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Reactions of 2- and 3-Methylpentane, Methylcyclopentane, Cyclopentane, and Cyclohexane on Activated Mo_2C

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Molybdenum carbide, prepared by a new synthetic route and further activated either by reductive or by oxidative treatments, has been studied as a catalyst for isomerization of 2- and 3-methylpentane and also for hydrogenolysis of cyclopentane, cyclohexane, and methylcyclopentane. The nature of this activating pretreatment dramatically modifies both the activity and the selectivity of the catalyst. Reductive pretreatments lead either to inactive, or to active but poorly selective, catalysts (Mo metal on the surface or pure Mo carbide), whereas oxidative treatment first inhibits the hydrogenolysis reaction present on oxygen-free molybdenum carbide, and second, enhances the isomerization rate of the catalyst. The branched molecules isomerize to give mostly acyclic isomers. No deactivation is observed with time on stream during isomerization of the branched molecules. The rate of hydrogenolysis of methylcyclopentane and cyclopentane is about four times lower than the rate obtained with branched molecules, and the catalyst is strongly deactivated. This phenomenon is attributed to the formation of highly dehydrogenated polyaromatics, and to the formation of CH_4, by demethylation of methylcyclopentane, which can irreversibly reduce the oxicarbide phase. The deactivated catalyst can easily be regenerated by a short oxidative treatment at 350°C. The results, in terms of both activity and isomer selectivity, obtained for *n*-hexane, 2-methylpentane, and 3-methylpentane isomerization are attributed to a bond-shift mechanism involving a metallocyclobutane ring intermediate which would take place on an oxicarbide phase.

1. INTRODUCTION

In the last 2 decades, several authors have shown that transition metal carbide catalysts resemble the noble metals for their high catalytic activities in a large range of reactions (*1–8*). Nevertheless, to be well suited for catalytic use, the carbides must exhibit a high specific surface area. So far, two main routes have been found to synthesize transition metal carbides with specific surface areas as high as 220 $m^2 g^{-1}$, i.e., reaction of hydrocarbon with the solid oxide (*9–11*) and reaction of the metallic oxide vapors with activated charcoal (*12*). However, the surface carbide is very sensitive and is quickly covered by oxidic species when handled in air, as revealed by XPS analysis (*14*). For this reason, it is necessary to reactivate the surface prior to its use as a catalyst. In previous articles, we reported different routes for reactivating the carbide before a catalytic reaction: reductive (*13, 14*) and oxidative activation (*15*) processes.

Three different reductive activation processes were tested to clean the surface carbide. These activations were carried out *in situ* before the catalytic reaction: (1) direct reduction under H_2 flow at 800°C and normal pressure for 2 h; (2) coreduction/carburization of the oxidic layer by an *n*-pentane/hydrogen mixture at 700°C followed by reduction under H_2 flow at 600°C for 2 h, in order to remove traces of carbonaceous residues; (3) same treatment as (2) but in the presence of trace amounts of Pt or Ir (ca.

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500 ppm). After the activation treatment the carbides were tested for *n*-hexane isomerization and characterized by several techniques such as XRD, TPR, XPS, and BET measurement. Full details of the application of these techniques and their results are given in Ref. (*14*). The first activation process yielded a surface carbide polluted by Mo metal which is known to be a very poor catalyst for isomerization. The second reductive process allowed the recarburization of the oxidic layer, but left a large amount of carbonaceous residue blocking access of the reactant to the active sites. When the reductive activation was performed in the presence of trace amounts of Pt or Ir, the specific activity of the catalyst was greatly increased while the selectivity for C_6 isomers was still very low (14% on Mo_2C) compared to the selectivity obtained on a conventional Pt catalyst (ca. 80–90%). It was concluded that on clean surface carbide (checked by XPS) the main reaction observed was hydrogenolysis (*14*). The same observation has been reported by several other authors (*16–18*).

A new activation process was also tested, using an oxidative treatment in order to investigate the effect of oxygen on the isomerization activity of molybdenum carbide (*15*). In this process, the carbide was calcined under air flow at 350°C for 14 h; this was followed by a stabilization period under the reacting mixture *n*-hexane/hydrogen at 350°C for 6 h. The molybdenum carbide treated in this way exhibited both a high specific activity and a high selectivity for isomerization (ca. 90%). Various physical analyses showed that the active phase is probably an oxicarbide which oxygen atoms penetrate by substitution or by saturation of vacancies in the carbide lattice (*15*). The increase in isomer selectivity after an oxidative treatment was also observed by Iglesia and co-workers (*16–18, 23*) for several reactions of alkanes on WC catalysts. These authors have shown that oxygen atoms selectively inhibited the cracking sites and they proposed a bifunctional mechanism for the isomerization reaction.

The aim of the present article is to report the activity and isomerization selectivity of other molecules such as 2-methylpentane, 3-methylpentane, methylcyclopentane, cyclopentane, and cyclohexane on molybdenum carbide and molybdenum oxicarbide catalysts. The results could be used to elucidate the reaction mechanism involved in the isomerization of alkanes on these catalysts. In this study, we also report the unique effect of methylcyclopentane on molybdenum oxicarbide catalysts; the methylcyclopentane molecule strongly deactivates molybdenum oxicarbide both by carbonaceous deposits and by reduction of the active phase itself, which affects both the activity and the selectivity of the catalyst for isomerization. The catalyst can, however, be easily regenerated by a short oxidative treatment.

