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Skeletal Isomerization of Hydrocarbons on Molybdenum Catalysts

III. Catalytic Study of Alumina-Supported Catalysts

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Catalytic results obtained at a reaction temperature of 350°C with an alumina-supported molybdenum catalyst (6% MoO_3/Al_2O_3) are presented. Before all catalytic experiments the catalyst was treated under hydrogen flow at temperatures ranging from 550 to 950°C. The effect of reduction temperature has been studied. Up to and including 750°C, the reaction mechanisms are essentially acidic. After reduction at 950°C, the reaction mechanisms change and become metallic. This supported catalyst reduced at 950°C behaves exactly like the unsupported metallic molybdenum powder reported on in Part II [*J. Catal.* **104**, 211–224 (1987)]. Isomerization occurs on metallic sites via a metallacycle intermediate evolving to a carbene–olefin intermediate giving exclusively bond shift migration. This mechanism accounts for the relative migration rates of the alkyl groups which have been studied by ^{13}C labeling experiments. © 1987 Academic Press, Inc.

INTRODUCTION

In Part II (*1*) we developed considerations about the mechanisms of skeletal rearrangement of hydrocarbons on molybdenum powder and films. The results on film and powder were quite different: the film produced extremely fast cracking reactions, whereas the powder produced largely isomerization reactions. The most important conclusion of this study was that the isomerizations prevalent on the powder most probably occur on metallic sites via a metallacycle intermediate precursor evolving to a carbene–olefin intermediate giving exclusively bond shift migration. On films, on the other hand, the metallacyclobutane species is preferentially oriented toward cracking and homologation probably due to modifications of the intrinsic character of molybdenum by electronic, ligand, or support effects.

This part presents the catalytic results on alumina-supported molybdenum catalysts. This type of catalyst has also been studied by XPS (*2*).

EXPERIMENTAL

Initially, the catalyst consists of molybdenum oxide, MoO_3, supported on γ-alumina (Ketjen CK 300) at 6% concentration. The alumina impregnation was performed with an alcoholic solution of molybdenum acetylacetonate for 72 h followed by solvent evaporation, drying at 120°C for 12 h, and then calcination in air at 550°C for 2 h. This method provides uniform coverage of the carrier by an oxide monolayer (*3–5*).

This supported catalyst was studied in the same flow system as the molybdenum powder (*1*). Before the reaction, the catalyst was reduced *in situ* under hydrogen flow at 550, 750, or 950°C under a pressure of 760 Torr (1 Torr = 133.3 N m^{-2}).

The reaction temperature was kept at 350°C; the weight of catalyst was between 200 and 500 mg.

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TABLE 1

Specific Surface Areas (m^2/g) of Pure Alumina and of Supported Catalysts in Oxidic Form and after 2 h Reduction in 760 Torr Hydrogen at 550, 750, or 950°C

Pure alumina	215
Mo6	202
Mo6—550	187
Mo6—750	172
Mo6—950	144

Pretreatments consisted of heating the catalyst under hydrogen flow at a rate of 150°C/15 min to the chosen reduction temperature (550, 750, or 950°C). The catalyst was kept at this temperature for 2 h and then cooled to 350°C in 30 to 45 min to perform the catalytic experiment. The hydrogen flow rate was 40 ml/min during pretreatment and 10 ml/min during the catalytic experiments.

The notation Mo6 designates the catalyst in its original oxide form (the number 6 indicates the percentage molybdenum oxide). Mo6—550, Mo6—750, and Mo6—950 represent the catalysts reduced at 550, 750, and 950°C, respectively.

Specific surface areas were determined using the BET method. The results are shown in Table 1. It can be noted that the specific surface area remained high after a high-temperature reduction, 144 m^2/g at 950°C. This method also allowed measurement of the pore volume, which varied relatively little, from 0.6 cm^3/g for pure alumina to 0.4 cm^3/g for Mo6—950. The pore radii were nearly all between 40 and 50 Å. Thus the C_6 and C_7 hydrocarbon molecules could move freely in the pores.

