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Catalytic Activity of Bulk Tungsten Carbides for Alkane Reforming

II. Catalytic Activity of Tungsten Carbides Modified by Oxygen

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The influence of oxygen on the reforming activity of bulk tungsten carbide (WC) has been studied for the reaction of pentanes, hexanes, heptanes, and two olefins (2-methyl-2-pentene and 4-methyl-1-pentene). Depending on the air treatment, at low (−78°C), moderate (350°C), or high (700°C) temperature, these alkanes lead to different reaction products as a result of different reaction mechanisms. Whatever the oxygen treatment, heptanes react faster than hexanes, which are more reactive than pentanes. Furthermore, cyclanes (methylcyclopentane or ethylcyclopentane) are less reactive than linear alkanes (*n*-pentane, *n*-hexane, or *n*-heptane), which react more slowly than the branched ones (isopentane, 2-methylpentane, 3-methylhexane). Whatever the oxygen treatment, no cyclic mechanism is involved and isomerization proceeds only through two kinds of bond-shift mechanisms. In order to obtain more information about the possible mechanisms, i.e., a bifunctional mechanism with dehydrogenation/hydrogenation on metallic sites and carbenium ion rearrangement on acidic sites, two unsaturated reactants (2-methyl-2-pentene and 4-methyl-1-pentene) have been tested. The reaction mechanisms and a kinetic model are discussed in detail in a forthcoming paper.

1. INTRODUCTION

Tungsten carbides exhibit interesting catalytic properties for many chemical reactions (1–3, and literature cited therein) and some of the properties of these materials can be compared to those of platinum (4). However, the presence of oxygen plays a determining role for the activity and selectivity of these catalysts, mainly for isomer products (5–7). In a previous paper we studied this problem for the reforming reactions of some hexanes and showed that there is a kinetic optimum for a specific O/W atomic surface ratio (8).

The results presented in Part I (9) clearly demonstrated that the reactions of 2-methylpentane, *n*-hexane, and methylcyclopentane on fresh bulk tungsten carbide without oxygen lead mainly to cracking. In the present work, it will be reported that fresh tungsten carbide samples exposed to different doses of oxygen at different temperatures show a decrease of the total activity accompanied by an increase in the selectivity for isomerization and a decrease of the hydrogenolysis rate.

The mechanism and intermediate species responsible for both the cracking and the isomerization distributions depending on the various oxygen treatments of the catalysts are discussed in a companion paper, Part III (10).

2. EXPERIMENTAL

The experiments were performed in the classical flow system already described in (11). Two kinds of catalyst samples (A and B) were used.

Series A Samples Modified by Chemisorbed Oxygen

The catalyst series designated A was prepared by a method already described in (12) in the same experimental setup used for the catalytic tests. For catalytic experiments, a sample of 300 mg WC powder with a specific BET surface area of 12 m^2/g was used. To avoid strong oxidation of the "fresh" tungsten carbide WC, oxygen was introduced by small successive controlled pulses of 0.05 cm^3 at −78°C and at atmospheric pressure up to surface saturation. Starting with a fresh carbide sample, 14 pulses were necessary to reach saturation, i.e., $14 \times 0.05 = 0.7$ cm^3 of oxygen. This result was checked by hydrogen adsorption: when hydrogen could no longer be adsorbed, the catalyst surface was assumed to be saturated with oxygen. Since 0.7 cm^3 of oxygen corresponds to 1.9×10^{19} molecules, if dissociative adsorption of oxygen occurs at this temperature, 3.8×10^{19} adsorption sites are necessary for the complete oxygen adsorption. The surface area of the sample ($0.3 \times 12 = 3.6$ m^2) implies 3.6×10^{19} available sites, assuming 10^{19} sites per m^2, so the agreement leads us to conclude that after 14 pulses of oxygen the surface is saturated.

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The sample was then progressively heated to 350°C under a helium flux, in order to avoid any decarburization of the surface under hydrogen. When this temperature was reached, the catalytic experiment was performed by introducing the mixture of hydrogen/hydrocarbon into the reactor for about 3 min. After this catalytic test, a cleaning treatment of the surface was performed: the catalyst was maintained under a hydrogen flux at 600°C for about 5 min in order to remove carbonaceous residues deposited by the reaction (we have already mentioned that the catalytic activity of "fresh" bulk tungsten carbides rapidly decreases by carbonaceous poison, resulting from a strong adsorption of the intermediates of the catalytic reaction on the surface (9)). After this last procedure, a slight recarburization of the catalyst was necessary. This was done by flowing a mixture of CH_4 20% H_2 80% for several minutes at 800°C through the reactor. The catalyst was then exposed to a helium flow at 750°C to remove residual hydrogen, and the next addition of oxygen at −78°C was performed ; 7 pulses, i.e., $7 \times 0.05 = 0.35$ cm^3 of oxygen, were necessary to reach saturation.

The procedure followed for the A samples, modified as described by chemisorbed oxygen at −78°C, can be summarized as follows:

1. "Fresh" bulk tungsten carbide was exposed to a helium flux at 350°C. At this temperature, the catalytic test was performed with hydrocarbon/hydrogen mixture for about 3 min.
2. After the catalytic test on the "fresh" bulk tungsten carbide, the surface was cleaned with H_2.
3. The catalyst was then exposed to the helium flux at −78°C, where the oxygen introduction was continued until surface saturation was achieved.
4. After the oxygen saturation, the sample was heated to the reaction temperature under helium flux and the reaction mixture was introduced.
5. The procedure from point 2 was repeated.

Series B Samples Modified by Oxygen at High Temperatures

Catalysts designated B were prepared by the Catalysis Laboratory of Lille (G. and L. Leclercq) in collaboration under a European Community Contract (C.E.E.ST2J 04607-CCTT). It was prepared from WO_3 by reduction followed by carburization with a mixture of 20% CH_4/H_2 80% at 800°C and passivated by the method already described (9, 11). Prior to the catalytic experiments in the laboratory, the sample was activated by a hydrogen flux at 700°C for 5 h. For these samples, oxygen was introduced by a controlled air leak of ≈ 1–2% O_2 in H_2 at different temperatures and for different times.

—by an air leak at 350°C for a few minutes; this sample will be denoted $WC_{(O\text{-}350)fm}$

—by an air leak at 350°C for 3 h; the sample will be denoted $WC_{(O\text{-}350)3h}$

—by an air leak at 700°C for 4 h; the sample will be denoted $WC_{(O\text{-}700)4h.}$

3. REACTIVITY OF HYDROCARBONS

3.1. Reactivity of Hexanes

As mentioned previously (9), the conversion or the catalytic activity, the selectivity, and the yield percentage for each molecule produced by the catalytic reaction are deduced from the gas phase composition determined by gas chromatography measurements. The conversion and the yield percentages are presented in figures in which, for convenience, the oxygen treatment is indicated along the x-axis by equidistant points. In reality, of course, the amount of oxygen on the catalyst surface does not increase linearly. However, it is reasonable to assume that this amount increases with the number of oxygen pulses for the catalyst A series or with the length and the temperature treatment for the catalyst B series. Moreover, in these figures, the representative points for each molecule have been connected with straight lines. This representation has been chosen for clarity and to help with comparison and discussion but it does not represent the actual variation of the parameters between the experimental points.

