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Highly Reduced MoO_3/Al_2O_3 Catalysts

II. Hydrogenolyses of Cyclopropane, Methylcyclopropane, and Propane

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The preparation of $Mo(0)/Al_2O_3$ by $Mo(CO)_6/DA;H_2,300–500°;H_2,650–950°$ ($Mo(CO)_6$ deposited on highly dehydroxylated alumina, heated in flowing He to 300–500°C and then in H_2 to 650–950°C) and by $MoO_3/Al_2O_3;H_2,950°$ give essentially equivalent results with respect to activity and selectivity in the hydrogenolyses of cyclopropane (CP) and methylcyclopropane (MCP) at 100°C and of propane at 250°C. Thus, one can prepare metallic Mo on alumina by the easier and more flexible preparation from MoO_3/Al_2O_3. MCP undergoes single hydrogenolysis to isobutane and butane and double hydrogenolysis to (a) $CH_4 + C_3H_8$ and to (b) $2C_2H_6$. The product ratio, butane/isobutane, is greater than unity which is uncommon on metals. After one to several pulses in a pulse reactor, catalyst samples were heated to 950°C in flowing H_2. The amount of liberated methane gave the amount of carbonaceous deposit. With one to seven pulses of CP or MCP in H_2, (C atoms in deposit)/(C atoms in product) was 0.03–0.04 but only 0.007 with propane. Activities usually declined with pulse number, but selectivities changed little. The $Mo(0)/Al_2O_3$ catalyst is initially metallic molybdenum and metallic molybdenum is catalytically active.

INTRODUCTION

Among the topics of earlier reports of catalytic reactions on unsupported molybdenum of low oxidation number (O.N.) were isotopic exchanges between cyclohexane and deuterium at 56 to 111°C (*1*) and between benzene and benzene-d_6 at 0°C (*2*), the hydrogenation of ethylene at −73 to 27°C (*3*), and the hydrogenolysis of cyclopropane at 0°C (*4*), all on evaporated molybdenum film, the hydrogenolysis of ethane at 375 to 400°C on MoO_2 reduced at 600°C (*5*), and the isomerization of hexane at 330°C on $Mo–MoO_2$ prepared by reducing MoO_2 at 500–600°C (*6*). The presence of both Mo and MoO_2 was required if isomerization was to occur. A temperature of 600°C is too low to produce a clean surface of molybdenum (*7*).

The first supported molybdenum catalyst in which the molybdenum was in low O.N. was prepared by Banks and Bailey by depositing $Mo(CO)_6$ on PDA (*8*) (for symbols see Ref. (*20*, Table 1)). Olefin metathesis was discovered by the authors on that material. The average O.N. of the Mo was probably in the range of *2–4* (*9*). The first supported metallic molybdenum catalyst, Mo/DA, was prepared by $Mo(CO)_6/DA;He,300–500°;H_2,650–950°$ (*7, 10*). The chemistry of these preparations is described in the preceding article.

In addition to metathesis, molybdenum in low oxidation number on Al_2O_3 prepared from $Mo(CO)_6/Al_2O_3$ was found to exhibit other striking catalytic properties. The hydrogenation of propylene was fast at −46°C, in particular, too fast to measure on $Mo(CO)_6/DA:He,300°;H_2,500°$ (*10, 11*). $Mo(CO)_6/Al_2O_3;He,500°$ is the most active supported catalyst so far reported for the isotopic exchange between cyclopentane and deuterium (*12*). Among supported catalysts, $Mo(0)/Al_2O_3$ is clearly exceeded in

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catalytic activity for the hydrogenolysis of alkanes only by Ru. Propane undergoes both single and double hydrogenolysis on Mo (*13*). Mo(0-2)/Al_2O_3 is active but less so than supported Pt (*11, 14*) for the hydrogenolysis of cyclopropane. Unlike Pt, Mo gives both single and double hydrogenolysis. $Mo(CO)_6/Al_2O_3$;He,300–500° and $Mo(CO)_6$/DA;He,300°;H_2,650° are good catalysts for the hydrogenation of CO at 300°C (*10*).

Other reports on Mo as a methanation catalyst have appeared. Murchison has reported good activity for Mo/Al_2O_3 and Mo/C although he considered the latter the better catalyst (*15*). Other reports appear in Refs. (*16–18*). The first of these papers dealt with Mo/Al_2O_3, the others with unsupported Mo.

Activated $W(CO)_6/Al_2O_3$ resembles similarly activated $Mo(CO)_6/Al_2O_3$ catalytically (*14*), for example, as a methanation catalyst (*10, 19*).

Although it had been generally considered that MoO_3/HA could not be reduced below about Mo^{4+}, it was found that MoO_3/HA;H_2,650° produced a material in which the Mo had an O.N. below 4+ and that MoO_3/HA;H_2,950° led to Mo(0) on Al_2O_3 (*7, 13, 14*). Further studies on this matter have supported these conclusions (*20*). A few preliminary studies on hydrogenation and hydrogenolysis had indicated that the catalytic behavior of these materials resembled that of $Mo(CO)_6/Al_2O_3$ activated to give the same O.N. as the reduced MoO_3/HA (*13*). Further work to check the validity of this initial conclusion appeared desirable. In addition, there was a serious question about the actual operating catalysts. One might start with a clean molybdenum surface, but in the presence of hydrocarbon or CO does the surface become converted to either carbide or oxycarbide and if so how fast? Indeed, there was a question as to whether the surface of molybdenum metal itself would be catalytically active. These questions go back to Ref. (*5*). There has been considerable interest in the preparation and catalytic properties of carbides and oxycarbides of Mo (*21*) and W, for example, for the hydrogenation of CO (*22*) and for the hydrogenation of ethylene (*23*). Further, $Mo(CO)_6$/DA;He,300° is a very active catalyst for a number of reactions, but C/Mo and O/Mo are 0.3 for this material (*14*); it could be considered a form of oxycarbide. Thus, while catalyzing the hydrogenation of CO, $Mo(CO)_6$/DA,He,300° and the oxycarbide of Ref. (*22*) might converge to a rather similar composition.