The presentation of the catalytic results and the parameters used were defined in Part II (*1*). Total conversion, denoted α_T, represents the percentage of reactant transformed on the catalyst. Isomer selectivity (S_i) is the percentage of isomers of the reactant present in the transformed products. Methylcyclopentane and cyclohexane are considered to be C_6 isomers. After S_i in the tables of results we show the percentage of the different products toward all the transformed molecules. This is the reaction product distribution itself. To compare the total activity of different catalysts, we introduce the absolute transformation rate, defined as

$$R_T = (1 - \alpha_T)\frac{F}{\omega}\ln\left(\frac{1}{1 - \alpha_T}\right)$$

where α_T = total conversion, F = hydrocarbon flow in microliters per second, and ω = catalyst mass in grams.

RESULTS AND DISCUSSION

This section presents successively the results obtained on the pure carrier (CK 300 alumina) and on Mo6.

I. Test Reactions on Pure Alumina

The activity of CK 300 alumina used as a carrier was determined with 2-methylpentane (injections of 3 μl) (Table 2). The mass of the catalyst was 200 mg. The activity (α_T) of the support was relatively high. This activity was influenced markedly by the pretreatment conditions. As expected, the reaction mechanisms on alumina were obviously acidic mechanisms and were not studied in detail. Considering Experiments 1 to 4, one observes that the activity reached a maximum (Experiment 2) after pretreatment at 550°C. This activity of the carrier must be taken into account in the study of the supported catalysts. It will also be seen that the most interesting and most studied catalysts are the ones which were reduced at 950°C. Table 2 shows that under such conditions the activity of the carrier was minimal.

II. Reactions on Mo6

A. Effect of Reduction Temperature

The activities and the reaction product distributions obtained from 2-methylpentane (2-MP) were determined on Mo6 without pretreatment (Experiment 1) and after pretreatment at 550, 750, and 950°C (Exper-

TABLE 2

Test Reactions on Pure Alumina at 350°C

Expt[a]	α_T[b] (%)	S_i[c] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[d]	$C_5 + C_1$ (i/n)							ΣC_7	
1	1.4	45.7	0	0.4	23	21.2 (2.2)	9.8 (2.5)	1.2	8.8	26.2	8.3	1.2	0	ε[e]	3.2
2	4	89.5	0	0	2.9	4 (1.5)	2.9 (2.1)	0.8	?	57.7	28.7	2.3	0	0.2	2
3	0.6	77.4	0	0	9.7	7.6 (2.1)	5.3 (1.5)	1.8	?	49.6	26.0	ε	0	0	1.9
4	0.3	89.6	0	0	10.5	ε	ε	0	?	53.7	35.9	0	0	0	1.5

[a] Reactant = 2-methylpentane. Weight of catalyst = 200 mg. (1) Without pretreatment. (2) Standard pretreatment at 550°C. (3) Standard pretreatment at 750°C. (4) Standard pretreatment at 950°C.

[b] Total conversion.

[c] Isomer selectivity. (see text).

[d] Isobutane (isopentane)/*n*-butane (pentane) ratio.

[e] ε signifies a very small amount of product.

iments 2 to 4, Table 3). The experimental conditions were the same as those used for the experiments on pure alumina (Table 2). Thus the results are directly comparable.

One can observe (Table 3) that the total activity, the selectivity, and the 3-methylpentane/*n*-hexane ratio increase appreciably for Mo6—950 (Experiment 4) in comparison with the other catalysts. Selectivity in isomerization reached a high value of 96%.