2. EXPERIMENTAL METHODS

2.1 Catalysts and Pretreatment

The molybdenum carbides used in these tests are synthesized by reaction between solid charcoal and oxide vapor under reduced pressure; the principle and the results have already been described (*12, 19*).

The X-ray diffraction patterns of the molybdenum carbide after synthesis (*14*) show that only hcp Mo_2C is present in the product and the *d*-spacings coincide well with those reported in the literature (*20*). Since XRD does not show any evidence of bulk molybdenum oxides, it is assumed that a significant proportion of the oxygen is either adsorbed on the surface or more probably, as shown by XPS (*15*) or by TPR analysis (*14*), present as suboxides or amorphous oxidic phases. A double elemental analysis gives a stoichiometric Mo_2C associated with the remaining unreacted carbon which is localized and buried in the heart of the particle (particle diameter: 0.250–0.450 mm). The low amount of oxygen cannot be accurately measured by elemental analysis.

Four activation processes are performed on this polluted Mo_2C. Details of these pro-

TABLE 1

Comparison of Activity and C_6 Isomer Selectivity for 2- and 3-Methylpentane Reaction on Mo_2C Catalysts, Activated by Different Reductive and Oxidative Treatments (α = Conversion; r = First-Order Apparent Rate)

Catalyst	Test molecule							
	2-methylpentane				3-methylpentane			
	α (%)	$r \times 10^{-10}$ (mol/s/g)	S_{C_6} (%)	$Y_i \times 10^{-10}$ (mol/s/g)	α (%)	$r \times 10^{-10}$ (mol/s/g)	S_{C_6} (%)	$Y_i \times 10^{-10}$ (mol/s/g)
Mo_2C reductive activation[a]	33.8	3032	5	152	34.5	2578	6	154
Mo_2C reductive activation[b]	1.4	219	20	44	1.04	137	28	38
Mo_2C reductive activation[c]	6.1	889	26	231	6.3	811	25	203
Mo_2C oxidative activation[d]	39.8	2499	90	2249	57.7	2408	91	2191

[a] Mo_2C, after synthesis and air exposue at RT, is reduced directly under H_2 flow at 800°C for 2 h and the reaction temperature is 600°C.

[b] Mo_2C, after synthesis and air exposure at RT, is treated under *n*-pentane/H_2 mixture up to 700°C and then further reduced by H_2 at 600°C for 2 h. The reaction temperature is 350°C.

[c] Mo_2C, after synthesis and air exposure at RT, is impregnated with 500 ppm of Pt and then treated under *n*-pentane/H_2 mixture up to 700°C and then further reduced by H_2 at 600°C for 2 h. The reaction temperature is 350°C.

[d] Mo_2C, after synthesis and air exposure at RT, is oxidized under air flow at 350°C for 14 h followed by a reactivation period under *n*-hexane/H_2 mixture at 350°C up to the steady state.

cesses were published in Refs. (*13–15*) and are presented in Table 1:

(a) Direct *in situ* reduction under pure H_2 flow at 800°C.

(b) *In situ* reduction by a mixture of *n*-pentane/H_2 at 700°C.

(c) *In situ* reduction by the same mixture at 700°C but the carbide is impregnated with 500 ppm of Pt or Ir.

(d) *In situ* oxidation under air at 350°C for 14 h, followed by a stabilization period under *n*-hexane/H_2 for 5 h at 350°C, after which *n*-hexane is replaced by the test molecule [2-methylpentane (2MP), 3-methylpentane (3MP), methylcyclopentane (MCP), cyclopentane (CyP), or cyclohexane (CyH)] without changing the catalytic reaction conditions. After reaction with 2MP, 3MP, MCP, CyP and CyH the flow is switched back to *n*-hexane; this last test is used to check if any deactivation or change in selectivity has occurred on the catalyst during isomerization with the test molecules.

2.2. Catalytic Reaction Conditions

Details of the catalytic reaction conditions and a description of the microreactor used were given in Ref. (*14*).

3. CATALYTIC RESULTS AND DISCUSSION

3.1. 2- and 3-Methylpentane Reactions

Table 1 shows the activity and the C_6 selectivity for 2- and 3-methylpentane reactions on Mo_2C activated by the four processes. Although these reactions are performed at different conversions, this cannot explain the large differences in selectivity. Moreover, an increase in the conversion should normally lead to a decrease in selectivity, but for the three tests at 350°C, large increases (~20 to 90%) are observed.

The Mo_2C activated by direct reduction under H_2 at 800°C for 2 h shows no activity up to 600°C. This lack of activity at temperatures below 600°C can be attributed to the presence of surface Mo metal, formed by the decomposition of Mo_2C by H_2 at 800°C. The main reaction at 600°C occurs through an hydrogenolysis mechanism (selectivity for isomers ≈5–6%). This low selectivity confirms that the catalyst is not able to isomerize.

