800°,0.5. The small numbers in the Figure show the sequence in which measurements were made.

TABLE 5

Values of N_t's after about 1 hr on Stream for Catalyst F3

	200°C	250°C	300°C
$N_t(1)$, sec^{-1}	0.0039	0.044	0.33
$N_t(2)$, sec^{-1}	0.00070	0.016	0.22

experiments which all involved rather low conversions. Table 5 gives values of N_t's for several temperatures which are characteristic of the period of one to several hours on stream as are those in Table 4. A similar run was made on a catalyst prepared like F3 but with a loading of 3.6 μmol Mo on 0.05 g DA. Since the turnover frequencies were nearly the same as in run F3, there is little effect of loading in the range 0.5 to 3.6 μmol Mo per 0.05 g DA.

After the measurements of N_t's on F2, the catalyst was exposed to a stream of propane and hydrogen (H_2/C_3H_8 = 2.6) at 580°C for 0.5 hr, flushed with H_2 at 580°C for 5 min and a new set of hydrogenolyses were run. $N_t(1)$ was nearly unchanged, but $N_t(2)$ declined to 60% of its original value.

Poisoning and Deactivation

Oxygen. Oxygen is a strong poison. A pulse of O_2, O/Mo = 1.5, injected into hydrogen passing at 250°C over a catalyst like F3 but consisting of 3.9 μmol of Mo and 0.05 g DA led to $N_t(1)$ with 0.5 times the normal value and $N_t(2)$ with 0.25 the normal value. Figure 2 shows the complete poisoning of catalyst P3 of the following paper by larger quantities of oxygen and its regeneration by heating in hydrogen.

Carbon monoxide. The regenerated catalyst P3 of the preceding paragraph was exposed to a pulse of carbon monoxide (CO/Mo = 9.6) in the same way as with O_2 in Fig. 2. The conversion of CO to CH_4 was 13%. The residual CO/Mo on the catalyst was 0.3 ± 0.3. The flow rate of hydrogen was then reduced to 60 cm^3 min^{-1}. A pulse of propane at 300°C was 0.18% hydrogenolyzed and a pulse of cyclopropane was 60% hydrogenolyzed. A pulse of propylene was 92% hydrogenated to propane and 0.63% hydrogenolyzed. At 25°C, the hydrogenation was 99.9%. This run was followed by a pulse of propylene in flowing helium at 25°C. No metathesis of propylene was observed in any of these runs.

A catalyst, 39 μmol/0.25 g DA;He,400°, H_2,500°, gave complete hydrogenolysis of a 40-μmol pulse of propane in a hydrogen flow of 30 cm^3 min^{-1} at 400°C, 96% to methane. Injection of a pulse of CO, CO/Mo = 1, reduced the conversion to 4%. Activity slowly increased with time and after three pulses of propane it was 11%. After H_2,400°,1, the conversion was 23%, after H_2,550°,1, it was 88% and after H_2,650°,1, it was 100% (98% methane). As shown by the methane yield, the activity of the initial catalyst was equivalent to a conversion of "several hundred" percents and the final catalyst was more active than the initial.

Water. Catalyst P2 (like P3 of Fig. 2) was exposed to pulses of water injected into hydrogen flowing over the catalyst at 250°C. At H_2O/Mo = 0.16, the activity for the pulse hydrogenolysis of butane had been reduced to 82% of its initial value and the

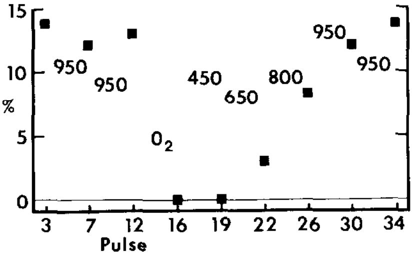

FIG. 2. Percentage hydrogenolytic conversion at 300°C of 25.1-μmol pulses of butane in hydrogen flowing at 300 cm^3 min^{-1} on catalyst P3 (4.2 μmol Mo/0.05 g DA;He,500°,1;He,650°,0.5;H_2,650°,1;H_2,950°,1) vs pulse number. The catalyst was heated in hydrogen for 1 hr at the temperature in degree centigrades indicated by the numbers on the graph before pulses 7, 12, 19, 22, 26, 30, and 34. The few pulses after each of these pulses were repetitions. A pulse of 10 μmol of oxygen was injected into the hydrogen flowing over the catalyst at 300°C just before pulse 16 and 6.8 μmol O_2 passed through the catalyst. The hydrogenolysis in pulse 16 was 0.00% and in pulse 19 it was 0.03%.

yield ratio CH_4/C_3H_8 from 4.55 to 3.94. After a cumulative total $H_2O/Mo = 0.58$, the activity and the yield ratio CH_4/C_3H_8 had been reduced to 61% and 3.5, respectively, and after $H_2O/Mo = 1.06$, to 42% and 2.9.