The first question arising is that of the evolution of the reaction mechanisms with the catalyst reduction temperature. The XPS results in Part I (*2*) have shown that up to and including a reduction temperature of 750°C, molybdenum on Mo6 remained strongly oxidized. On the other hand, Table 2 shows that up to 750°C the contribution of the acidic carrier to the catalytic activity was important. For these reasons, one may say that up to and including 750°C, the reac-

TABLE 3

Effect of Reduction Temperature on 6% Mo/Al_2O_3 (Mo6) Catalyst

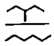
Expt[a]	α_T[b] (%)	S_i[c] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[d]	$C_5 + C_1$ (i/n)							ΣC_7	
1	1.1	48.2	0.4	0	7.9	27.4 (2.1)	16 (4.7)	1.1	?	30.2	12.8	4.1	0	0	2.4
2	1.8	35.4	0	0	10.6	31.3 (1.6)	22.7 (3.6)	0.8	?	20.1	14	0.5	0	0	1.4
3	1.2	83.7	0.6	0	5.8	6.2 (1)	3.8 (1.6)	2.4	?	51.3	26.3	3.7	0	0	2
4	2.4	96.4	0.6	0.07	1.1	1.1 (1.1)	0.8 (1.5)	2.2	?	74.8	19.4	0	0	0	3.9

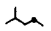
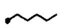
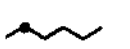
[a] Reactant = 2-methylpentane. Weight of catalyst = 200 mg. Reaction temperature = 350°C. (1) Without pretreatment. (2) Standard pretreatment at 550°C. (3) Standard pretreatment at 750°C. (4) Standard pretreatment at 950°C.

[b-d] See footnotes *b–d* in Table 2.

TABLE 4

Labeling Experiment on Mo6—750 (500 mg)

Expt[a]	α_T[b] (%)	S_i[c] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[d]	$C_5 + C_1$ (i/n)							ΣC_7	
1	2.8	71.1	0.5	13.4	8.6	3.9 (1.7)	2.4 (2.6)	1.8	3.5	35.9	28.5	1.4	ε[e]	0	1.3

											
2	26	74	1	97	2	8	23	69	21	45	34

[a] Reactant = 2-methyl[2-^{13}C]pentane. Reaction temperature = 350°C. 1) Reaction product distribution. (2) Isotopic distribution.

[b–e] See footnotes b–e in Table 2.

tions on Mo6 are probably largely dominated by acidic mechanisms. A tracing experiment on Mo6—750 (Table 4) confirms this assertion. Table 4 shows the results of an experiment performed on Mo6—750 (500 mg) starting from 2-methyl[2-^{13}C]pentane. The distribution obtained corresponds to a quasi-statistical distribution of the ^{13}C atom in the isomeric products. This means that each molecule undergoes many rearrangement reactions before desorption, which is, in this case, the rate-determining step in skeletal isomerization. This result can easily be explained on an acidic system. The reaction through carbenium ions, as shown in Scheme 1, is fast. On the other hand, desorption of the reaction products is much more difficult.

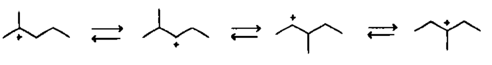
This system presents a potential complication. It has been shown by binding energies (XPS) and calculations of reaction enthalpies that on molybdenum and chromium, metallacyclobutane formation is favored by the presence of an oxygen atom double-bonded to the metal (a "spectator metal oxo bond") (*6*). Thus it is possible that on Mo6—750 (and Mo6—550), reactions linked to that kind of intermediate also take place.

The case of Mo6—950. The kinetics for Mo6—950 are totally different from those for Mo6—750 or Mo6—550. The tracer experiments (see Table 6) reveal that the statistical distribution disappeared. The rate-determining step is not the desorption but the skeletal rearrangement process. XPS analysis (*2*) has shown that the molybdenum was, under such conditions, very close to the metallic state. An increase of the metallic character leads to a greater desorption rate. A precise study of the reaction mechanisms becomes all the more possible in that the metallic character increase accompanies a clear increase in the catalytic activity (Table 3) and the contribution of the carrier becomes negligible (Table 2).