A major purpose of this research was to shed some light on these questions. MoO_3/HA seemed a particularly appropriate precursor since the resulting Mo(0)/Al_2O_3 catalyst should be free of carbide. This paper reports studies of the hydrogenolysis of propane at 250°C, and of cyclopropane (CP) and methylcyclopropane (MCP) at 50 and 100°C. A subsequent paper will report a study of the hydrogenation of propene at −63 to −30°C. Some of this material has been the subject of a preliminary communication (*24*). This set of reactions will provide a temperature interval of 300°C over which to assess conversion to carbide. The amounts of carbon retained by catalysts consequent to the various reactions have been measured after various times on stream.

Methylcyclopropane hydrogenolysis has the advantage that the selectivity ratio, butane/isobutane, may provide information about the presence of acid-catalyzed reactions (*25*) which would lead only to products with an unbranched chain, perhaps directly, perhaps via preliminary desorption of normal butenes followed by their hydrogenation.

EXPERIMENTAL

MCP contained about 1% butane and 0.1% *i*-butane for which corrections were made in calculating conversions. MCP, CP, and propane were used without purification, but pulses of these materials passed over MnO/SiO_2 before reaching the catalyst.

The hydrogenolyses of MCP, CP, and propane were investigated in a pulse reactor (*20, 11, 13*) on catalysts which have been described previously (*20*). Usually, 30-μmol pulses were passed over a catalyst sample which contained ca. 10 μmol of surface molybdenum atoms, Mo_S. The contents in O_2 of the H_2 and the He employed were kept low by use of traps of MnO/SiO_2. The actual content in O_2 at the reactor was measured as before (*20*). Any oxygen leak into the system was less than 0.01 μmol h^{-1}.

After insertion into the apparatus, samples of MoO_3/HA were treated O_2,500°,1; He,500° and then exposed to a further pretreatment. Only the further pretreatment will be listed.

In a number of cases the amount of carbonaceous deposit resulting from passing pulses of hydrocarbon over a catalyst in a catalytic run was measured by heating the catalyst in hydrogen to 950°C while the hydrocarbon formed, mostly methane, was collected in a silica gel trap at −196°C (*20*). By warming the trap, the collected hydrocarbon was liberated as a pulse into the flowing H_2 and analyzed by passage through a 1.2-m column of bis(2-2-(methoxyethoxy)ethyl) ether on Chromosorb P and then a catharometer. The catalysts were heated finally at 950°C for 1 h, but stops of 10 min in the heating ramp were made at 300 and 500°C following which the collected hydrocarbon was released and analyzed.

Approximate values of N_t (the turnover frequency per second per atom of Mo) were calculated from conversions by use of the pulse width measured at the reactor by the technique described in Ref. (*13*),

$$N_t = \frac{\mu\text{mol converted per pulse}}{(\text{pulse width in sec})(\mu\text{mol Mo})}\,.$$

The pulse width at the reactor of a 30-μmol pulse of MCP injected into hydrogen flowing at 60 $cm^3\ min^{-1}$ was 4.2 sec. Pulse width was inversely proportional to flow rate.

EXPERIMENTAL RESULTS

Reaction of Cyclopropane and Methylcyclopropane on Alumina

To provide a blank, conversions were measured of three pulses of CP and MCP in hydrogen flowing at 45 $cm^3\ min^{-1}$ over 0.25 g of PHF alumina at 100°C. There was usually some decrease in conversion between the first and the last pulse. The conversion of CP to propene (the only product) was 0.7% after H_2,950°, 1.8% after H_2,650°, and 1.3% after He,500°. The total conversion of MCP under the same conditions was 5, 20, and 24%. The main products were *cis*- and *trans*-2-butene, but there were 2–3% alkanes except after He,500° and H_2, 950°;He,950°. In the latter case, the carrier was helium and the total conversion was 19%.

Hydrogenolysis of Cyclopropanes on Mo/Al_2O_3

Hydrogenolysis of MCP on Mo(O.N. = 0)/Al_2O_3 was much faster and very different in kind. For example, on 0.0442 g (34 μmol Mo) 7.4% MoO_3/HA;H_2,950°;cool in H_2, flow rate of H_2 = 60 $cm^3\ min^{-1}$, the conversion was 1.9% at 25°C; 4.6% at 53°C; and 29% at 105°C. There were no olefin products, the main product was butane, and there was substantial isobutane, and, from double hydrogenolysis, methane and propane in equal amounts, and ethane.

Rates and selectivities at 100°C given by various catalysts pretreated H_2,950°,1 are presented in Table 1. Results on the last two catalysts, prepared from $Mo(CO)_6$/DA, are presented for comparison. Similar experiments were run on the first three catalysts of Table 1 pretreated H_2,650° (for their oxidation numbers see Ref. (*20,* Table 1)). Turnover frequencies of total reaction were 70–90% of those in Table 1, but selectivities to isobutane were only about one-half as large and those to equal amounts of methane and propane were one-quarter to one-half as large.