Nitrogen. Even nitrogen is a poison for hydrogenolysis. A catalyst, 30 μmol Mo/0.25 g DA, regenerated by H_2,950°, hydrogenolyzed 99% (93% methane) of a pulse of propane at 300°C at a total flow rate of 30 cm^3 min^{-1}. After injection of a pulse of nitrogen, $N_2/Mo = 1.3$, the conversion was 79% (72% methane). After three more pulses of nitrogen, the conversion was 40% (67% CH_4). The catalyst was fully regenerated by H_2,950°.

Deactivation and regeneration. In our most protracted flow reaction, that on the catalyst like F3 but with 3.6 μmol on 0.05 g DA, 250°C, total flow rate equal to 150 cm^3 min^{-1}, the conversion of propane was 7.1% at 5 min, 6.6% at 20, 6.3% at 185, 6.1% at 530, and 5.9% at 650 min. Of the 3.6 μmol of Mo, about 1.0 μmol was on the surface of the small Mo(0) particles (*4*). During the run 5.2 mol of hydrogen and 0.2 mol of propylene passed over the catalyst. It is not easy completely to avoid poisoning in such experiments where 0.1 ppm of strong poison can be serious.

The liberation of methane was measured during the regeneration of a catalyst which had become deactivated by exposure to a series of pulses of alkanes. The regeneration was effected by heating to 900°C in hydrogen at 40°C min^{-1}. The rate of liberation of CH_4 became detectably non-zero at about 500°C, maximized at about 600°C, continued to be significant to 900°, but dropped nearly to zero after 20 min at 900°C. The total liberation of methane corresponded to $CH_4/Mo = 0.04$. About 10% as much carbon was evolved in the form of ethane and propane.

The rate of deactivation in pulse experiments was variable and usually faster than deactivation in flow experiments. We believe that deactivation in our experiments resulted from a combination of deposition of unreactive carbon species and from poisons. The treatment H_2,950°, or sometimes even H_2,650°, regenerated the catalyst with negligible loss in activity as shown in Fig. 2. In one set of pulse experiments carried out to a time on stream of days, H_2,950° finally failed to regenerate the catalyst.

Reduced MoO_3/HA Catalysts

Since MoO_3/HA reduced at 800°C in hydrogen was found to catalyze the hydrogenolysis of propane (F6 in Table 4), reduced MoO_3/HA was further investigated. The catalyst was prepared by impregnation to incipient wetness of alumina with a solution of MoO_3 in dilute ammonia and followed by drying at 55°C. The material was then calcined O_2,500°,1.

Oxygen titration. After H_2,660°,0.5;He, 660°,0.05, cool to 500°C in helium, oxygen titration as described under Experimental Results gave an average ON of 1.96. Four runs were made on samples exposed to H_2 at 800–840°C. The resulting ON were −0.16, −0.14, +0.14, and +0.01, i.e., close to zero.

Catalysts of MoO_3/HA;H_2,800° were black like those prepared by activating $Mo(CO)_6/DA$. Upon exposure to air, they stayed black for several days. MoO_3/HA; H_2,650° was dark brown, but it became white within an hour when exposed to air, that is, Mo(II) became oxidized to Mo(VI).

Hydrogenation of propylene. The hydrogenation of propylene in a flow reactor at −46°C and $H_2/C_3H_6 = 7.3$ was investigated on 5.0 μmol MoO_3/0.048 g HA activated either H_2,650°,0.5 or H_2,800°,0.5. The catalysts had nearly the same activity; N_t was 0.5 sec^{-1} for H_2,650° and 0.4 sec^{-1} for H_2, 800°. On H_2,650°, the conversion was 57% at a flow rate of 60 cm^3 min^{-1} and 27% at 120 cm^3 min^{-1}.

Metathesis of propylene. Pulses of 16 μmol of propylene in helium flowing at 30 cm^3 min^{-1} were passed over a catalyst containing 5 μmol of Mo in ON + 2 (H_2,640°) at 60°C. The amount of metathesis

$$2C_3H_6 \rightarrow C_2H_4 + C_4H_8$$

increased with pulse number, but the rate of increase had become slow by pulse 8 in which the percentage metathesis was 6.1%. This activity is of the same order of magnitude as that found for Mo^{2+}/PDA prepared from Mo(CO)$_6$/PDA by He,300°,1 (*4, 5*).