The importance of the extensive cracking can be determined by the average carbon atom number $\bar{n}$ in the hydrogenolysis products as previously mentioned in (9). For hexanes, $\bar{n}$ is given by the following relationship:

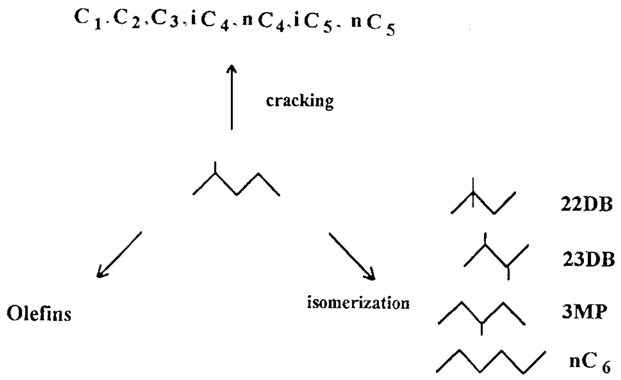
$$\bar{n} = \frac{\sum_{c=1}^{c=5} c \times S_c}{\sum_{c=1}^{c=5} S_c}, \qquad [1]$$

where S_c and c are respectively the selectivity and the carbon atom number of each cracked product. From the mean value $\bar{n}$, the mean carbon–carbon bond cleaved $\overline{X}$ can be deduced for hexanes by the following relationship:

$$\overline{X} = \frac{6 - \bar{n}}{\bar{n}}. \qquad [2]$$

3.1.1. Reactivity of 2-methylpentane (2MP). The reaction of 2MP on both A and B catalyst series leads to cracking and isomerization. The cracking products are methane (C_1), ethane (C_2), propane (C_3), isobutane (iC_4), and n-butane (nC_4), isopentane (iC_5), and n-pentane (nC_5). The isomerization products are 2,2-dimethylbutane (22DB), 2,3-dimethylbutane (23DB), 3-methylpentane (3MP), and n-hexane (nC_6), as shown in Scheme 1.

The total yield percentages of cracking and isomerization as well as the total conversion percentage are reported in Figs. 1a and 1b for the A and B sample series respectively. Starting from 100% on the fresh carbide, the total yield



SCHEME 1. Different reaction products of 2MP.

percentage of cracking decreases when oxygen additions are made on catalyst A and reaches 16% after the second addition, as shown in Fig. 1a. For the same experiment, the isomerization yield percentage increases from zero on the fresh carbide to 14% after the second oxygen addition.

On catalyst B, the same general features are observed for the total yield percentages of cracking and isomerization as oxygen treatments become more severe (from $WC_{(O\text{-}350)fm}$ to $WC_{(O\text{-}350)3h}$ and finally to $WC_{(O\text{-}700)4h}$). The yield percentage of cracking decreases from 100% on the fresh carbide (result not represented in Fig. 1b) to 2% on the $WC_{(O\text{-}700)4h}$ sample. The yield percentage in isomerization increases from zero on the fresh carbide to 23% on the $WC_{(O\text{-}700)4h}$ sample, a value slightly higher than the A series after the second addition. Moreover, on catalyst B, the cracking reactions are the main processes on the fresh carbide without oxygen, but on $WC_{(O\text{-}700)4h}$ the isomerization reactions are predominant and the cracking becomes negligible. Looking at the conversion on each sample, strong differences can be observed:

—on A series catalysts, the corresponding values are 100% on the fresh carbide and 30% after the second oxygen addition, as shown in Fig. 1a.

—on B series catalysts, the conversion is also 100% on the fresh carbide, 25% and 16% on $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$, respectively, but 25% on $WC_{(O\text{-}7000)4h}$ (cf. Fig. 1b), where isomerization reactions are the main processes, as already mentioned. Note that on the $WC_{(O\text{-}350)3h}$ sample and on the A series sample after the second oxygen addition, the yield percentage of cracking and isomerization are of comparable importance, but high temperature oxygen treatment deeply changes the surface state of the catalyst, leading to the results given in Fig. 1b for the $WC_{(O\text{-}700)4h}$ sample.

TABLE 1

Isomerization Yield Percentage for the 2MP Reaction at 350°C

Oxygen treatment	22DB	23DB	3MP	nC_6
		a. A Samples		
Fresh carbide	0.00	0.00	0.00	0.00
First addition	0.01	0.10	0.50	0.20
Second addition	0.20	0.50	12.55	0.70
		b. B Samples		
$WC_{(O\text{-}350)fm}$	0.002	0.007	0.50	0.08
$WC_{(O\text{-}350)3h}$	0.10	0.25	4.90	0.60
$WC_{(O\text{-}700)4h}$	1.15	1.55	12.95	7.75

The variations with oxygen treatments of the yield percentages of the various isomerized products are given in Table 1 for the A and B series. For each isomer produced during the reaction, the corresponding yield percentage increases as the adsorbed oxygen amount increases, or as the oxygen treatments become more severe. It is worth noting that 3-methylpentane (3MP) is the most important isomer formed on both series of catalysts and the corresponding yield percentage is 12% for the A series after the second oxygen addition and for the $WC_{(O\text{-}700)4h}$ sample of the B series. However, the $3MP/nC_6$ ratio is greater than 7 on the A series and on the $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$ samples of the B series and is close to 1 on the $WC_{(O\text{-}700)4h}$ sample of the B series.

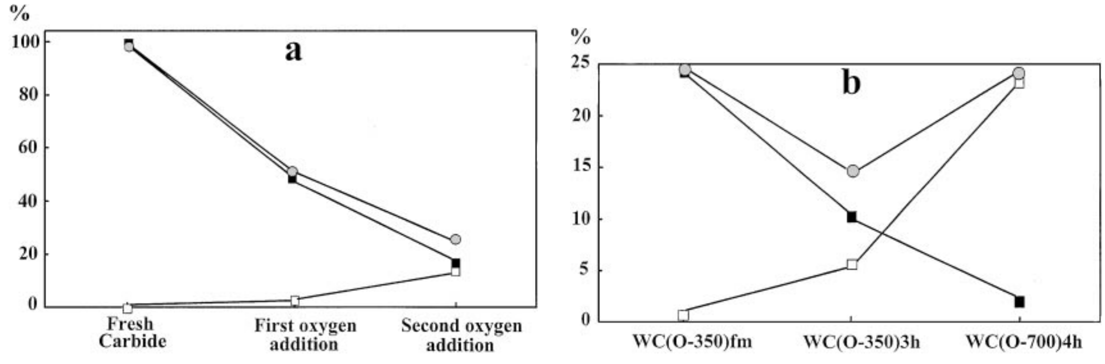


FIG. 1. Conversion, total yield % for cracking and isomerization of 2MP on (a) catalyst A and (b) catalyst B series at 350°C: (■) cracking, (□) isomerization, (●) conversion.