Table 2 presents results of the hydroge-

TABLE 1

Hydrogenolysis at 100°C of MCP on Various Catalysts[a] Pretreated H_2,950°

Catalyst Mo (%)	Mo (μmol)	Pulse No.	Selectivity (mol%)					Conversion (%)	N_t[c] (sec^{-1})
			C_1 (%)	C_2 (%)	C_3 (%)	i-C_4 (%)	n-C_4[b] (%)		
0.89[d]	20	1	11	4	11	17	58	55	0.15
		3	12	5	13	18	52	48	0.13
		5	14	5	14	18	49	46	0.12
7.4[d]	93	1	20	7	20	20	33	85	0.05
		3	21	7	21	19	31	84	0.05
		5	21	8	21	20	31	84	0.05
4.8[d]	74	1	15	4	15	21	45	32	0.021
		3	14	4	14	19	49	23	0.015
		5	13	3	13	18	53	19	0.013
0.84[e]	22	1	10	25	10	5	50	68	0.11
		3	11	25	11	7	46	61	0.10
		5	11	25	11	7	46	61	0.10
0.84[e]	22	1	14	5	14	10	57	41	0.07
		3	14	4	14	10	58	41	0.07

[a] Fresh samples of catalysts prepared from MoO_3/HA were used in the first three experiments after pretreatment O_2,500°,1;H_2,950°,1. The last two experiments employed $Mo(CO)_6$/DA (*10, 13*) which was pretreated He, 400°,1 for the first of these experiments and then further treated H_2,950° for the last.

[b] C_1, C_2, C_3, n-C_4, and i-C_4 are alkanes. No olefinic products were detected.

[c] Turnover frequency in molecules reacting per second per atoms of Mo (not per surface atom of Mo).

[d] Pulses (30 μmol) of MCP into H_2 flowing at 46 cm^3 min^{-1}.

[e] Pulses (20 μmol) of MCP into H_2 flowing at 42 cm^3 min^{-1}.

nolysis of CP on Mo(0)/Al_2O_3 at 100°C and also results of injection of CP into He carrier. Injection of MCP into He gave nearly the same results as CP. There has been controversy as to whether Mo(0)/Al_2O_3 consists initially of carbide or of metallic Mo and, if metallic Mo initially, whether the surface of the catalyst is so rapidly carbided that it constitutes the actual catalyst present in catalytic runs. Therefore, the amount of hydrocarbon released on heating to H_2 to 950°C was measured. This gives the amount of carbon present on the catalyst at the end of a pulse sequence. The pulse reactor provides the ideal way to investigate this matter since observations can be made at very low effective times on stream. After a certain number of pulses, the catalyst was heated in stages to 950°C and the hydrocarbon collected was measured. At 300 and 500°C there was a 10-min halt in the 5–10°C min^{-1} temperature ramp and at 950°C, there was a 1-h hold before releasing the collected hydrocarbon. Results are presented in Table 3 as carbon atoms per Mo atom although an unknown fraction of the "coke" may be on the alumina surface. Where successive series of pulses were employed, after H_2,950°,1 the catalyst was cooled to the reaction temperature and a new sequence of pulses was passed.

Hydrogenolyses were run at 100°C on two 7.4% Mo catalysts which had been heavily exposed to CP in helium at 300°C. Conversion of CP in H_2 was drastically inhibited, being reduced from 76% (Table 2) to 0.2%. Conversion of MCP was much less inhibited, from 84% (Table 1) to 18%, but selectivity was completely altered. Products consisted of 90% butenes and 9% n-butane. Thus, the coked catalyst appears to promote ring opening almost exclusively via an acid-catalyzed process. Coke on

TABLE 2

Reaction of Cyclopropane at Various Temperatures on Mo(0)/DA

Catalyst Mo (%)	Mo (μmol)	Run T (°C)	Pulse No.	Selectivity (mol%)			Conversion (%)	N_t[a] (sec^{-1})
				C_1 (%)	C_2 (%)	C_3 (%)		
			Hydrogen carrier[b]					
0.89[c]	18.6	50	1	19	19	62	3.9	0.0073
			5	19	19	62	3.6	0.0068
			10	19	19	62	3.1	0.0060
	11.6	50	1	19	19	62	2.3	0.0091
			5	19	19	62	2.1	0.0084
4.8[d]	74	100	1	39	19	42	6.9	0.0024
7.4[e]	93	100	1	29	29	42	76	0.017
0.84[e]	22	100	1[f]	37	37	26	40	0.046
			1[g]	31	31	38	33	0.031
			Helium carrier[h]					
7.4	93	100	1	6	17	77	10.8	0.0022
			3	0	0	100	1.1	0.0002
			5				0.0	0

[a] Turnover frequency (sec^{-1}/atom of Mo).

[b] Fresh samples of catalyst pretreated H_2,950°,1;cool in H_2 except for the 0.84% catalyst which was prepared from $Mo(CO)_6/Al_2O_3$. Only alkane products were detected in these runs.

[c] Pulse (18 μmol) of CP in 50 cm^3 min^{-1} of H_2 in the first series, 11.6 μmol and 51 cm^3 min^{-1} in the second series.

[d] Pulse (30 μmol) in 53 cm^3 min^{-1} of H_2.

[e] Pulse (30 μmol) in 46 cm^3 min^{-1} of H_2.

[f] $Mo(CO)_6$/DA pretreated He,400°,1.

[g] After the preceding run, pretreated H_2,950°,1;cool in H_2.