A low specific rate is observed at 350°C (219 and 137 × 10^{-10} mol s^{-1} g^{-1}) on molybdenum carbide, activated under an *n*-pentane/hydrogen (20 Torr/740 Torr) mixture without traces of platinum. Selectivity is improved (20–28% instead of 5%), which can be attributed to the difference in temperature, but is still low when compared to conventional Pt/Al_2O_3 catalyst. This low activity is similar to that obtained when *n*-hexane was used (*14*) and is attributed to the presence of polymeric carbon, formed by decomposition of *n*-pentane which covers the active sites. Much higher activities are obtained by using the same gaseous treatment but in the presence of traces (ca. 500 ppm) of noble metals, such as Pt or Ir, which can catalyze the recarburization and also the hydrogenation of the polymeric carbon, to give "clean" surface carbide. The specific rate is greatly improved (889 and 811 × 10^{-10} instead of 219 and 137 × 10^{-10} mol s^{-1} g^{-1}) but the selectivity is still low (ca. 25%) showing that clean carbide surfaces mainly catalyze the hydrogenolysis of C–C bonds.

When the catalyst is treated with air and then "reactivated" under an *n*-hexane/hydrogen mixture at 350°C for a few hours, it can be seen that, both specific rate and isomer selectivity are strongly increased. Details of these reactions are reported in Tables 2 and 3. This phenomenon has already been observed for the case of *n*-hexane isomerization in a previous article (*15*).

The branched molecules (2- and 3-methyl-

TABLE 2

2-Methylpentane Reaction on Molybdenum Oxicarbide Catalyst (Air Calcination at 350°C for 14 h)

	Test molecule											
	n-Hexane				2-Methylpentane						*n*-Hexane	
Time on stream (h):	0.8	1.7	3.3	5.8	6.3	7.5	10.3	25.8	26.8	30.3	30.6	31.6
$r \times 10^{-10}$ (mol/g/s)	537	1025	1478	1559	1928	2194	2087	2495	2614	2499	1513	1648
S_i (C_6) (%)	81	83	87	87	87	89	89	90	90	90	89	88
$Y_i \times 10^{-10}$ (mol/g/s)	435	851	1278	1356	1677	1953	1857	2246	2353	2249	1347	1450
Σ Cracking (%)	19	17	13	13	13	11	11	10	10	10	11	12
	Selectivity of reaction products											
Isomer selectivity (%)												
2,2-DMB	2	2.2	2.4	2.4	3.6	3	3	3	3	3	2	2
M2P	63	63	63.2	63.4	—	—	—	—	—	—	63	62
M3P	33	33	33.3	33	40	44	44	51	52	51	34	35
HEX	—	—	—	—	56.4	52	53	46	45	45	—	—
MCP	1.6	1.5	0.7	0.8	0.6	1	0	0	0	1	1	0.5
BEN + CYC	0.4	0.3	0.4	0.4	0.4	0	0	0	0	0	0	0.5
Cracking selectivity (%)												
C5 + C1	18	19	22	24	22	29	25	38	39	37	41	36
C4 + C2	22	22	24	24	22	23	23	27	27	27	25	31
2 C3	59	58	53	52	53	48	47	33	31	32	29	32
3 C2	0.5	0.5	0.5	0	2	0	5	1	2	3	4	1
6 C1	0.5	0.5	0.5	0	1	0	0	1	1	1	1	0

TABLE 3

3-Methylpentane Reaction on Molybdenum Oxicarbide Catalyst (Air Calcination at 350°C for 14 h)

	Test molecule											
	n-Hexane			3-Methylpentane						*n*-Hexane		
Time on stream (h):	0.5	2.5	5	5.5	7.5	22	24	26	29.5	31	48	49
$r \times 10^{-10}$ (mol/g/s)	363	1473	1639	2257	2361	2321	2382	2390	2408	1643	1611	1624
S_i (C_6) (%)	81	87	88	90	91	92	91	91	91	89	90	86
$Y_i \times 10^{-10}$ (mol/g/s)	294	1282	1442	2031	2149	2135	2168	2175	2191	1462	1450	1397
Σ cracking (%)	19	13	12	10	9	8	9	9	9	11	10	14
				Selectivity of reaction products								
Isomer selectivity (%)												
2,2-DMB	2	2	3	2	3	2.3	2.4	2.4	2.5	2	1.8	2
M2P	63	64	62	61	62	63.6	63.7	64	64	59	61.5	61
M3P	33.5	33	34	—	—	—	—	—	—	38.5	36.2	36.4
HEX	—	—	—	36.5	34.5	33.7	33.3	33	33	—	—	—
MCP	1.2	0.5	0.5	0.3	0.3	0.3	0.4	0.4	0.3	0.3	0.3	0.4
BEN + CYC	0.3	0.5	0.5	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2
Cracking selectivity (%)												
C5 + C1	20	23	27	29	31	35	37	36	38	37	39	37
C4 + C2	21	24	26	27	27	28	29	30	30	29	29	31
2 C3	53	51	46	43	41	32	31	29	29	28	26	24
3 C2	2	1	0.5	0.5	0.5	2	2	2	2	3	2	4
6 C1	4	1	0.5	0.5	0.5	3	1	3	1	3	4	4

pentane) are more reactive than the linear molecule for isomerization (2499 vs 1559 × 10^{-10} and 2408 vs 1639 × 10^{-10} mol s^{-1} g^{-1} for 2- and 3-methylpentane, respectively). In addition, no deactivation versus time on stream is observed during the test period and the C_6 selectivity remains very high, ca. 90–91% (cf. Tables 2 and 3). The tests carried out under *n*-hexane at 350°C after reaction with the branched isomers show that the catalyst is unchanged in terms of activity and selectiviy. Only a small difference is observed in the selectivity of the cracked products, less 2 C_3 and more C_5 + C_1 are formed. But this difference is not due to the reaction with the branched molecules because it is also observed when *n*-hexane is run alone for a long period (see, for instance, in Table 7, the selectivity for the *n*-hexane reaction after regeneration of the catalyst). The formation of C_3 is generally attributed to strong Bronsted acidic centre on the surface. It is possible that such sites are present at the beginning of the reaction and are poisoned with time.