TABLE 2

Cracking Yield Percentage for the 2MP Reaction at 350°C

Oxygen treatment	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5
a. A Samples							
Fresh carbide	100.00	0.00	0.00	0.00	0.00	0.00	0.00
First addition	8.45	7.55	13.45	10.55	3.90	1.50	4.00
Second addition	1.05	3.60	6.25	0.90	1.80	1.00	1.50
b. B Samples							
$WC_{(O\text{-}350)fm}$	1.75	5.50	10.90	3.75	0.45	1.05	1.05
$WC_{(O\text{-}350)3h}$	1.20	2.45	4.00	1.35	0.45	0.50	0.35
$WC_{(O\text{-}700)4h}$	0.25	0.25	1.00	0.35	0.10	0.10	0.15

The variations of the yield percentages corresponding to the various molecules formed by cracking for the series A and B catalysts are given in Table 2. The general feature of the results appears to be the same for both catalyst series: starting from zero on the fresh carbide, the yield percentages of all the cracking products except methane increase, go through a maximum, and then decrease when the amount of oxygen adsorbed increases or when the oxygen treatment becomes more severe. In contrast the methane yield percentage decreases continuously from 100% on the fresh carbide to low values, around a few percent, for high oxygen amount on the surface. In addition to cracking and isomerization reactions, traces of homologation reactions giving 2,2-dimethylpentane and 2,4-dimethylpentane occur at a very low level (0.5% of the total products formed).

From the relationships [1] and [2], $\bar{n}$, the mean carbon atom number in the cracking products, and $\overline{X}$, the mean value of the number of carbon–carbon bonds cleaved, can be calculated. This determination is valid only when the isomerization reactions can be neglected in comparison with the importance of the cracking reactions. This is the reason why this determination has only been made for the $WC_{(O\text{-}350)fm}$ sample for the catalyst series B, for the fresh carbide without oxygen, and for the sample of catalyst series A after the first oxygen addition. The $\bar{n}$ and $\overline{X}$ values are respectively 3.0 and 1.0 for $WC_{(O\text{-}350)fm}$; 1.0 and 5.0 for the fresh carbide free of oxygen; 3.2 and 0.9 for the catalyst series A after the first oxygen addition. The values for the first $WC_{(O\text{-}350)fm}$ and the A series sample modified by the first oxygen addition are not very far apart and the results given in Fig. 1 and in Tables 1 and 2 can be compared for these two samples. The catalytic behavior of catalyst series A, saturated by the first oxygen addition at −78°C and tested under the reaction mixture at 350°C, is also comparable to the catalyst series B sample, modified by air at 350°C for a few minutes. However, catalyst series B treated by air at 700°C, $WC_{(O\text{-}700)4h}$, shows results completely different from those obtained on all the other samples (either catalyst series A or B).

3.1.2. Reactivity of n-hexane (nC_6). The conversion and the total yield percentages in cracking and isomerization are given in Figs. 2a and 2b for the catalysts of series A and B, respectively. As the oxygen amount increases on catalyst series A, the conversion and the cracking yield percentages decrease from 100% on the fresh tungsten carbide down to 25% after the third oxygen addition. On the same sample, isomerization increases slowly from zero to 3% after the third oxygen addition. On catalyst series B (cf. Fig. 2b) the same general trends for conversion, cracking, and isomerization yield percentages as for 2MP are observed. For low oxygen temperature treatment, cracking reactions are the main processes, whereas for high oxygen temperature treatment (for the $WC_{(O\text{-}700)4h}$ sample), isomerization reactions are the main processes and cracking becomes negligible. Comparison of the results given in Figs. 2a and 2b shows that the conversion and yield percentages for cracking and isomerization for the $WC_{(O\text{-}350)fm}$ sample of catalyst series B and for

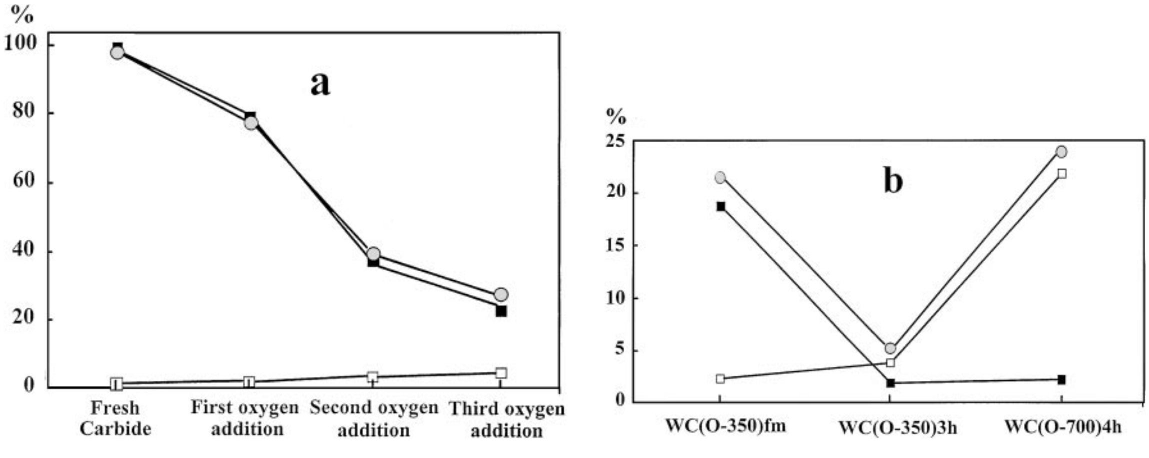


FIG. 2. Conversion, total yield % for cracking and isomerization of nC_6 on (a) catalyst A and (b) catalyst B series at 350°C: (■) cracking, (□) isomerization, (●) conversion.

TABLE 3

Isomerization Yield percentage for the nC_6 Reaction at 350°C

Oxygen treatment	22DB	23DB	2MP	3MP
a. A Samples				
Fresh carbide	0	0	0	0
First addition	0	0	0.55	0.25
Second addition	0	0	1.40	1.00
Third addition	0.02	0.03	2.15	1.50
b. B Samples				
$WC_{(O\text{-}350)fm}$	0.002	0.01	1.55	0.95
$WC_{(O\text{-}350)3h}$	0.15	0.15	2.20	1.50
$WC_{(O\text{-}700)4h}$	0.65	1.45	11.15	8.65

catalyst series A after the third oxygen addition are very close to each other. Here, too, as for the 2MP reaction, oxygen treatments at high temperature lead to completely different results from those observed when oxygen is introduced to the catalyst at low temperature or at 350°C.

The yield percentages for the various isomerization products obtained as a function of oxygen treatments for the catalysts of the A and B series are given in Table 3. The yield percentages for each isomer increase as the amount of oxygen on the sample increases (for catalyst series A) or when the oxygen treatment becomes more severe (for catalyst series B). 3MP and 2MP are the main isomers produced by the reaction, 22DB and 23DB being present in very small amounts. As for the 2MP reaction, MCP has never been detected from nC_6, implying that the isomerization of acyclic hexanes does not proceed through a cyclic mechanism such as that observed on metals [14].