[h] After a preceding run with pulses of MCP in carrier helium, the catalyst was pretreated H_2,950°,1;He,950°,1;cool to 25°. Pulse (39 μmol) in 45 cm^3 min^{-1} of helium was employed. Only alkane products were detected in these runs.

SiO_2–Al_2O_3 has also been reported to act as a proton acid in this reaction (*25*).

Hydrogenolysis of Propane

These experiments were run primarily to determine the degree of deposition of carbonaceous residues during the hydrogenolysis of propane. Rate and selectivity data at 250°C are presented in Table 4. Selectivities are presented as the fractions of single and double hydrogenolysis in the overall reaction as calculated from the observed mole fractions of CH_4 and C_2H_6 in the products.

single hydrogenolysis:

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4$$

double hydrogenolysis:

$$C_3H_8 + 2H_2 \rightarrow 3CH_4$$

For example, in the pulse 1 of the first run with the 0.89% Mo catalyst, the product was 37% ethane and 63% methane, whence single hydrogenolysis was 0.81 of the overall reaction and double hydrogenolysis was 0.19.

Table 5 reports the results of measuring the amount of carbonaceous deposit formed during the hydrogenolysis of propane by procedures analogous to those employed in Table 3.

Catalyst Regneration at 950°C

After a series of pulses of CP, MCP, or propane, a number of catalysts were treated H_2,950°,1 and a second pulse series was passed. This cycle was then repeated. Reproducibility was good. For example, at 250°C, with propane pulses over 7.4% Mo, successive values of N_t in pulse 1 were 0.011, 0.016, 0.013, 0.015; with MCP at 100°C, 0.019, 0.020, 0.020; and with 0.89% Mo and CP at 50°C, 0.0073, 0.0068, 0.0077.

DISCUSSION

Catalytic Identity of MoO_3/HA;H_2,950° and $Mo(CO)_6$/DA;He,400°;H_2,650°

Reference (*20*) supports the view that MoO_3/HA;H_2,950° (I), $Mo(CO)_6$/DA;He,300–500°;H_2,950° (II), and $Mo(CO)_6$/DA;He,300–500°;H_2,650° (III) are physically similar and consist of metallic Mo supported on highly dehydroxylated alumina. In this paper it is shown that the hydrogenolysis of MCP has very nearly the same rate and selectivity on I, II, and III. This paper in conjunction with previous work shows that the same situation obtains for the hydrogenolyses of CP (*11*) and propane (*13*). The close agreement in rates is shown in Table 6. The alumina of catalysts I, II, and III is a mixture of γ- and δ-alumina, but that of I and II is a slightly reduced, defect alumina which can be represented by $Al^{2+}/Al^{3+} = 0.0012$. Further, in III, C/Mo is ~0.01 rather than 0.00. Neither of these differences is evident in catalytic behavior.

TABLE 3

Carbonaceous Residues Formed during Hydrogenolysis of Cycloalkanes[a]

	Methylcyclopropane				Cyclopropane		
Mo (%)		7.4		0.84		0.89	
Source		MoO_3/HA		$Mo(CO)_6$/DA		MoO_3/HA	
Pretreatment		H_2,950°,1		He,400°,1; H_2,950°,1		H_2,950°,1	
Mo (μmol)		90		22		18.6	
T of run (°C)		100		100		50	
Pulse No.[b]	1	3	5	2	10	5	1
Conversion (%)	30	33	36	41	3.5	3.7	3.9
C_{prod}/Mo[c]	0.40	1.31	2.42	5.3	1.02	0.54	0.11
C_{react}/Mo[c]	1.34	4.02	6.70	13.1	29	14.5	2.90
C_{res}/Mo[c]	0.011	0.039	0.076	0.178	0.045	0.019	0.005[f]
C_{res}/C_{prod}[c]	0.028	0.030	0.031	0.034	0.044	0.036	0.044
100 → 300°C[d]	0.007	0.021	0.051	0.064	0.0127[e]	0.0024	
300 → 500°C[d]	0.001	0.002	0.005	0.064	0.0037	0.0036	
500 → 950°C[d]	0.003	0.016	0.020	0.050	0.0282	0.0134	

[a] The H_2 flow rate was about 45 cm^3 min^{-1} and the pulse size was 30 μmol with the 7.4% Mo catalyst and 24 μmol with the others.

[b] The pulse sequences 1, 3, 5 and 10, 5, 1 were run in those orders.

[c] For a given pulse series, C_{react} is micromoles of carbon in total reactant passed; C_{prod} is micromoles of carbon in the product of reaction; and C_{res} is micromoles of carbon in the carbonaceous residue deposited on the catalyst.

[d] Micromoles of carbon in the hydrocarbon collected between $T_{reaction}$ and 300°C, between 300 and 500°C, and between 500 and 950°C.

[e] CH_4 0.0027 μmol, C_2H_6 0.0004, C_3H_8 0.0031. These are micromoles of alkane not of carbon. Similar but smaller yields of ethane and propane were obtained with CP on 7.4% Mo but only traces elsewhere.

[f] The quantity of methane formed was so small that it was collected as one sample in unbroken heating to 950°C.

These results confirm the earlier conclusion which was based on rather sparse data that I, II, and III are catalytically equivalent materials. Thus, Mo(0)/Al_2O_3 can be prepared in the simpler fashion by reduction of MoO_3/Al_2O_3 rather than from $Mo(CO)_6$/DA.

$Mo(CO)_6$/DA;He,400° can be considered to be an oxycarbide in which C/Mo and O/Mo are about 0.25. It is considerably less active for the hydrogenolysis of propane than this material from which the carbon and oxygen have been removed by H_2,650–950° (*13*). However, as shown in Table 1, the "oxycarbide" is somewhat more active than the carbon-free material for the hydrogenolysis of MCP. (see also Ref. (*11*)).