The distribution of the C_6 isomers shows high selectivity for the linear and branched molecules (2MP → 3MP + *n*-HEX, 3MP → 2MP + *n*-HEX); very few cyclic molecules (methylcyclopentane and benzene) are observed (less than 1% of the total C_6 molecules). Only traces of olefins are detected amongst the reaction products (<1%, mainly C_4 olefins).

3.2. *Methylcyclopentane Reaction*

As shown in Table 4, the specific rate of isomerization drastically decreases after half an hour of reaction, from 1614 to 356 × 10^{-10} mol g^{-1} s^{-1}. The catalyst continues to deactivate during the course of the reaction but not so rapidly and reaches a steady state after four hours at 350°C. The rate of isomerization observed for methylcyclopentane at this steady-state is about ten times lower than that of the linear or

TABLE 4

Methylcyclopentane Reaction on Molybdenum Oxicarbide Catalyst (Air Calcination at 350°C for 14 h)

	Test molecule											
	n-Hexane				Methylcyclopentane					*n*-Hexane		
Time on stream (h):	0.5	1	3	5	5.5	7	8	24	26	28	45	47
$r \times 10^{-10}$ (mol/g/s)	133	643	1386	1614	356	278	189	174	182	339	541	606
S_i (C_6) (%)	80	84	88	90	94	94	92	85	84	76	75	72
$Y_i \times 10^{-10}$ (mol/g/s)	106	540	1220	1452	335	261	174	148	153	258	406	436
Σ cracking (%)	20	16	12	10	6	6	8	15	16	24	25	28
	Selectivity of reaction products											
Isomer selectivity (%)												
2,2-DMB	1	2	2	1	1	0	0	0	0	1	1	0
M2P	59	63	62	61	10	10	11	15	14	40	51	50
M3P	32	32	33	34	4	4	4	7	6	25	33	31
HEX	—	—	—	—	13	14	16	10	10	—	—	—
MCP	7	2	2	2	—	—	—	—	—	33	14	17
BEN + CYC	1	1	1	2	72	72	69	68	70	1	1	2
Cracking selectivity (%)												
C5 + C1	18	18	19	18	26	29	30	34	27	42	41	38
C4 + C2	24	23	22	23	28	29	35	26	24	27	27	28
2 C3	51	56	58	56	22	21	23	16	15	19	21	20
3 C2	2	1	0.5	2	9	4	2	5	6	4	4	5
6 C1	6	2	0.5	1	15	17	10	18	21	8	7	9

branched molecules such as *n*-hexane or the methylpentanes. This low reactivity is attributed to the fast formation of carbonaceous residues. These residues are obtained by extensive dehydrogenation of methylcyclopentane to give methylcyclopentadienyl or cyclopentadienyl which, by condensation, form polymethylcyclopentadienyl or polycyclopentadienyl which are known to be good coke precursors (*21*), according to the diagram shown in Fig. 1a.

The distribution of the C_6 products shows that molybdenum oxicarbide preferentially forms benzene and cyclohexane from MCP (72%). This may be explained by the mechanism presented in Fig. 1b: the methylcyclopentane is transformed into cyclohexane (*21*) which dehydrogenates to give benzene. The formation of methane is attributed to a demethylation of MCP to form cyclopentane which itself dehydrogenates and condenses to give polycyclopentadienyl. If methylcyclopentane adsorbs via a metallocyclobutane which splits into a methylidene radical and an adsorbed cyclopentene molecule as presented in Fig. 1b, the formation of a large amount of C_1, in excess of the C_5, can be understood. The methylidene radical is hydrogenated to CH_4 while cyclopentene polymerizes and does not desorb. The same intermediate can also yield C_5 ring opening but at a slower rate, followed by insertion of the C_1 radical and desorbtion of cyclohexane.

The C_6 selectivity slightly decreases from 94 to 84% after 21 h under the methylcyclopentane/hydrogen mixture (Table 4). This phenomenon can be attributed to a slight recarbidation of the oxicarbide surface induced by the decomposition of the methylidene adsorbed radical.