The variations of the yield percentages for each of the cracked molecules of the catalysts of series A and B are given in Table 4. On the fresh sample of the catalysts of series A, the yield percentages for all the molecules are zero, except for methane, which is 100%. The results obtained on the fresh carbide for catalysts of series A and B are the same. Concerning the products formed by cracking, the general features appear similar to those obtained with 2MP. These results are not reported in this paper but have been detailed in previous work (13).

TABLE 4

Cracking Yield Percentage for the nC_6 Reaction at 350°C

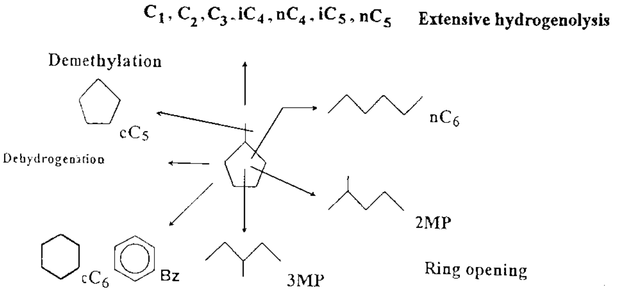
Oxygen treatment	C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5
a. A Samples							
Fresh carbide	100.00	0.00	0.00	0.00	0.00	0.00	0.00
First addition	14.35	21.60	17.30	0.00	11.35	0.00	14.35
Second addition	5.50	10.80	8.80	0.05	6.65	0.10	5.95
Third addition	1.95	6.95	5.75	0.05	4.60	0.050	2.45
b. B Samples							
$WC_{(O\text{-}350)fm}$	1.20	6.45	4.60	0.09	4.20	0.04	2.40
$WC_{(O\text{-}350)3h}$	0.30	0.40	1.05	0.08	0.15	0.03	0.04
$WC_{(O\text{-}700)4h}$	0.40	0.30	0.65	0.10	0.20	0.30	0.25

The mean carbon atom number of the total cracked products ($\bar{n}$) and the mean carbon–carbon bond cleaved ($\overline{X}$) can again be calculated on the A series catalysts and on the $WC_{(O\text{-}350)fm}$ sample of the B series catalysts. For all these samples, $\bar{n}$ is around 2.9 and $\overline{X}$ is between 1.0 and 1.1. The similarity of these values leads one to assume that all these samples have very comparable properties giving very similar cracked product distributions and very low isomerization yield percentages.

3.1.3. Reactivity of methylcyclopentane (MCP). For these experiments catalysts of the A series, after being treated by oxygen additions at −78°C have been reduced under a hydrogen flow (around 50 cm^3/min) at atmospheric pressure, first at 600°C for 15 min, then at 700°C for 20 min. Methylcyclopentane can undergo several kinds of reactions, represented in Scheme 2. The conversion and the total yield percentages in single and extensive hydrogenolysis and in ring enlargement are given in Figs. 3a and 3b for catalysts of series A and B, respectively.

As for the two other molecules studied previously, oxygen addition on the catalyst reduces the conversion and the extensive hydrogenolysis. This is clearly visible in Fig. 3a for catalyst series A. For the catalysts of series B, the results obtained on the fresh carbide are not given in Fig. 3b, but as for those of series A, on the fresh carbide, all the yield percentages are zero except for extensive hydrogenolysis leading to methane.

Single hydrogenolysis goes through a maximum after the first oxygen addition, then decreases to a value lower than 1% after the third oxygen addition, as shown in Fig. 3a for the catalyst series A. This is also true for the catalyst series B (cf. Fig. 3b), where the corresponding values are 2.4 for $WC_{(O\text{-}350)fm}$, 0.8 for $WC_{(O\text{-}350)3h}$, and around 2 for $WC_{(O\text{-}700)4h}$. As for the two other hydrocarbons studied, the catalyst series A after several oxygen additions and the $WC_{(O\text{-}350)fm}$ sample of catalyst series B can be compared; the corresponding results for single and extensive hydrogenolysis as well as for ring enlargement are very close. The



SCHEME 2. Different reaction products of MCP.

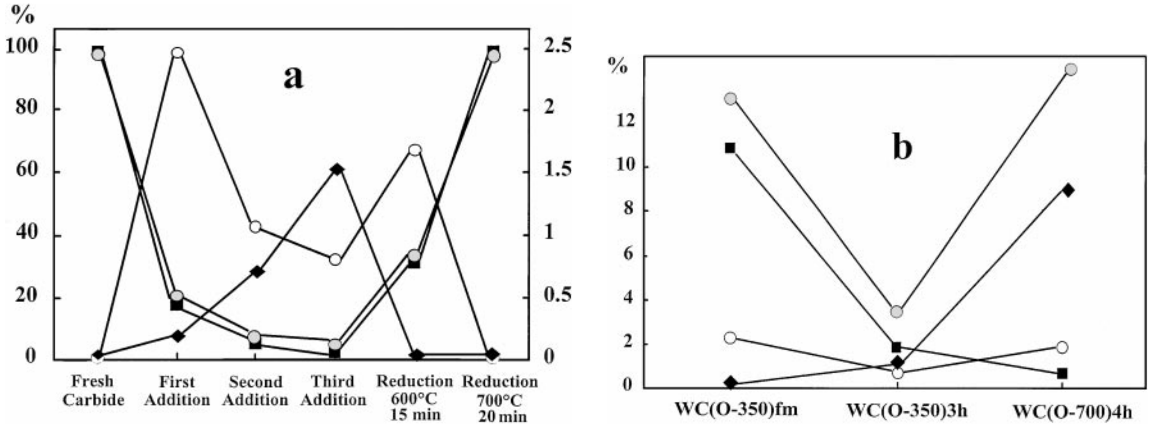


FIG. 3. Conversion, total yield % for single and extensive hydrogenolysis and for ring enlargement of MCP on (a) catalyst A and (b) catalyst B series at 350°C. Left *Y*-axis: (■) extensive hydrogenolysis, (●) conversion; right *Y*-axis: (○) single hydrogenolysis, (◆) ring enlargement.

results obtained on the WC$_{(O-700)4h}$ sample of catalyst series B differ for single hydrogenolysis, increasing slightly in comparison with the value obtained on the WC$_{(O-350)3h}$ sample. Oxygen treatment at high temperature completely changes the catalytic activities of the tungsten carbide, which differ greatly from the activity observed when oxygen is adsorbed at lower temperatures.

Ring enlargement giving benzene and cyclohexane does not occur at all on the fresh carbide, and oxygen must be on the surface to allow this reaction to happen. The corresponding yield percentages increase as the amount of oxygen adsorbed increases on catalyst series A and there is a high value on the WC$_{(O-700)4h}$ sample of catalyst series B.