B. Reaction Mechanisms on Mo6—950

Catalytic results on Mo6—950 (200 mg) and on metallic molybdenum powder (1 g) have been compared in Tables 5 and 6: product distributions obtained from several hydrocarbons and isotopic distributions in tracer experiments are shown. The analogy between the results is obvious.

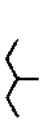
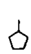
The similarities between Mo6—950 and Mo powder in total activities of several saturated hydrocarbons, in reaction product distributions, and in isotopic distributions



SCHEME 1

TABLE 5

Comparison between Mo6—950 and Mo Powder

		$R_T \times 10^3$ [a]	α_T [b] (%)	S_i [c] (%)	$6C_1$	$3C_2$	$2C_3$	$C_4 + C_2$ (i/n)[d]	$C_5 + C_1$ (i/n)										
	Mo6	1.06	2.3	92.1	1.1	0.1	3	1.6 (1.4)	2.1 (2)	1.8	?	—	75.6	14.4	0.2	ε[e]	5.25	—	—
	Mo p	1.09	12.5	91	0	0	2.1	2.6 (1.8)	4.2 (1.7)	1.4	?	—	82.2	7.4	ε	0	11.1	—	—
	Mo6	1.21	2.9	93.4	2.2	1	0.9	1.3 (0.4)	1.2 (2.4)	0.7	?	86.7	—	6	ε	0	—	14.4	—
	Mo p	1.31	18.1	92.8	0	0.2	1	2.2 (0.5)	3.9 (2.6)	0.6	1.4	84.4	—	4.3	2.1	ε	—	19.6	—
	Mo6	0.18	0.75	43.8	4.9	0	4.6	11.1 (0.7)	35.5 (4)	0.6	?	4.9	4.3	15.4	—	18.6	0.3	0.3	1.1
	Mo p	0.16	3.8	50	0	0	5.5	14.2 (0.9)	30.4 (3.9)	0.2	ε	9.1	5	5.4	—	30.3	0.9	1.7	1.8
	Mo6	0.30	1.1	74.3	3.9	0.8	6.8	7.7 (0.04)	6.4 (0.1)	0.8	?	41.5	32	—	ε	ε	—	—	1.3
	Mo p	0.33	6.4	45.4	0	2.2	12.8	18.5 (0.05)	21.2 (0.08)	0.2	0.3	24.6	19.1	—	0.8	0.4	—	—	1.3

[a] Reaction temperature = 350°C. R_T= Total rate (see text).

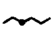
[b–e] See footnotes b–e in Table 2.

lead to the conclusion that the isomerization sites are the same on metallic molybdenum and on Mo6—950. All the mechanistic considerations developed on Mo powder (*1*) are also valid on Mo6—950.

Table 7 shows the average percentages (over three experiments) of each isomer in comparison with all the C_6 products obtained from 2-methyl[2-^{13}C[pentane (2-MP-2^{13}C), 2-methyl[4-^{13}C]pentane (2-MP-4^{13}C), 2-methyl[1-^{13}C]pentane (2-MP-1^{13}C), and 3-methyl[3-^{13}C]pentane (3-MP-3^{13}C). We call self-isomerization a reaction which moves the ^{13}C atom without changing the structure of the molecule. For example, 3-MP-3^{13}C becomes 3-MP-2^{13}C by a 1,2 ethyl shift. The self-isomerization percentages are very imprecise; therefore these reactions have not been taken into account in the study of the 2-methylpentanes. On the other hand, it was necessary to consider them in the 3-methylpentane study to determine the ethyl shift rate. One can see in Table 7 that starting with 3-MP-3^{13}C, we obtained four times more 3-MP-2^{13}C, the product of a 1,2 ethyl shift, than 2-MP-3^{13}C, the product of a 1,2

TABLE 6

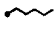
Comparison between Mo6—950 and Mo Powder: ^{13}C Labeling Experiments[a]

											
	Mo6	11	89	0	100	0	2	18	80	78	22
	Mo p	0	100	1	98	1	0	17	83	81	19
	Mo6	6	94	0	4	96	0	21	79	80	20
	Mo p	11	89	0	4	96	0	12	88	90	10
	Mo6	43	57	3	80	17	0	93	8	47	53
	Mo p	53	47	0	84	17	0	91	9	37	63

[a] Reaction temperature = 350°C.