The test under the *n*-hexane/hydrogen mixture performed afterwards under the same conditions, confirms the large deactivation of the catalyst (factor 5). In addition, the isomerization rate of *n*-hexane rises

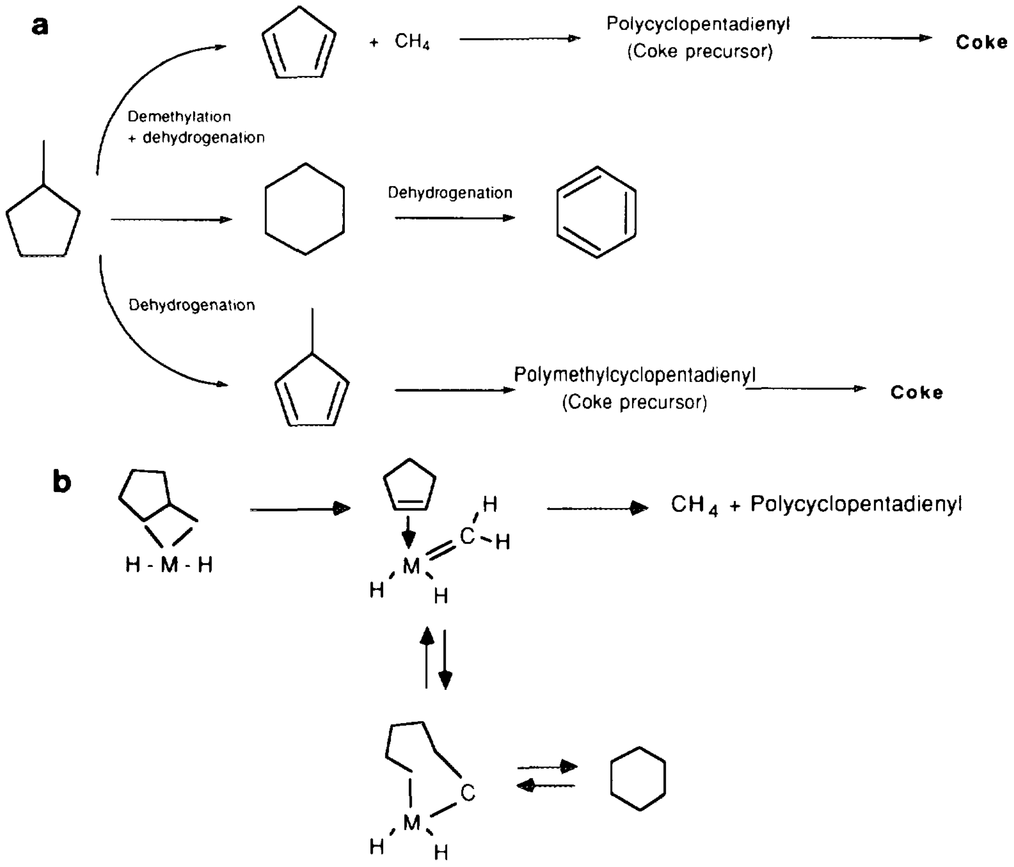

FIG. 1. (a) Coke formation from methylcyclopentane. (b) Reaction mechanism for cyclic molecules.

slowly after the methylcyclopentane tests, from 339 to 606 × 10^{-10} mol s^{-1} g^{-1}, showing that the catalyst itself catalyzes the gasification of the coke deposited on the surface (this phenomenon is illustrated by the formation of abnormal extensive cracked products such as C_1 and C_2 molecules, which have never been observed before). The isomer selectivity is decreased from 90 to 75% after MCP exposure and remains unchanged after about 20 h under the *n*-hexane/hydrogen mixture at 350°C. This shows that the nature of the active phase has been irreversibly modified, probably because of the recarbidation of the oxicarbide phase.

The low reactivity of MCP compared to the reactivity of the linear and branched molecules again, confirms that the isomerization mechanism on this catalyst does not involve a cyclic intermediate such as methylcyclopentane.

3.3. Cyclopentane and Cyclohexane Reactions

As explained above, the deactivation observed during the MCP reaction is attributed to two phenomena: (1) condensation of highly dehydrogenated C_5-rings to give coke which blocks access to the active sites and (2) formation of significant amounts of methylidene radicals, by demethylation of MCP, which irreversibly recarbides the oxicarbide phase and significantly decreases the isomer selectivity.

In order to check this hypothesis, two other cyclic molecules, cyclopentane and cyclohexane, are tested under the same reaction conditions. The specific rate of the

TABLE 5

Cyclopentane Reaction on Molybdenum Oxicarbide Catalyst (Air Calcination at 350°C for 14 h)

	Test molecule										
	n-Hexane			Cyclopentane					*n*-Hexane		
Time on stream (h):	1.5	4.5	7		9.5	12.5	24	26.5	29	31	34
$r \times 10^{-10}$ (mol/g/s)	771	1623	1674		98	110	94	93	667	634	746
S_i (C_6) (%)	86	89	90	Si (C5) (%)	82	79	69	67	88	87	86
$Y_i \times 10^{-10}$ (mol/g/s)	663	1444	1507		80	87	65	62	587	551	642
Σ cracking (%)	14	11	10		18	21	31	33	12	13	14
			Selectivity of reaction products								
Isomer selectivity (%)											
2,2-DMB	2	2.6	2.8	Isopentane	41	34	24	24	0.5	1	1
M2P	64	63.4	62	*n*-Pentane	59	66	76	76	76	64	67
M3P	33	33.3	34.6						22.5	34	31
HEX	—	—	—						—	—	—
MCP	0.7	0.4	0.4						0.5	0.5	0.5
BEN	0.3	0.3	0.2						0.5	0.5	0.5
Cracking selectivity (%)											
C5 + C1	19	24	27	C4 + C1	51	51	44	46	42	40	39
C4 + C2	22	25	26	C3 + C2	40	40	42	41	30	29	29
2 C3	57	50	46	2 C2 + C1	3	3	5	3	20	23	24
3 C2	1	0.5	0.5	5 C1	6	6	9	10	3	4	4
6 C1	1	0.5	0.5						5	4	4