Hydrogen reduction at high temperature (700°C) can completely remove the chemisorbed oxygen added onto the surface at −78°C and the initial results obtained on the fresh carbide are found again: conversion and extensive hydrogenolysis to methane reaching 100%, and single hydrogenolysis and ring enlargement being zero, as shown in Fig. 3a. It can be observed in this figure that the ring enlargement decreases to zero after the first step of reduction by hydrogen at 600°C for 15 min, but the extensive hydrogenolysis has not reached 100% and single hydrogenolysis reaches its maximum value near 1.5%. So, by reducing the catalyst at 600°C, oxygen is still present on the surface, but for the ring enlargement the oxygen species still present do not play any part for this reaction and the results are the same as on the fresh carbide. Finally, hydrogen reduction at 700°C for 20 min gives the same results as those on the fresh carbide; the reduction of the sample at 600°C for 15 min evidently leads to an incomplete reduction.

As on the fresh tungsten carbide, dehydrogenation of MCP giving methylcyclopentenes can occur. If the corresponding yield percentages, not given in the curves and tables, are very low on the fresh carbide, the presence of oxygen increases the corresponding amount mainly on the WC$_{(O-350)fm}$ sample, but this amount is zero on the WC$_{(O-700)4h}$ sample. Some amount of oxygen is necessary to optimize this reaction and to favor the corresponding dehydrogenation mechanism.

Analyzing the results obtained with 2MP, nC$_6$, and MCP, we conclude that the catalytic behavior of bulk tungsten carbides modified by chemisorbed oxygen additions at −78°C and then being placed at 350°C under hydrogen flux for the catalytic test is close to the behavior observed by treating the sample at 350°C (WC$_{(O-350)fm}$). These analogies are correct concerning both the total cracking and isomerization and each product distribution; for example, starting from 2MP, the 3MP/nC$_6$ ratio is higher on WC modified by oxygen at −78°C, on WC$_{(O-350)fm}$, and on WC$_{(O-350)3h}$ (greater than 7 on these three catalysts) than on WC$_{(O-700)4h}$. In this last case, the ratio is close to 1. That is the reason why, in the following, we will compare the catalytic activity of some hexanes, heptanes, and pentanes only on the WC$_{(O-350)fm}$, WC$_{(O-350)3h}$, and WC$_{(O-700)4h}$ of the catalyst B series. The difference between these two kinds of samples appears also by comparison of the results obtained with 2MP for the conversion and the total yield % of cracking and isomerization as a function of time (given in Figs. 4a and 4b for WC$_{(O-350)fm}$ and WC$_{(O-700)4h}$, respectively). Although these parameters are very stable for WC$_{(O-700)4h}$, a strong decrease of the corresponding values is noted for the WC$_{(O-350)fm}$ sample.

3.1.4. Reactivity of 2,2-dimethylbutane (22DB). 2,2-Dimethylbutane can undergo cracking giving isopentane (iC$_5$), neopentane (neoC$_5$), isobutane (iC$_4$), and isomerization leading to 2-methylpentane (2MP), 3-methylpentane (3MP), and 2,3-dimethylbutane (23DB), as shown in Scheme 3. The total conversion and the yield percentages for the total cracking and isomerization are represented in Fig. 5a. For all three catalyst samples, the yield percentages for isomerization remain at a low level; cracking is important on WC$_{(O-350)fm}$ and on the WC$_{(O-700)4h}$ samples and is minimal on WC$_{(O-350)3h}$.

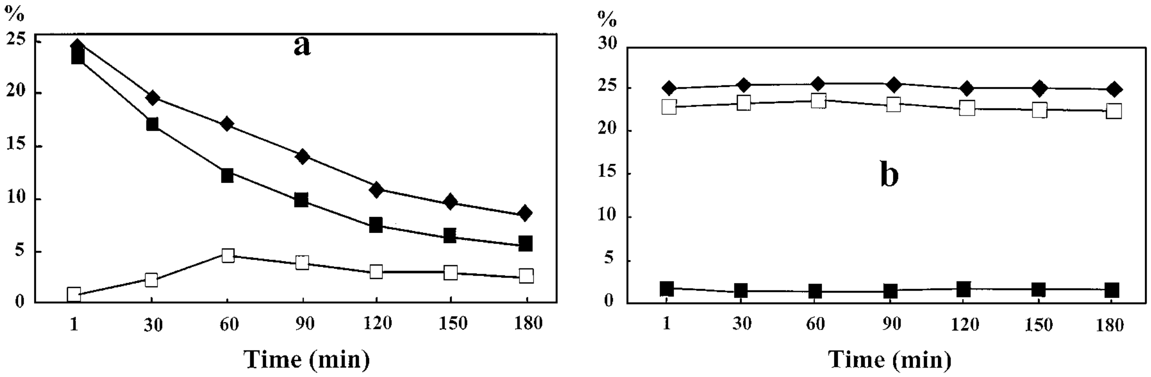


FIG. 4. Conversion, total yield % for cracking and isomerization of 2MP as a function of time on (a) $WC_{(O\text{-}350)fm}$ and (b) $WC_{(O\text{-}700)4h}$ samples of catalyst B series at 350°C: (■) cracking, (□) isomerization, (◆) conversion.

For cracking reactions (Fig. 5b), $\bar{n}$, the mean carbon atom number and $\overline{X}$, the carbon–carbon bonds cleaved, are respectively 2.0 and 2.0 for the three catalysts used. This result clearly demonstrates that multiple bond cleavages occur starting from 22DB. That was never the case for the other hexanes (2MP, nC_6) and MCP on the two less modified samples, $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$. This is confirmed by the fact that there is a high proportion of cracked products coming from more than one carbon–carbon bond rupture, like C_3, nC_4, and nC_5. Only iC_4, iC_5, and neoC_5 are due to single carbon–carbon bond rupture, as shown in Scheme 3. On all three carbide samples, neopentane (rupture C_I–C_{II}) was never detected under our experimental conditions.

Among the isomers (Fig. 5c), the 2,3-dimethylbutane is the only one formed on $WC_{(O\text{-}350)fm}$. On $WC_{(O\text{-}700)4h}$ the presence of 2MP and 3MP is noted and the 23DB is in this case detected in minor amounts; the other isomer observed, the nC_6, is not an initial product but results from repetitive processes.

3.1.5. Reactivity of benzene (Bz) and cyclohexane (cC_6). The activity of cyclohexane has been measured only for $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$. The benzene reaction has only been studied on the $WC_{(O\text{-}700)4h}$ catalyst. The yield percentage distributions are given in Table 5. The yield percentages for the conversion, the total cracking, and the formation of methylcyclopentane, cyclohexane, and benzene are given.

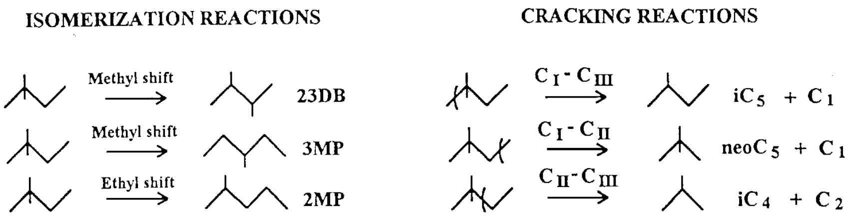
Starting from cyclohexane, this molecule is more easily converted in $WC_{(O\text{-}350)fm}$ than in $WC_{(O\text{-}700)4h}$ (34% against 15%). No cracked products were detected on these two samples only methylcyclopentane and benzene. This last product is present in a very large amount on the $WC_{(O\text{-}350)fm}$ sample. In contrast, the methylcyclopentane appears in a greater proportion on the $WC_{(O\text{-}700)4h}$ sample.