Hydrogenolysis of propane. In Fig. 1, $N_t(1)$ and $N_t(2)$ for Mo(CO)$_6$/DA;H$_2$,650° (catalyst F3 of Table 4) and MoO$_3$/HA;H$_2$, 800° (catalyst F6 of Table 4) are compared as functions of temperature and shown to be nearly the same. Conversions of pulses of propane in flowing hydrogen at 200–300°C were also nearly the same on the two types of catalysts.

Hydrogenolysis of cyclopropane. This was investigated in the pulse reactor with 26-μmol pulses of cyclopropane injected into H$_2$ flowing at 60 cm^3 min^{-1}. Only MoO$_3$/HA;H$_2$,640°,0.5 (av ON of Mo = +2) was investigated and at temperatures between 30 and 200°C. N_t (interpolated) was 0.008 sec^{-1} at 65°C, whereas it was 0.041 sec^{-1} at 65°C on Mo(CO)$_6$/PDA;He,300°,1 (*5*). Further, at 100°C the ratio of the conversion in the first reaction below to that in the second was 3.5 for reduced MoO$_3$/HA, in fair accord with

$$\text{Cyclopropane} + H_2 \rightarrow C_3H_8$$

$$\text{Cyclopropane} + 2H_2 \rightarrow C_2H_6 + CH_4$$

the ratio found for the other catalyst which was 2.5 (*5*).

Poisoning and regeneration. Table 6 shows the results of an experiment in which a reduced MoO$_3$/HA catalyst was poisoned by O$_2$ and CO and regenerated by heating in hydrogen.

DISCUSSION

Catalysts

The catalysts of principal concern here have been described in the Introduction: clean Mo(0)/DA, Mo(0.3)/DA containing $\sim$0.3 C/Mo and probably also 0.3 0/Mo, Mo$^{\sim 2+}$/PDA, and Mo$^{\sim 3+}$/PDA.

TABLE 6

Poisoning and Regeneration in the Hydrogenolysis of Propane at 300°C on 4.9 μmol MoO$_3$/0.05 g HA

Treatment	Conversion,[a] %
H$_2$,810°,0.5	31
O$_2$[b]	20
O$_2$[b]	12
H$_2$,800°,0.25	36
H$_2$,860°,0.25	43
CO[c]	3.7
CO[c]	0.3
H$_2$,860°,0.25	44

[a] Percentage of propane hydrogenolyzed in the pulse mode at a flow rate of H$_2$ of 60 cm^3 min^{-1}.

[b] Injection of a pulse of O$_2$, O$_2$/Mo = 0.3, into flowing hydrogen at 300°C.

[c] Injection of a pulse of CO, CO/Mo = 1.0, into flowing hydrogen at 300°C. Conversion of CO to CH$_4$ was 41% in the first pulse and 25% in the second.

Clean Mo(0)/DA turned out to be the most interesting catalyst for the hydrogenolysis of propane. As previously reported (*4, 5*), this material consists of small particles of metallic Mo supported on alumina. The percentage exposed of Mo will be taken to be 30% (*4, 5*), but this number is subject to some uncertainty since it is derived from measurements of the chemisorption of CO and it is not clear what fraction of CO is dissociatively adsorbed so as to occupy two surface sites.

The yields of H$_2$, CH$_4$, CO, and CO$_2$ liberated during each stage of one preparation of Mo(0)/DA, Mo(CO)$_6$/DA;He,650°,0.5; H$_2$,650°,0.5;H$_2$,950°,0.3, are shown in Table 1. After He,650°,0.5 the catalyst had retained carbon to C/Mo = 0.25, but H$_2$,650°, 0.5 reduced C/Mo to 0.01. Although the catalyst appears to consist of supported metallic molybdenum (EXAFS, TEM), it differs in one aspect from bulk molybdenum. Adsorption of N$_2$ on Mo(0)/DA is slow at 25°C. The equivalent of several minutes' exposure of Mo(0)/DA to N$_2$ led to the adsorption of N$_2$ only to N/Mo = 0.017. However, at 300°C, adsorption of N_2 had saturated in an exposure of 15 sec at N/Mo $\simeq$ 0.07. Adsorption of N_2 on the (100) plane of bulk Mo is fast at 25°C (*10*).

Hydrogenolysis of Propane

Preliminary experiments in a pulse reactor (Table 3) established that clean Mo(0)/DA had a high activity for the hydrogenolysis of propane at 250–300°C. At these temperatures, both single and double hydrogenolyses, Eqs. (1) and (2), occurred simultaneously to convert C_3H_8 into CH_4 + C_2H_6 or into $3CH_4$, respectively. The ethane formed in Eq. (1) was subsequently hydrogenolyzed to methane but at a rate slower than that of propane in Eq. (1). At 400°C, essentially complete hydrogenolysis to methane was observed as shown by the last entry in Table 3.