TABLE 7

Labeling Experiments on Mo6—950[a]

	α_T[b] (%)														
1. 	1–3	1.9	0.3	3				0	18.2	57.5	14.1		5	ε[c]	0
2. 	1–3	1.9	0.3	3.9				0	17.6	57.1	15.2		4	ε	0
3. 	1.1	2.2	?	?				25.6	1.9	41.9	13.8	3.9	10	0.6	0
4. 	1–3	0.2	0.4	0.6	1	15.7	5.4	10.2		64.7	0.9		0.9	ε	0

[a] Percentage of each isomer toward all C_6 products. Lines 1–3: 2-methylpentane, self-isomerization not taken into account. Line 4: 3-methylpentane, self-isomerization taken into account.

[b] See footnote *b* in Table 2.

[c] See footnote *e* in Table 2.

methyl shift. It can be concluded that the ethyl shift is 4(±1) times faster than the methyl shift on molybdenum.

For comparison, on platinum, the ethyl shift is faster than the methyl shift for C_5 hydrocarbons (*7*), and the shift rate is the same for C_6 and C_7 (*8*).

The chain-shortening (CS) methyl shift produces 2,3-dimethyl[1-^{13}C]butane from 2-MP-4^{13}C. We observe 0.3 mol of this product for 100 mol of isomers (Table 7); thus the corresponding reaction is absolutely negligible.

A comparison between 3-MP-2^{13}C and 2,3-dimethyl[2-^{13}C]butane (Table 7, lines 1 and 2) shows that the methyl shift is about 20 times faster than the isopropyl shift. Table 7 also allows one to assert that the methyl shift is 30 times faster than the CS ethyl shift which produces neohexane from 2-MP.

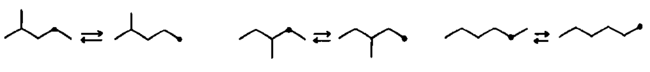
The order of theoretical bond shift rates stated in Part II (*1*), Et > Me > iPr = nPr > Et-CL > Et-CS > Me-CS > Me-CL, is thus confirmed and to some extent quantified. (CS signifies chain shortening and CL, chain lengthening). However, because the nPr and Et-CL shifts cannot be isolated, it is not possible to verify or clarify the sequence iPr = nPr > ET-CL > Et-CS.

If we apply to the 2-MP-1^{13}C the model established for 2-MP, we obtain the diagram in Fig. 1. We note that none of the proposed reactions account for *n*-[2-^{13}C]hexane. This product can be explained by reactions which we call intra-extra shifts (Scheme 2). These reactions are relatively facile according to Figs. 6 and 7 in Part II (*1*). An accurate study of this kind of shift is not possible because products such as 2-MP-5^{13}C and 3-MP-5^{13}C are very difficult to characterize by mass spectrometry.

CONCLUSION

The reference catalyst of this study (Mo6) consists in its original form of 6% molybdenum oxide supported on alumina. It undergoes an *in situ* reduction under hydrogen flow before all catalytic experiments.