Starting from benzene, the $WC_{(O\text{-}700)4h}$ sample is not very active and exclusively converts benzene into methylcyclopentane. No hydrogenation products leading to cyclohexene and cyclohexadienes have been detected. Furthermore, starting from both $WC_{(O\text{-}700)4h}$ no methylcyclopentenes were observed.

3.2. Reactivity of Heptanes

The reactivity of heptanes has been studied under the same experimental conditions as those used for hexanes. As for hexanes, the comparison of a linear (*n*-heptane), a branched (3-methylhexane), and a cyclic (ethylcyclopentane plus methylcyclohexane) hydrocarbon shows the influence of the structure of the molecule on its activity for cracking and isomerization. Only the reactions of ethylcyclopentane and methylcyclohexane are described in this paper; the results concerning *n*-heptane and 3-methylhexane, which are similar to those of *n*-hexane and 2-methylpentane, have been detailed elsewere (13).

3.2.1. Reactivity of ethylcyclopentane (ECP). As for MCP, ECP can react giving dehydrogenation products,



SCHEME 3. Isomerization and cracking products of the 22DB reaction.

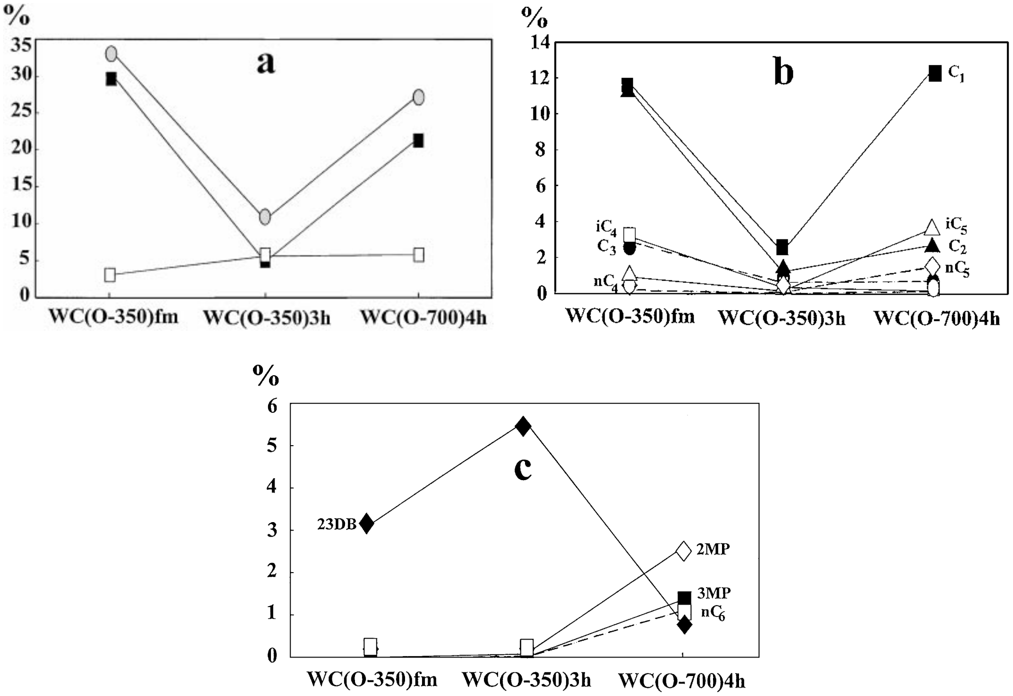


FIG. 5. (a) Conversion, total yield % for cracking and isomerization of 22DB on catalyst B series at 350°C: (■) cracking, (□) isomerization, (●) conversion. (b) Yield % for cracking of 22DB on catalyst B series at 350°C: (■) C_1, (▲) C_2, (●) C_3, (□) iC_4, (○) nC_4, (△) iC_5, and (◇) nC_5. (c) Yield % for isomerization of 22DB on catalyst B series at 350°C: (◆) 23DB, (◇) 2MP, (■) 3MP, (□) nC_6.

extensive hydrogenolysis ($C_1 \rightarrow C_6$), single hydrogenolysis by exocyclic carbon–carbon bond rupture (cyclopentane (cC_5) and methylcyclopentane (MCP)), and single hydrogenolysis of the carbon–carbon bonds of the cyclopentanic ring (*n*-heptane (nC_7), 3-methylhexane (3MH), and 3-ethylpentane (3EP)), ring enlargement (methylcyclohexane (MCH) and toluene (Tol)), and isomerization (dimethylcyclopentanes).

The total conversion, and the total yield percentages for extensive and single hydrogenolysis as well as for ring enlargement are shown in Fig. 6. The extensive hydrogenolysis is the process most strongly modified by the oxygen treatment.

The comparison of the ring enlargement yield percentages (Tol plus MCH) shows a small change from 17% on $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$ to 21% on $WC_{(O\text{-}700)4h}$ in the case of ECP (Fig. 6), whereas these percentages change from 0.5% on $WC_{(O\text{-}350)fm}$ to 1.3% on $WC_{(O\text{-}350)3h}$ and to 8.2% on $WC_{(O\text{-}700)4h}$ in the case of MCP (Fig. 3b).

TABLE 5

Conversion, Total Cracking, Methylcyclopentane, Cyclohexane, and Benzene Yield (%) at 350°C

	Reactant	Conversion Yield (%)	Cracking Yield (%)	MCP Yield (%)	cC_6 Yield (%)	Bz Yield (%)
$WC_{(O\text{-}350)fm}$	cC_6	34.0	0.0	0.8	—	33.0
$WC_{(O\text{-}700)4h}$	cC_6	15.0	0.0	11.2	—	3.7
	Bz	1.0	0.0	1.0	0.0	—

3.2.2. Reactivity of methylcyclohexane (MCH). The hydrocarbon has only been studied on the $WC_{(O\text{-}700)4h}$ sample. The yield percentage distributions are given in Table 6. The main product formed is Tol, followed by ECP. This tendency is completely different from the one observed with cC_6. Indeed, the cC_6 (Table 5) was mainly converted into MCP (11.2%) and only 3.7% into Bz on the $WC_{(O\text{-}700)4h}$ sample. This point is important for the discussion concerning the mechanisms [10].

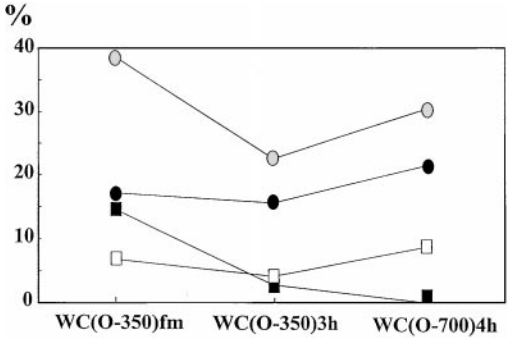


FIG. 6. Conversion, total yield % for single and extensive hydrogenolysis and for ring enlargement of ECP on catalyst B series at 350°C: (■) extensive hydrogenolysis, (□) single hydrogenolysis, (●) conversion, (●) ring enlargement.