These results conflict with reports of the hydrogenolysis of alkanes on what was believed to be clean metallic molybdenum, both a commercial molybdenum powder; H_2,500°,15 (*26*) and MoO_3/HA;H_2,950° (*27*). The activity for hydrogenolysis was very small at 350°C, many orders of magnitude lower than that reported in Refs. (*7*, *13*, *28*). The hydrogenolysis of alkanes on Mo(0)/Al_2O_3 is extremely sensitive to poisons such as O_2, CO, H_2O, and even N_2 (*13*). Oxygen is extracted from flowing H_2 at 300°C by Mo(0)/Al_2O_3 and the resulting adsorbed oxygen is removed by H_2 only at temperatures considerably in excess of 500°C (see Ref. (*13*, Fig. 2)). We suggested that the catalysts of Holl *et al.* were poisoned by oxygen or other contaminants extracted from the gases flowing over the cat-

TABLE 4

Hydrogenolysis of Propane at 250°C on Mo/Al_2O_3[a]

Mo (%)	Mo (μmol)	H_2 at[b] (°C)	Pulse No.	Double[c]	Single[d]	Conversion (%)	N_t (sec^{-1})
0.89	17.8[e]	950	1	0.19	0.81	12.5	0.035
			5	0.23	0.77	16.8	0.048
			10	0.23	0.77	17.7	0.050
7.4	89[f]	950	1	0.22	0.78	23.3	0.011
			3	0.24	0.76	24.2	0.012
			5	0.24	0.76	24.3	0.012
		950	1	0.26	0.74	33.1	0.016
			3	0.26	0.74	31.2	0.015
			5	0.24	0.76	30.5	0.015
4.8	90	1000	1	0.26	0.74	31.3	0.017
			3	0.27	0.73	29.3	0.015
			5	0.27	0.73	28.5	0.015
0.86[g]	22.4	650	1	0.26	0.74	6.3	0.014
	ex $Mo(CO)_6$/DA		3	0.26	0.74	7.3	0.016
			5	0.26	0.74	7.3	0.016
0.89	17.8[e]	650	1	0.21	0.79	1.7	0.0045
			3	0.16	0.84	2.2	0.006
			5	0.16	0.84	2.2	0.006

[a] The flow rates of hydrogen were 44 cm^3 min^{-1} except 41 cm^3 min^{-1} for the first run with the 7.4% Mo catalyst. All injections were 30 μmol.

[b] Pretreatment temperature in hydrogen for 1 h.

[c] Fraction of double hydrogenolysis.

[d] Fraction of single hydrogenolysis.

[e] Following an initial H_2,650°, the hydrogenolysis of 5 pulses of propane was measured (last entry) and the carbonaceous residue was then determined (see Table 5). The catalyst was treated O_2,500°;H_2,950°. The 10 pulses of propane shown above were then injected following which the carbonaceous residue was determined (see Table 5).

[f] After an initial H_2,950° the first 5 pulses were run and the catalyst was treated H_2,950°, 15 pulses were injected (not shown) and the carbonaceous residue was measured (Table 5). The lower set of 5 pulses shown was injected and the residue was measured again (Table 5).

[g] Made from $Mo(CO)_6$/DA; He,400°.

TABLE 5

Carbonaceous Residues after the Hydrogenolysis of Propane[a]

Catalyst Mo (%)	0.89	7.4	7.4	4.8	0.89
Mo (μmol)	17.8	89	89	90	17.8
H_2 to °C	950	950	950	1000	650
No. of pulses	10	5	15	5	5
Av conversion (%)	15.5	31.6	27.1	29.7	2.1
C_{react}/Mo[b]	50.6	5.1	15.3	5.0	25.3
C_{prod}/Mo[c]	7.84	1.61	4.15	1.49	0.53
C_1/Mo 250 → 300°C[d]	—	—	0.005	—	—
C_1/Mo 300 → 500°C	0.030	0.0054	0.0060	0.010	0.00
C_1/Mo 500 → 950°C	0.021	0.0050	0.0169	0.003	0.035
C_{res}/Mo[e]	0.051	0.0104	0.0279	0.013	0.041
C_{res}/C_{prod}	0.0065	0.0064	0.0067	0.0087	0.077

[a] Reaction temperature = 250°C, pulse size = 30 μmol, flow rates = 44 cm^3 min^{-1}; symbols and catalyst history as in Table 4.

[b] The amount of propane passed over the catalyst in the given number of pulses expressed as (mol of C in propane)/(mol of Mo on catalyst).

[c] The amount of products formed by hydrogenolysis expressed as (mol of C in products)/(mol of Mo on catalyst).

[d] CH_4/Mo in interval 250 to 300°C.

[e] Total carbon liberated during heating to 950°C = total carbon in residue, expressed as C/Mo.

alysts (*29*), but Holl *et al.* reject this view (*30*). It seems unlikely that metallic molybdenum can exist in two forms of such divergent catalytic activity, particularly in view of the catalytic near identity of samples of $Mo(0)/Al_2O_3$ prepared from MoO_3/HA and $Mo(CO)_6$/DA.