TABLE 6

Cyclohexane Reaction on Molybdenum Oxicarbide Catalyst (Air Calcination at 350°C for 14 h)

	Test molecule												
	n-Hexane			Cyclohexane					*n*-Hexane				
Time on stream (h):	2	3	5.5	6.5	10.5	13.5	15	25	26.5	29.5	34.5	37	38
$r \times 10^{-10}$ (mol/g/s)	1375	1559	1666	1345	916	986	958	979	836	975	1155	1223	1251
S_i (C_6) (%)	88	89	90	99	98.5	99	99	98	90	91	90	89	89
$Y_i \times 10^{-10}$ (mol/g/s)	1210	1387	1499	1331	902	976	948	959	752	887	1039	1088	1113
Σ cracking (%)	12	11	10	1	1.5	1	1	2	10	9	10	11	11
				Selectivity of reaction products									
Isomer selectivity (%)													
2,2-DMB	2.5	2.6	2.8	ε	ε	ε	ε	ε	1	1.2	1.2	1.3	1.3
M2P	63.5	63.4	63	3	2	1.4	1.3	1.4	54	61	61	61	61.6
M3P	33.2	33.3	33.3	1.5	0.6	0.6	0.5	0.6	31	34.5	34.7	34.9	35.3
HEX	—	—	—	15.5	3.8	1.6	1.3	1.1	—	—	—	—	—
MCP	0.5	0.5	0.5	64	75.6	76.7	77.2	76.3	1.5	1	1.2	1.1	0.8
BEN	0.3	0.2	0.4	16	18	19.7	19.7	20.6	12.5	2.3	1.9	1.7	1
Cracking selectivity (%)													
C5 + C1	22	25	28	32	31	35	36	32	38	38	38	36	37
C4 + C2	24	25	25	30	27	28	27	30	30	30	30	29	29
2 C3	53	49	46	20	17	16	18	19	26	28	26	27	27
3 C2	0.8	1	0.8	5	6	4	5	4	3	2	3	3	4
6 C1	0.2	0	0.2	13	19	17	14	16	3	2	3	5	3

reactions of these molecules and the product selectivities are presented in Tables 5 and 6.

The rate of cyclopentane hydrogenolysis on molybdenum oxicarbide catalyst is about twenty times lower than the rate observed for the linear or branched molecules (see Table 5). This low activity is attributed both to the formation of polycyclopentadiene yielding coke on the surface and to the absence of the sixth carbon atom which could allow the molecule to condense into a cyclic C_6 by ring enlargement (insertion of the methylidene radical). After 20 h under cyclopentane at 350°C, the catalyst is strongly deactivated. The rate of *n*-hexane isomerization recorded after this cyclopentane run is about three times lower than the rate obtained before. These results show that the deactivation of the catalyst is highly dependent on the presence of the C_5-rings. However, the isomer selectivity in the *n*-hexane reaction, performed after the cyclopentane run, remains unchanged (ca. 89%). This result confirms the role of the methylidene intermediate.

The molybdenum oxicarbide is a better catalyst for cyclohexane than for MCP and CP reactions as shown in Table 6. In addition, the selectivity for C_6 molecules, is very high (between 98 and 99%). A large amount of MCP is produced by the reaction (about 77% of the total C_6 products). This observation suggests a mechanism which allows the interconversion of cyclohexane to methylcyclopentane and vice versa as presented in Fig. 1b. The *n*-hexane reaction carried out on the catalyst after the cyclohexane run shows that the deactivation is less pronounced than that observed after the hydrogenolysis of MCP and CP. These results confirm that the deactivation of the catalyst is directly due to the presence of a C_5-ring. In addition, the selectivity for C_6 isomers is unchanged (ca. 90%). The direct formation of methylidene radicals from cyclohexane requires a preliminary step, the C_6-ring opening which is slower than their direct formation from MCP. In consequence there is never a large enough concentration of these radicals to allow the recarbidation of the oxicarbide surface responsible for the decrease in selectivity. As soon as the metallocyclobutane is formed from the C_6-ring, it can yield MCP, this reaction being as fast as the polymerisation of cyclopentene, a very different situation to that when the starting molecule is MCP.

3.4. Oxidative Regeneration of Molybdenum Oxicarbide Catalyst after Methylcyclopentane Isomerization Tests

The deactivation of the oxicarbide surface when MCP is reacted over it, is attributed (i) for loss of activity, to the formation of polycyclopentadienyl residues, and (ii) for loss of selectivity, to its recarbidation (or reduction) by methylidene radicals. If this deactivation is superficial, it should be possible to re-establish both the activity and the selectivity by a light oxidative treatment. To check this hypothesis the catalyst is treated under air flow (rate = 10 cm^3 min^{-1}) at 350°C for 2 h, and then tested using the *n*-hexane reaction; the results are given in Table 7. Both the activity and the selectivity for C_6 isomers have returned to their initial values. The distributions of the C_6 isomers and of the cracked products approach those obtained before the MCP run.