TABLE 6

Conversion and Product Distribution Yield (%) of Methylcyclohexane on $WC_{(O\text{-}700)4h}$ at 350°C

Conv. (%)	Yield (%) Primary Products cC_6	ECP	Tol	2MH	3MH	Secondary Products C_1–C_6	33DP	23DP	3EP
26.4	0.3	3.4	16.9	1.3	0.4	0.0	0.4	0.3	2.7

TABLE 7

Total Rate Constant, k_{tot}, Expressed in 10^7 mol/s · g_{cata} for Pentanes, Hexanes, and Heptanes on $WC_{(O\text{-}350)fm}$, $WC_{(O\text{-}350)3h}$, and $WC_{(O\text{-}700)4h}$ at 350°C

	$WC_{(O\text{-}350)fm}$	$WC_{(O\text{-}350)3h}$	$WC_{(O\text{-}700)4h}$
nC_5	1.1		1.3
nC_6	1.8	0.4	1.9
nC_7	4.3	2.0	2.6
iC_5	1.1		0.99
3MP	2.3	0.6	2.2
3MH	5.1	1.9	2.6
MCP	0.9	0.2	0.7
ECP	1.3	0.7	1.0
MCH			1.0
cC_6	1.1		0.4
Bz			0.01

3.3. Comparison of the Catalytic Activities of C_5, C_6, and C_7 Alkanes

In order to compare the activity of these three hydrocarbons, the rate constants for total conversion (k_{tot}), for total cracking (k_{cra}), and for total isomerization (k_{iso}) have been determined by use of the following relationship, previously mentioned in (3),

$$k = \frac{F}{\omega} \times \ln\left(\frac{1}{1-\alpha}\right),$$

where α is the total conversion or the selectivity of the total cracking or of the total isomerization, F and ω being respectively the hydrocarbon flux and the catalyst weight.

The rate constants (k_{tot}) for the total conversion of linear (nC_5, nC_6, and nC_7), branched hydrocarbons with a tertiary carbon (iC_5, 3MP, and 3MH) and with a quaternary carbon (22DB), of cyclic hydrocarbons with a five-membered ring (methyl- and ethylcyclopentane), and of Bz, cC_6, and MCH are given in Table 7. The total rate constant (k_{tot}) and the total cracking (k_{cra}) and the isomerisation (k_{iso}) rate constants for the hexanes (see Section 3.1) are shown for comparison in the Fig. 7.

The following may be noted:

(a) The longer the hydrocarbon chain, the higher the k_{tot}; heptanes are more reactive than hexanes which are more reactive than pentanes. This difference is the most marked in the $WC_{(O\text{-}350)fm}$ sample and the least marked in the $WC_{(O\text{-}700)4h}$ sample. The difference is more pronounced for branched than for linear hydrocarbons.

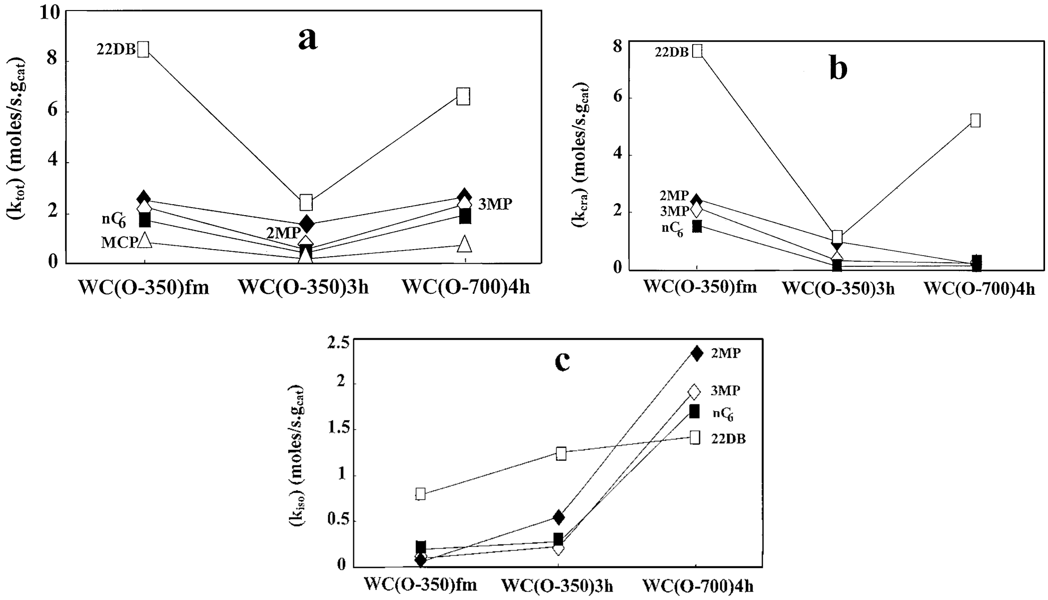


FIG. 7. (a) Total rate constant (k_{tot}, in mol/s · g_{cat}) of hexanes on catalyst B series at 350°C. (b) Total cracking rate constant (k_{cra}, in mol/s · g_{cat}) of hexanes on catalyst B series at 350°C. (c) Total isomerization rate constant (k_{iso}, in mol/s · g_{cat}) of hexanes on catalyst B series at 350°C. (□) 22DB, (◆) 2MP, (◇) 3MP, (■) nC_6, (△) MCP.

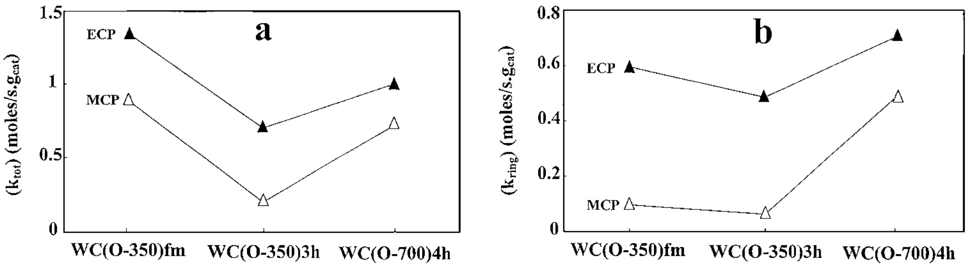


FIG. 8. (a) Total rate constant (k_{tot}, in mol/s · g_{cat}) on catalyst B series at 350°C. (b) Ring enlargement rate constant (k_{ring}, in mol/s · g_{cat}) on catalyst B series at 350°C. (△) MCP, (▲) ECP.