Mo(0.3)/DA [(Mo(CO)$_6$/DA;He,300°,1; H_2,300°,1)] was less active as shown by the first entry under DA in Table 3. Mo^{2+}/PDA was still less active although it had substantial activity at 400°C. Mo^{3+}/PDA was even less active.

The hydrogenolysis of propane was then investigated in a flow reactor in order to measure rates more accurately. Figure 1 shows $N_t(1)$ (turnover frequency per sec per atom of Mo) for single hydrogenolysis and $N_t(2)$ for double hydrogenolysis in the temperature range 225–280°C for catalyst F3 (Table 4). Table 5 shows the values of $N_t(1)$ and $N_t(2)$ at 200, 250, and 300°C. N_t' per Mo_s would be ~3 times larger. Thus, N_t'(total) at 250°C would be about 0.2 sec^{-1}. Double hydrogenolysis has a larger E_a than single hydrogenolysis, 131 vs 101 kJ mol^{-1}, but in the temperature range studied the single hydrogenolysis was always the faster reaction.

Catalyst F3 and a catalyst differing only in containing 3.6 μmol Mo on 0.05 g DA led to nearly the same turnover frequency. Thus, loading in the range 0.5 to 3.6 μmol per 0.05 g of DA seems to have little effect on N_t. Catalyst F2 was pretreated like catalyst F3 but with an additional 0.25 hr at 950°C. It led to rates which were nearly the same as those on catalyst F3. Thus, H_2,950°C after H_2,650°C had little catalytic effect.

The Mo(0)/DA clearly starts as metallic Mo, but it might well become converted to carbide during hydrogenolysis runs (*11*). After the run on catalyst F2, the catalyst was exposed to hydrogen + propane (H_2/C_3H_8 = 2.6) at 580°C for 0.5 h which should be rather strongly carbiding conditions. This treatment led to almost no change in $N_t(1)$ but $N_t(2)$ declined to 60% of its original value. In the pulse reactor at 250–300°C with propane or butane the activity of a fresh catalyst declined slightly between pulses 1 and 2. The subsequent rate of decline was slow. Thus, if the operating catalyst is actually a molybdenum carbide and unless clean Mo and carbide have similar activities, carbiding must occur rapidly.

Poisoning, Deactivation, and Regeneration

The catalyst is very sensitive to poisoning. Figure 2 shows an experiment in a pulse reactor at 300°C which involved poisoning by a pulse of oxygen, O_2/Mo = 2.4, in hydrogen carrier. Before this the Mo(CO)$_6$/DA had been activated in hydrogen at 650°C and then heated in hydrogen at 950°C after pulses 3, 6, and 9. Conversions were nearly the same in pulses 1–9. After a pulse of oxygen, the catalytic activity was too small to measure. H_2,450° raised the conversion of propane to 0.03%, H_2,650° to 3%, H_2,800 to 8.2%, and H_2,950° restored the activity to its initial value. Thus, adsorbed oxygen begins to be removed at $T >$ ~500°C, but exposure to hydrogen at $T >$ 800°C is necessary to remove essentially all adsorbed oxygen. Further, the catalysts can be heated several times to 950°C without loss of activity and presumably without coarsening of the distribution of particle sizes of the molybdenum. The unusual stability at high temperatures probably results from the very high lattice energy of metallic molybdenum.

After pulse 34 in Fig. 2 the catalyst was exposed to a pulse of carbon monoxide. The conversion of propane was reduced from ~13% to the equivalent of ~0.04%. However, the catalyst was still active for the hydrogenation of propylene at 25°C but not for the metathesis of propylene at that temperature. Mo^{2+}/PDA has considerable activity for hydrogenation (*5*). In hydrogenolysis at 400°C, CO also drastically reduced conversion, but the conversion increased as hydrogen continued to pass over the catalyst at 400°C. H_2,650°C restored initial activity. The poisoning of hydrogenolysis by CO explains why significant amounts of ethane and propane can be formed during hydrogenation of CO at 300°C (*3*) even though clean molybdenum is an active hydrogenolysis catalyst at 300°C.

Water is also a poison for hydrogenolysis and even nitrogen is a poison although a much less effective poison than oxygen or carbon monoxide.