Hydrogenolyses of Cyclopropane and Methylcyclopropane

Study of the hydrogenolysis of MCP has an advantage over that of CP in that MCP has two possible products, butane and isobutane. This might help in detecting the intrusion of a ring opening process catalyzed by acids, since that would result in cleavage of the bond between the ring carbon attached to methyl and an adjacent carbon atom and not of the C–C bond opposite the methyl group (*25*). Consequently the product of hydrogenolysis would be butane and not isobutane. In hydrogenolyses, butane might be an initial product or butene might be an intermediate. It would be difficult to decide between the two possibilities because the rate of hydrogenation of butene would vastly exceed that of its formation. Since PHF alumina catalyzes the isomerization of MCP exclusively to unbranched butenes, the isomerization by PHF Al_2O_3 is acid catalyzed.

A primary carbenium is such a high energy species that one would hardly expect to form $CH_3–CH_2–CH_2^+$ by direct proton-

TABLE 6

Some Turnover Frequencies per Surface Atom of Molybdenum, N_t^s, for $Mo(0)/Al_2O_3$

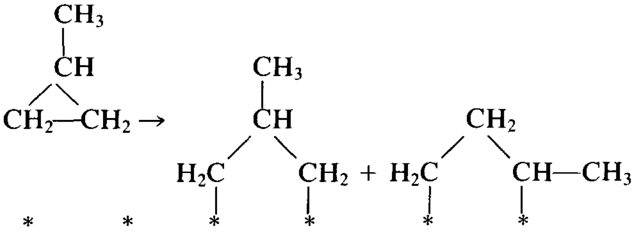
Catalyst Mo (%)	D_{CO} (%)	N_t^s in molecules reacting per second per Mo_s		
		Methylcyclopropane at 100°C	Cyclopropane at 100°C	Propane at 250°C
0.89	58	0.26		0.060
4.8	37	0.058	0.02	0.046
7.4	25	0.19	0.17	0.044, 0.064
0.84[a]	31	0.22	0.20	0.045

[a] From $Mo(CO)_6$/DA;H_2,650 or 950°.

ation of CP in acid-catalyzed reactions. The most likely initial intermediate is the lower energy, edge, or corner CPH^+ (*31, 32*). No activation energy appears to separate the edge and the corner-protonated forms (*31*). In the acetolysis of substituted cyclopropanes in acetic acid catalyzed by *p*-toluenesulfonic acid, the rate ratio, MCP/CP, was 91 at 100°C (*33*). MCP reacted to form exclusively unbranched-chain products. CP and MCP probably react to form protonated cyclopropanes as initial products, but $MCPH^+$ may well rearrange to the *s*-butyl carbenium ion before further reaction (*33*). CPH^+ is unlikely to rearrange since that would lead to a much larger rate ratio on alumina, MCP/CP, than the observed value of ~15 (*33*).

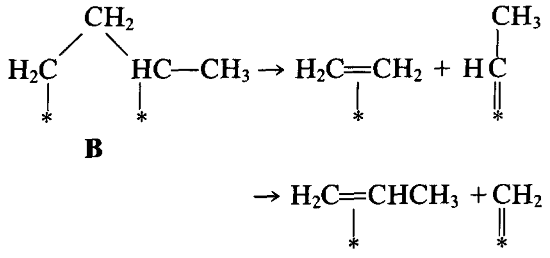
If study of MCP has an advantage over that of CP, study of both is still more advantageous. As shown by comparison of Tables 1 and 2, the rates of reaction of MCP and CP are nearly the same on the 7.8% Mo catalyst and on one derived from $Mo(CO)_6$. Thus, any substantial contribution of acid-catalyzed reactions on these materials is unlikely.

The hydrogenolysis of CP on a number of catalysts derived from $Mo(CO)_6$ involves both single and double hydrogenolysis (*11*) like Ni (*34, 35*) but unlike Pt, Pd, and Rh which give only single hydrogenolysis (*36*). The most likely mechanism for single hydrogenolysis of cyclopropanes on metals involves initial adsorption with ring opening (*11*). Unlike the situation with CP, two different products of adsorption can be formed from MCP as shown below.



A **B**

Perhaps **A** and **B** should be written as metallocyclobutanes with only one *. Intitial adsorption is followed by hydrogenolysis of the M–C bonds to liberate isobutane from 1,3-diadsorbed 2-methylpropane (**A**) and butane from 1,3-diadsorbed butane (**B**). Thus, intermediate **B** could be converted to *n*-butane or it could decompose to give intermediates which would lead to ethane or to methane plus propane.



(1)

(2)

Double hydrogenolysis of intermediate **A** would give only methane plus propane.

All $MoO_3/Al_2O_3;H_2,950°$ catalysts behave similarly in the hydrogenolysis of

MCP as shown in Table 1. Reaction was fast at 100°C, but the rate of further hydrogenolysis of alkane products is negligible. Considerable double hydrogenolysis to form ethane and equal amounts of methane and propane occurred. The amount of double hydrogenolysis (C_3 + $0.5C_2$) was roughly equal to the amount of i-C_4 and methane was always exactly equal to propane as required in the cleavage of **A** and **B**. 0.84% $Mo(CO)_6$/DA;He,400°;H_2,950° (the last entry in Table 1) behaved catalytically much like the first catalyst in the table, 0.89% MoO_3/HA,H_2,950°. However, the oxycarbide catalyst, 0.84% $Mo(CO)_6$/DA;He,400°C, which would have had retained C/Mo and O/Mo of ~0.25, differed substantially from the others in giving a much smaller value of $S_{i/n}$ and a much larger value of S_{2C_2/C_1+C_3}. These values would accord with a favored formation of **B** vs **A** on the oxycarbide catalyst.