(b) All of the hexanes except 2,2-dimethylbutane exhibit a comparable behavior on all three samples studied; for example, there is

—a minimum of the (k_{tot}) value observed on the $WC_{(O\text{-}350)3h}$ sample (Fig. 7a)

—a slight decrease of the (k_{cra}), which is almost nil on the $WC_{(O\text{-}700)4h}$ sample (Fig. 7b)

—a marked increase of the (k_{iso}) on the $WC_{(O\text{-}700)4h}$ sample (Fig. 7c)

—an influence of the structure of the molecule can be seen: (k_{tot}) is the lowest for MCP and increases for the linear hydrocarbon (nC_6) and for the branched hydrocarbons with a tertiary carbon atom (2MP and 3MP). The same influence can be seen for (k_{cra}) and (k_{iso}), as shown in Fig. 7. The presence of a quaternary carbon atom in 22DB leads to the highest (k_{tot}) and (k_{cra}) values on all three samples, with a marked minimum on $WC_{(O\text{-}350)3h}$. However, the difference is the most pronounced on the $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$ samples. As regards (k_{iso}) for 22DB (Fig. 7c), on the $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}350)3h}$ samples the corresponding value is higher than for 2MP, 3MP, and nC_6. In contrast, for the $WC_{(O\text{-}700)4h}$ catalyst the corresponding value for 22DB is lower, the most important being the 2MP one, followed by 3MP, nC_6, and the 22DB.

The (k_{tot}) obtained with MCP and ECP on the three samples is smaller starting from MCP (Fig. 8a), and the relative difference between MCP and ECP remains almost constant. However, in the case of the ring enlargement rate constants (Fig. 8b), the relative difference between MCP and ECP becomes smaller for a more severe oxygen treatment. Indeed, on the $WC_{(O\text{-}700)4h}$ sample, the rate constant for ring enlargement is 1.4 times higher for ethyl- than for methylcyclopentane, whereas on the $WC_{(O\text{-}350)fm}$ sample it is about 7.5 times higher.

The rate constants for total conversion (k_{tot}), for dehydrogenation (k_{deh}), and for isomerization (k_{iso}) of MCH and of cC_6 on the $WC_{(O\text{-}700)4h}$ sample are presented in Table 8. The dehydrogenation of MCH and of cC_6 leads respectively to Tol and Bz, whereas the isomerization of MCH gives ECP and dimethylcyclopentanes, and the isomerization of cC_6 gives MCP. No dimethylcyclopentanes are detected. On this $WC_{(O\text{-}700)4h}$ sample, (k_{tot}) and (k_{deh}) are higher for MCH than for cC_6 (about 2 times in each case), but (k_{iso}) is favoured when starting from cyclohexane.

3.4. *Reactivity of Olefins*

The catalytic activity of two olefins (2-methyl-2-pentene (2M2Pen) and 4-methyl-1-pentene (4M1Pen)) was checked on $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$ and compared with the activity of 2MP.

The values of the isomerization rate constant (k_{iso}) are summarised in Table 9. It can be deduced from this table that the most remarkable difference is obtained for the $WC_{(O\text{-}350)fm}$ sample. On this catalyst, the 2M2Pen reacts about 10 times faster than the 2MP and the 4M1Pen reacts 6 times faster than the 2M2Pen, which means that 4M1Pen is about 60 times more reactive than 2MP. On the $WC_{(O\text{-}700)4h}$ sample, the isomerization of 2M2Pen and of 4M1Pen respectively proceeds 1.25 and about 3 times faster than for 2MP. On the other hand, 4M1Pen is isomerized only 2.6 times faster than 2M2Pen on this sample.

TABLE 8

Rate Constants for Total Conversion, (k_{tot}), for Dehydrogenation, (k_{deh}), and for Isomerization, (k_{iso}) of MCH and cC_6, Expressed in 10^7 mol/s · g_{cat} at 350°C

Reactants	(k_{tot})	(k_{deh})	(k_{iso})
MCH	1.03	0.66	0.13
cC_6	0.42	0.10	0.32

TABLE 9

Isomerization Rate Constants, k_{iso} of 2-Methylpentane, 2-Methyl-2-Pentene, and 4-Methyl-1-Pentene, Expressed in 10^7 mol/s · g_{cat} at 350°C

	2MP	2M2Pen	4M1Pen
$WC_{(O\text{-}350)fm}$	0.06	0.6	3.5
$WC_{(O\text{-}700)4h}$	2.0	2.5	6.4

4. CONCLUSIONS

Oxygen addition strongly modifies the catalytic behavior of pure bulk tungsten carbides by lowering the total activity, which is very high on a "fresh" carbide (9), and by increasing the selectivity in isomerization. Among the isomerization products, which become more important with the quantity of oxygen added and with the temperature treatments, MCP was never detected starting from acyclic hydrocarbons, which means that the isomerization does not proceed through a cyclic mechanism, as observed on Pt or Pd catalysts. The reactivity of hydrocarbons is strongly dependent on their structure. Linear alkanes react more slowly than branched ones, and cyclic hydrocarbons (five carbon atom ring) react less easily than linear ones. This difference is less marked when the catalysts are treated at high temperature in the presence of traces of oxygen.

The oxygen treatments lead to catalysts with different characteristics: those treated under oxygen at the highest temperature show a "modified metallic" behavior, while those treated at low and moderate temperature seem to show more "acidic" properties for cracking and isomerization reactions. In the following paper (10), the corresponding mechanisms and intermediates species for cracking and isomerization reactions are discussed in detail.

REFERENCES

1. Muller, J. M., and Gault, F. G., *Bull. Soc. Chim. Fr.* **2**, 416 (1970).
2. Levy, R. B., and Boudart, M., *Science* **81**, 547 (1973).
3. Keller, V., Cheval, M., Maire, F., Wehrer, P., Ducros, R., and Maire, G., *Catal. Today* **17**, 493 (1993).
4. Colton, R. J., Huang, J. T. J., and Rabalais, J. W., *Chem. Phys. Lett.* **34**, 337 (1975).
5. Ribeiro, F. H., Dalla-Betta, R. A., Boudart, M., Baumgartner, J., and Iglesia, E., *J. Catal.* **130**, 86 (1991).
6. Ribeiro, F. H., Boudart, M., Dalla-Betta, R. A., and Iglesia, E., *J. Catal.* **130**, 498 (1991).
7. Iglesia, E., Baumgartner, J. E., Ribeiro, F. H., and Boudart, M., *J. Catal.* **131**, 523 (1991).
8. Muller, A., Keller, V., Ducros, R., and Maire, G., *Catal. Lett.* **35**, 65 (1995).
9. Keller, V., Wehrer, P., Garin, F., Ducros, R., and Maire, G., *J. Catal.* **153**, 9 (1995).
10. Keller, V., Garin, F., Ducros, R., and Maire, G., *J. Catal. in press* (1996).
11. Frennet, A., Leclercq, G., Leclercq, L., and Maire, G., *in* "Proceedings of the 10th International Congress of Catalysis, Budapest July 19–24, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 927, Elsevier, Amsterdam, 1993.
12. Wehrer, P., Vennegues, P., Bastin, J. M., and Maire, G., *Ann. Chim Fr.* **18**, 128 (1993).
13. Keller, V., P.h.D. thesis, Strasbourg, 1993.
14. Gault, F. G., *Adv. Catal.* **30**, 81 (1981).