Up to and including a reduction temperature of 750°C, the reaction mechanisms on Mo6 are essentially acidic. The study of the catalytic properties of the pure carrier showed an important participation of the



SCHEME 2

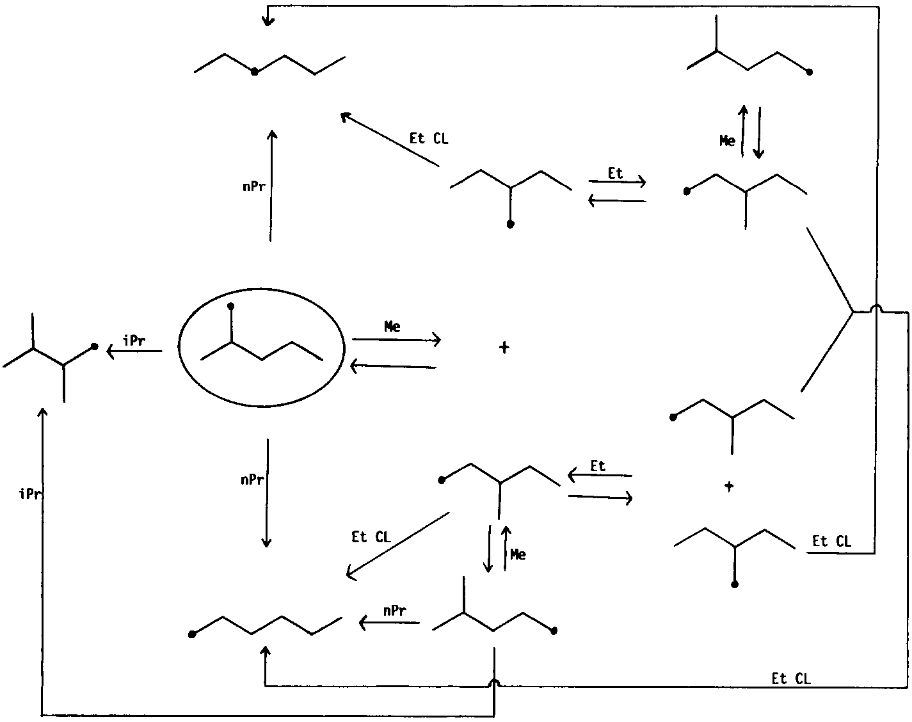


FIG. 1. Isomerization of 2-methyl[1-^{13}C]pentane on Mo6—950.

acidic sites of the alumina in the catalysis. The XPS study (*2*) clearly showed the existence of many oxidized sites, MoOx. A ^{13}C labeling experiment on Mo6—750 indicated particular kinetics in which the slow step is the desorption of the products. A hydrocarbon undergoes many skeletal isomerization reactions before desorbing.

When the reduction temperature reaches 950°C the kinetics are completely modified: the carbon–carbon bond rupture becomes the slow step of the reaction process. According to the XPS study (*2*), molybdenum is very close to the metallic state. The Al_2O_3 carrier has negligible activity. This kind of catalyst is more active and more selective toward isomerization than catalysts reduced at lower temperatures. The isomerization mechanisms on Mo6—950 have been thoroughly studied. A parallel has been drawn between reaction mechanisms on Mo6—950 and on metallic molybdenum in powder form. The main goal of this study was to establish that metallic molybdenum has isomerizing properties which could also be found on Mo6—950. On metallic molybdenum, isomerization occurs solely by a bond shift. The cyclic mechanism, very important on platinum, iridium, and palladium, is completely missing, which reinforces the mechanism of Garin and Gault (*7, 8*) proposing a metallacyclobutane species to explain the bond shift mechanism. It must be noted that at a reaction temperature of 350°C molybdenum is about 1000 times less active than platinum. This mechanism accounts for the relative migration rates of the groups which are in the order Et > Me > iPr = nPr > Et-CL > Et-CS. The ethyl shift is four times faster than the methyl shift, which itself is 20 times faster than the isopropyl shift and 30 times faster than the chain-shortening ethyl shift.

It will be shown later (*9*) that other pretreatment conditions on supported molybdenum can lead to very different catalytic properties by analogy with the results obtained on evaporated Mo films where cracking and homologation are enhanced. However, the behavior is still in agreement with the general mechanistic proposals of Maire and Garin (*10*) for explaining the isomerization, cracking, and homologation reactions.

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