Catalytic activity for the hydrogenolysis of propane at 250–300°C slowly declined with time on stream. For example, in a flow reactor at 250°C, the conversion declined from 7.1% at 5 min to 6.3% at 185 min and then to 5.9% at 650 min. In view of the high sensitivity of the catalyst to poisons, we do not know what fraction of the decline is due to poisoning and what fraction to deposition of "carbon." During a regeneration of a partially deactivated catalyst by heating to 900°C in hydrogen, alkanes (mainly methane) were liberated in an amount, C/Mo = 0.04–0.05. This matter needs further investigation.

Reduced MoO_3/PDA

Since H_2,500° converts MoO_3/HA only to Mo^{4+}/PDA and since H_2,500° removed little adsorbed oxygen from M(0)/DA whereas H_2,950° removed all adsorbed oxygen, the question arose as to whether treatment of oxidized Mo/PDA by H_2 at high temperatures would reduce the molybdenum to Mo(0). In one experiment the Mo in Mo^{2+}/PDA prepared by $Mo(CO)_6$/PDA;He,300°, 1;H_2,300°,0.5 was still Mo^{2+} after H_2,650°, but the Mo^{2+} had been reduced to Mo(0) after a subsequent H_2,800°,0.5.

$Mo(CO)_6$/PDA was then treated H_2,650° which should lead to an ON of about +2. In the flow reactor, this material had an activity for hydrogenolysis of about 5% that of Mo(0)/DA (Table 4, run F4). Subsequent treatment by H_2,800° raised the hydrogenolytic activity to that observed for Mo(0)/DA. A similar experiment (run F5) in which Mo^{2+}/PDA was treated H_2,800° directly led to the same result. Therefore, MoO_3/HA was heated directly in hydrogen to 800°C. The resulting catalyst (run F6) had the same hydrogenolytic activity as Mo(0)/DA prepared from $Mo(CO)_6$/DA (Fig. 1). Thus, Mo(0)/DA can be readily prepared from MoO_3/HA as confirmed by titration by oxygen at 500°C and it has the same catalytic activity for the hydrogenolysis of propane as catalysts prepared from $Mo(CO)_6$/DA. Oxygen titration also showed that the av ON of Mo in MoO_3/HA;H_2,650° was ~ +2.

Since the hydrogenolytic activities of Mo(0)/DA and of Mo(2+)/Al_2O_3 appeared to be independent of whether they were prepared from MoO_3/HA or $Mo(CO)_6$/DA, a few experiments were run to determine catalytic activities of highly reduced MoO_3/HA for other reactions. At −46°C, MoO_3/HA;H_2,650° or 800° gave activities for the hydrogenation of propylene similar to those observed for Mo(0)/DA prepared from $Mo(CO)_6$/DA (*5*). Mo(2+)/Al_2O_3 prepared from MoO_3/HA had an activity for the metathesis of propylene equivalent to its counterpart and the same was true for the hydrogenolysis of cyclopropane on Mo(2+)/Al_2O_3. These reactions need further investigation.

In addition, poisoning and regeneration of Mo(0)/Al_2O_3 prepared from MoO_3/HA were very similar to that noted for Mo(0)/DA prepared from $Mo(CO)_6$/DA as shown for O_2 and CO in Table 6.

Thus, Mo(2+)/Al_2O_3 and Mo(0)/Al_2O_3, materials which have outstanding activity for a number of hydrocarbon reactions, are readily prepared by MoO_3/HA;H_2,650° and MoO_3/HA;H_2,~900°, respectively. In practical use, Mo(0)/Al_2O_3 would have the disadvantage that it is easily poisoned by O_2, H_2O, and CO. However, because of the extraordinary resistance of Mo(0)/Al_2O_3 to high temperatures in H_2, poisoned catalysts can be completely regenerated by H_2,950°.

$W(CO)_6/Al_2O_3$

A few pulse experiments like those of Table 3 were run at 300°C on activated $W(CO)_6/Al_2O_3$ at loadings of about 2.8 μmol of W, loadings less than 0.1 of those by Mo in Table 3. On $W(CO)_6$/DA;He,300°;H_2, 650°, pulses of propane and of propylene were completely hydrogenolyzed to 95% CH_4 and 5% C_2H_6. Similar activity was exhibited by $W(CO)_6$/DA;He,300°;H_2,300° and injection of CO (CO/Mo = 2.1) depressed conversion to 1%. $W(CO)_6$/PDA; He,250°;H_2,300° converted about 5% of a pulse of propylene to CH_4 + C_2H_6 ($CH_4/C_2H_6 = 1.4$). Comparison of these data with those of Table 3 indicates that $W(CO)_6/Al_2O_3$ leads to substantially more active hydrogenolysis catalysts than $Mo(CO)_6/Al_2O_3$, but this matter needs further examination.

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