3.5. Isomerization Mechanism

The high isomerization rate of the linear and branched molecules (HEX, 2MP, and 3MP), compared to the hydrogenolysis rate of MCP, on molybdenum oxicarbide catalyst, leads to the conclusion that the mechanism involved during isomerization proceeds through a bond-shift and not via a methylcyclopentanic intermediate. Ribeiro (*22*) has rejected a mechanism involving the formation of a metallocyclobutane intermediate preferring a bifunctional mechanism (dehydrogenation–carbocation rearrangement–hydrogenation) on the oxygen-treated WC. However on the catalyst studied in this article, Mo_2C treated by air

TABLE 7

Oxidative Regeneration of Molybdenum Oxicarbide Catalyst after Methylcyclopentane Reaction (Test Molecule *n*-Hexane)

	Treatment											
	Air/350°C/14 h				Methylcyclopentane 350°C/21 h[a]			Air/350°C/2 h[b]				
Time on stream (h):	0.5	1	3	5	1	17	19	1.5	2.5	5	6	22
$r \times 10^{-10}$ (mol/g/s)	133	643	1386	1614	339	541	606	726	1013	1516	1446	1470
S_i (C_6) (%)	80	84	88	90	76	75	72	86	87	90	90	91
$Y_i \times 10^{-10}$ (mol/g/s)	106	540	1220	1452	258	406	436	624	881	1364	1301	1338
Σ cracking (%)	20	16	12	10	24	25	28	14	13	10	10	9
	Selectivity of reaction products											
Isomer selectivity (%)												
2,2-DMB	1	2	2	1	1	1	0	2	2.1	2.7	2.4	2
M2P	59	63	62	61	40	51	50	64	64	63	63	62.4
M3P	32	32	33	34	25	33	31	33	32	33.6	33	35
HEX	—	—	—	—	—	—	—	—	—	—	—	—
MCP	7	2	2	2	33	14	17	1	0.6	0.4	0.4	0.4
BEN + CYC	1	1	1	2	1	1	2	0	0.3	0.3	0.2	0.2
Cracking selectivity (%)												
C5 + C1	18	18	19	18	42	41	38	22	22	27.2	24	36
C4 + C2	24	23	22	23	27	27	28	23	24	24	25	28
2 C3	51	56	58	56	19	21	20	53	52	48	50	31
3 C2	2	1	0.5	2	4	4	5	0.5	0.4	0.4	0.2	2
6 C1	6	2	0.5	1	8	7	9	1.5	1.6	0.4	0.8	3

[a] *n*-Hexane reaction after 21 h under methylcyclopentane/hydrogen mixture at 350°C.

[b] *n*-Hexane reaction after [a] followed by an oxidative regeneration under air flow at 350°C for 2 h.

followed by the formation of a probable oxicarbide superficial phase, the metallocyclobutane mechanism can fully explain the results. The specific rate of reaction on this later system was approximately ten times lower than the rate on the Ribeiro system, which is consistent with a different mechanism. In addition, distribution of the cracked products obtained from *n*-C7 reaction and small amounts of metathesis products always observed (especially for the *n*-C4 reaction giving 1 to 2% of C5 molecules), experimental results which will be published separately, strongly support the metallocyclobutane mechanism.

A step-by-step description of this mechanism applied to the reaction of *n*-HEX, 2MP and 3MP is presented in Figs. 2, 3, and 4.

It is necessary to define three general rules to explain the different isomeric distributions observed when *n*-HEX, 2MP, and 3MP are reacted.

(i) In these three hexanes all the $\alpha\gamma$ positions are equivalent; in other words, the fact that a carbon atom is primary, secondary or tertiary does not change the probability of formation of a metallocyclobutanic intermediate.

(ii) The formation of a methylidene radical is more facile than the formation of ethylidene, propylidene, etc., radicals; the formation of these other radicals is equally facile.

(iii) The insertion of one of these radicals (methylidene, ethylidene, etc.) after rotation of the π-olefinic fragment around the π-bond is very easy on a primary, easy on a secondary and difficult on a tertiary carbon atom, mainly due to steric hindrance.

These three rules are logical and do not imply the introduction of fragile hypotheses. They support the following observations: the amount of dimethyl-2,2- and -2,3-butane

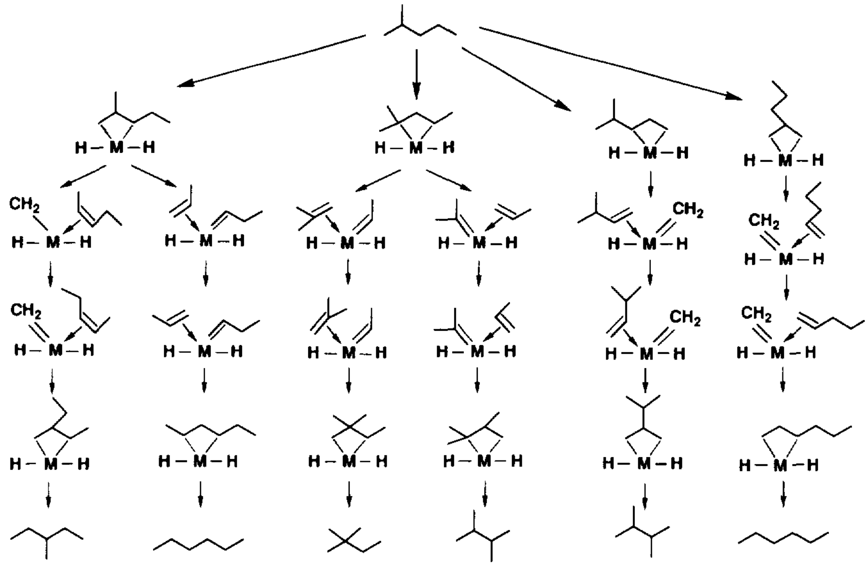

FIG. 2. Elemental steps during 2-methylpentane isomerization on molybdenum oxicarbide at 350°C.