Table 6 gives initial turnover frequencies per surface atom of molybdenum calculated from chemisorption of CO (*20*). These values are, of course, of low precision. Conversions were large in many cases and calculation of N_t^s assumes that the hydrogenolysis is zero order in MCP and that all reaction occurs at Mo_s. However, in the hydrogenolysis of propane good agreement was observed between N_t^s measured in this fashion and N_t^s measured in a flow reactor (*13*). Relative values of N_t^s should be fairly good. The activity of the catalyst prepared by the equilibrium method was lower for the hydrogenolyses of both MCP and CP.

Origin of n-Butane in the Hydrogenolysis of MCP

As shown in Table 1, the selectivity $S_{i/n}$ is less than unity, whereas on Pt, Pd, and Rh (*36*) it is considerably greater than unity. Were ring C–C bonds cleaved randomly, $S_{i/n}$ would be 0.5. One might conclude that isobutane, methane, ethane, and propane were formed at Mo(0), but that much of the butane was formed by an acid-catalyzed reaction on alumina. Against such a conclusion are the following considerations. The 7.4% Mo catalyst of Table 1 converted 84% of a pulse of MCP and 76% of a pulse of CP (Table 2), whereas the equivalent amount of Al_2O_3;H_2,950° would have converted 2.5% of a pulse of MCP and 0.3% of one of CP. Thus, the conversion of MCP on the alumina surface would be very small and that of CP, negligible. The runs with CP in carrier helium in Table 2 provide another argument to the same effect. There, the conversions in pulses 1, 3, and 5 were 11, 1.1 and 0.0%. However, on Al_2O_3 alone, decline in conversion with successive pulses was small. This would indicate that conversion in the run of Tables 1 and 2 occurred on Mo and not on Al_2O_3 and that Mo in the absence of H_2 is rapidly poisoned by decomposition products of hydrocarbon. These arguments may not be conclusive. The conditions of catalyst preparation might generate sites on the alumina surface not present on pure alumina. However, rather improbably, the very different conditions of preparation of MoO_3/HA and $Mo(CO)_6$/DA would have to generate the same active (acidic?) sites on alumina. Alternatively, hydrogen spillover from Mo(0) might somehow generate active sites on the alumina. It has been reported that hydrogen spilled over onto δ-Al_2O_3 from a subsequently removed Pt/δ-Al_2O_3 leads to a very slow isomerization of MCP at 25°C (*37*). However, the rate of hydrogenolysis of MCP on 7.4% Mo(O) in the pulse reactor at 25°C was much larger.

In the hydrogenolysis of 1,1-disubstituted cyclopropanes on Pd/C (*38*), electron-releasing groups (alkyl, $-CH_2OH$, alkoxyl) result in cleavage opposite the substituents (between C-2 and C-3 in the ring), whereas cleavage adjacent to the substituents results from electron-attracting groups (carboxy, acyl, CN). This accords with the theory for the effect of substitutents on the various bond strengths and lengths in the cyclopropane ring. In this, an electron-releasing group results in the bonds adjacent to the substituent being strengthened and shortened vs the bond opposite the substitutent, whereas an electron-attracting group has the opposite effect (*39, 40*). The weakest bond is assumed to be preferentially cleaved. If this is so, as in general seems to be the case, it is hard to see how any cleavage via species **A** and **B** can lead formation of *n*-butane to predominate with MCP. Perhaps, formation of some butane occurs by cleavage at acidic sites located at the interface between Mo and Al_2O_3 and which are not present on Al_2O_3 alone. A firm choice between this explanation (to which the authors incline) and the assumption that the excess *n*-butane is formed on Mo does not appear possible with present data.

Carbonaceous Residues and Carbiding

In previous work with $Mo(CO)_6$/DA;H_2, 650° the striking observation had been made that catalysts which had lost activity could be fully restored by H_2,950°, a temperature unprecedented for a supported catalyst. In the present work it was found that MoO_3/HA;H_2,950° behaved identically. One would suspect that deposition of carbonaceous residues originates the decline of conversion with time or pulse number when P_{O_2} and P_{H_2O} are very low. To examine this matter and also the question of carbiding of molybdenum, the amounts of carbonaceous residues resulting from runs with MCP and CP at 100°C were measured by heating in hydrogen to 950°C and measuring evolved hydrocarbon (Table 3).

The amount of MCP passed over a catalyst expressed in terms of carbon atoms per Mo varied from 1.34 to 16.5 and the turnover *number* expressed as carbon atoms in products per Mo (C_{prod}/Mo) varied from 0.40 to 6.5. With the 4.8% Mo catalyst, C_{res}/C_{prod}, the atoms of C in the carbonaceous residue per atom of C in products, was 0.050. With the other catalysts, C_{res}/C_{prod} varied only between 0.028 and 0.040 even including the first 0.84% Mo catalyst of Table 2 (oxycarbide) if one corrects for its initial content in C. With the 7.4% catalyst, the ratio was the same for 1, 3, and 5 pulses and after pulse 5 the surface contained 0.076 atoms of carbon per total Mo. Expressed in terms of Mo_s, the ratio would be four times larger. Similar results were obtained with CP (Table 3). Initially, then, a substantial fraction, 3–5%, of the total reaction leads to carbonaceous deposits although we are unable to apportion the deposit between the surfaces of Mo and Al_2O_3. C_{res}/C_{prod} was nearly the same on 4.8% Mo;H_2,650° as on catalysts pretreated H_2,950°.

Is Mo(0) itself catalytically active? Is Mo(0) converted to carbide during exposure to pulses of MCP? As for the first question, consider the 7.4% Mo catalyst in Table 3. C_{res}/Mo was only 0.011 after the first pulse, or C_{res}/Mo_s was 0.044. Coverage increased roughly linearly with pulse number and, after five pulses, C_{res}/Mo_s was 0.3 and total *molecules* of MCP reacted per Mo_s was 2.4. Clearly then, catalytic hydrogenolysis of CP or MCP at 50–100°C can occur on bare molybdenum metal and does occur on bare molybdenum initially.

Following runs with MCP, only CH_4 was liberated during H_2, 500–950°, but some C_2H_6 and C_3H_8 appeared at lower temperatures with the 4.8% Mo catalyst and the oxycarbide. Hydrocarbon liberation during H_2,100–200° was small, but carbon removed during H_2,200–300° amounted to about one-half of total carbon deposit. The interval 300–500°C led to little liberation of methane, but 500–950°C led to considerable removal of carbon, the majority of which was liberated during the 1-h hold at 950°C. One would conclude that the carbon removed at $T \leq 300$°C is not carbide, but that carbon removed at $T \geq 500$°C is carbide (surface or bulk) although it may not have been present as carbide after reaction at 100°C. Overbury has reported that ethylene adsorbs with a high degree of dissociation on clean Mo(111) at 25°C and that the noncarbidic surface carbon so formed is transferred to a subsurface position at 600 K

(*41*). The subsurface carbon (within 5 Å of the surface) is carbidic and diffuses into the bulk only at $T \geq 1500$ K.

The literature provides few data from which one can clearly determine the temperature at which H_2 would convert high area molybdenum carbide to essentially carbon-free molybdenum metal. Perhaps the clearest are the temperature-programmed reduction data of Ref. (*42*) which indicate that all carbon should be removed by H_2,950°,1. The TPR data of Ref. (*21*) are also consistent with this conclusion. Thus, the Mo(0) in MoO_3/HA;H_2,950° is free of carbide.

On MoO_3/HA;H_2,950°, the fraction of carbon in reacted molecules which is converted to carbonaceous deposit expressed as C_{res}/C_{prod} was much smaller in the hydrogenolysis of propane at 250°C (Table 5) than in the hydrogenolysis of CP at 50°C (Table 3) or of MCP at 100°C (Table 3), 0.007, 0.04, and 0.03, respectively. Judging from the data for 5 and 15 pulses of propane in Table 5, C_{res}/Mo would have been 0.002 for one pulse, or C_{res}/Mo_s would have been 0.008. At lower temperatures it would appear that H_2, perhaps that present during a pulse or perhaps that present between pulses, is less effective in removing the carbonaceous deposit which forms on the catalyst than at higher temperatures. However, even 15 pulses (C_{res}/Mo_s = 0.11) corresponded to exposure of the catalyst to propane for only about 1 min. The linear increase in C_{res}/Mo observed between 5 and 15 pulses unaccompanied by a drastic decline in activity could not be continued for many minutes. Yet in a run in a flow reactor at 250°C on $Mo(CO)_6$/DA;He,650°;H_2,650°, conversion of propane was 7.1% at 5 min, 6.6% at 20 min, and 5.9% at 650 min (*13*). After a run of several hours on $Mo(CO)_6$/DA;H_2,950°, the catalyst was exposed to a mixture of H_2 and CH_4 (2.6 : 1) at 580°C and the hydrogenolysis of propane was remeasured at 250°C. The rate of single hydrogenolysis was nearly unchanged but that of double hydrogenolysis had been reduced to 60% of its original value (*13*). If the catalyst was not converted to carbide before the 580°C treatment and became carbided during that treatment, then one must conclude that carbiding has no large effect upon overall rate, but that it selectively suppresses double hydrogenolysis. This would be reminiscent of the observation that sulfiding Ni(111) and (100) reduced the rate of double hydrogenolysis of CP much more than that of single hydrogenolysis (*43*). Even exposing 7.4% MoO_3/HA;H_2,950° to five pulses of CP in He carrier at 300°C (Table 2) produced little true carbiding judging by the fact that total C_{res}/Mo was 0.241 and yet CH_4/Mo between 500 and 950°C was only 0.012.

During the hydrogenolysis of ethane at 300°C on hcp Mo oxycarbide (*44*), the oxygen content of the oxycarbide was gradually reduced to zero and the catalytic activity for hydrogenolysis increased markedly. The terminal material was $Mo_2C_{0.83}$ which may have involved particles with a carbide core and a metallic molybdenum skin. In such a case metallic molybdenum and carbide would have similar catalytic activities.

CONCLUSION

As judged by their catalytic character in the hydrogenolyses of CP and MCP at 50–100°C and of propane at 250°C, $Mo(CO)_6$/DA;He,300–500°;H_2,650–950° and MoO_3/HA;H_2,950° are essentially equivalent catalysts, metallic Mo(0) on Al_2O_3.

The hydrogenolysis of MCP on Mo(0)/Al_2O_3 involves both single and double hydrogenolysis. The ratio, *i*-butane/butane, resulting from single hydrogenolysis is much smaller than usually seen on metals. Most of the *n*-butane must be formed on Mo, but some might be formed by initial reaction at other sites.

The reactions reported in this paper lead to deposition of carbonaceous residues, but under the conditions studied the catalysts could not have been converted to bulk carbide. Bare metallic molybdenum is clearly active. Perhaps longer times on stream would result in formation of "surface carbide" although it is not entirely clear what surface carbide means. In particular, it can be noted that surface carbon species move subsurface and become "carbidic" only at $T \geq 327°C$ (*41*).

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