formed by the reactions is small; almost equivalent amounts of 3MP and *n*-HEX should be formed from 2MP (observed ratio 3MP/*n*-HEX = 1.1); more 2MP than *n*-HEX should be formed from 3MP (observed ratio 2MP/*n*-HEX = 1.9); similarly, more 2MP than 3MP should be formed from *n*-HEX (observed ratio 2MP/*n*-HEX = 2). Many other little effects can be explained by carefully examining the mechanism described in Figs. 2, 3, and 4. For instance, we should expect more 3MP than *n*-HEX from 2MP

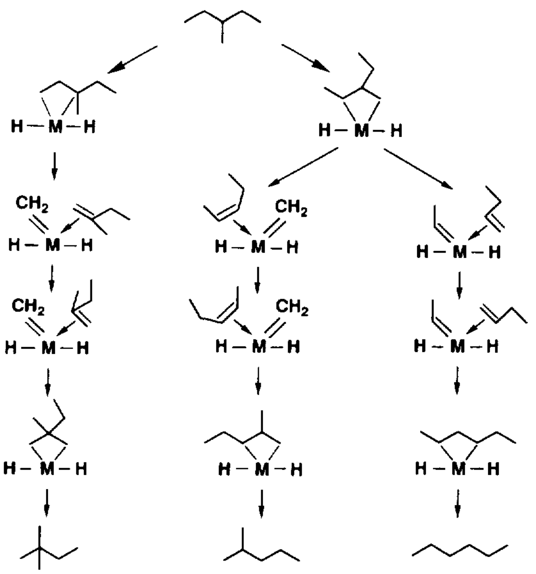

FIG. 3. Elemental steps during 3-methylpentane isomerization on molybdenum oxicarbide at 350°C.

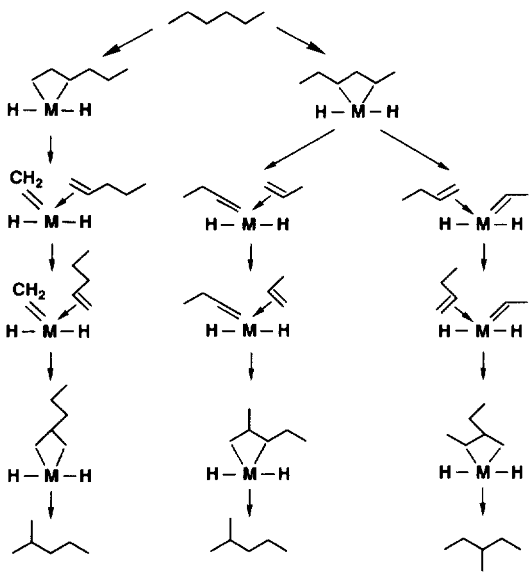

FIG. 4. Elemental steps during *n*-hexane isomerization on molybdenum oxicarbide at 350°C.

because of the double possibility of adsorption at positions 1–3 instead of the single possibility at 1–6. But the insertion of the methylidene is much easier on the primary carbon atom (insertion leading to *n*-HEX) than on the secondary carbon atom (leading to 3MP). This difference almost totally compensates for the double possibility of adsorption. Finally, it should be recalled that the intervention of the same metallocyclobutane intermediate very well explains the reaction of the cyclic molecule previously described.

4. CONCLUSION

Molybdenum carbide activated by reduction mainly leads to cracked molecules, as already found when the test molecule was *n*-hexane (see Part I (*14*)). When this carbide is activated by a mild oxidation, it is transformed into a new reactive phase which is probably a molybdenum oxicarbide. Further experiments which are soon to be published strongly support the existence of such a phase.

The oxygen modifies the catalytic properties of molybdenum carbide, i.e, it drastically decreases the hydrogenolysis reaction and increases the isomerization. These catalysts are very reactive and selective for isomerization of branched molecules such as 2- and 3-methylpentane and no deactivation is ever observed with time on stream at 350°C. This stability is explained by (i) the fact that the molybdenum oxicarbide surface is self-cleaning by catalytic elimination of carbonaceous deposits and (ii) the absence of cyclic intermediate species which can condense to form coke on the surface.

The rate of MCP and CyP reaction is about four to five times lower than the reaction rate of the branched molecules. Cyclic C_5 hydrocarbons strongly deactivate the catalyst by extensive deposition of carbonaceous compounds during the course of the reaction, which cannot be totally eliminated by autocatalysis. In addition, the methylidene intermediate formed by demethylation of MCP reduces the catalyst surface and decreases its isomer selectivity. The molybdenum oxicarbide deactivated in this way, can easily be regenerated by a short oxidative treatment.

Cyclohexane reacts moderately on molybdenum oxicarbide catalyst with very high selectivity (ca. 98%) for methylcyclopentane and benzene.

The different selectivities observed during the reactions of 3MP, 2MP, *n*-HEX, and MCP are well explained by an isomerization mechanism proceeding via a metallocyclobutane intermediate.

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