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Catalytic Activity of Bulk Tungsten Carbides for Alkane Reforming

I. Characterization and Catalytic Activity for Reforming of Hexane Isomers in the Absence of Oxygen

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Hydrogenolysis of 2-methylpentane, *n*-hexane and methylcyclopentane has been studied on tungsten carbide WC between 150 and 350°C. The experiments have been performed in a classical flow reactor under a great excess of hydrogen ($p_{H_2}/p_{HC} = 150$) flowing at atmospheric pressure. The catalyst samples have been prepared *in situ* in the flow reactor system by reduction and carburization of WO_3 powder by a mixture of $CH_4(20\%)/H_2(80\%)$ at T = 850°C for 4 h. The BET surface area is around 12 m^2/g. The reactions of these three hydrocarbons give mainly cracking, leading to molecules with less and less carbon atoms as temperature increases. At *T* = 350°C, only methane is observed. Isomerization products, due to skeletal rearrangement, are mainly observed at low temperature, but they represent only a few percent of the total reaction process. The results show that tungsten carbide exhibits catalytic properties close to those of metals like ruthenium, iridium, and nickel in the field of cracking reactions. © 1995 Academic Press, Inc.

1. INTRODUCTION

In 1970 Muller and Gault (1) showed that tungsten carbides possess very interesting properties for the reaction of hydrocarbon hydrogenolysis. They observed on clean tungsten films the complete decomposition of 1,1,3-trimethylcyclopentane at 350°C into methane and traces of ethane. After an induction period of several minutes, new products appear, mainly xylenes resulting from aromatization. According to the authors, this modification of the catalytic activity of tungsten films was due to the formation of superficial tungsten carbide.

Levy and Boudart (2) have shown that tungsten carbides catalyze the formation of water from hydrogen and oxygen at room temperature and isomerization of 2,2-dimethylpropane to 2-methylbutane, reactions which are normally thought to be possible only on platinum and palladium. These authors suggested that the presence of carbon in tungsten carbides modifies the electronic surface properties of tungsten in such a way that they resemble those of platinum. X-ray photoelectron spectra of W, WC, and Pt presented by Colton *et al.* (3) have confirmed this idea.

Other interesting catalytic reactions have been studied on transition metal carbides: these include CO hydrogenation on TaC and TiC (4), on WC and W_2C (5), giving mainly CH_4, ethylene hydrogenation on TiC, WC, and TaC (6, 7), carbon monoxide oxidation on TaC, WC, and Mo_2C (8), and ammonia synthesis (9).

The activity and selectivity of these materials are very sensitive to the presence of impurities like carbon and oxygen, which can act as poisons and deeply reduce the activity of these materials.

Previous results obtained in our laboratory clearly demonstrated the importance of the surface composition of these materials for skeletal rearrangements of hydrocarbons (10, 11). Boudart *et al.* (12) have shown the importance of the surface composition of tungsten carbide for hydrogen adsorption. Polymeric carbon is a poison for this absorption but oxygen enhances it. Ribeiro *et al.* (13, 14) and Iglesia *et al.* (15, 16) have shown the strong influence of oxygen on the activity and selectivity of these catalysts. Chemisorbed oxygen reduces alkane hydrogenolysis and increases the selectivity for isomerization. This reaction would result from a bifunctional mechanism due to the presence on the surface of two kinds of sites, acidic sites due to the presence of oxygen and metallic sites coming from the tungsten carbide.

In a series of four papers, we will report a study of the activity and selectivity of tungsten carbides for hexane reactions in relation with the presence of amorphous carbon or oxygen on the surface. Three hydrocarbons have been chosen in order to test the influence of oxygen: 2-methylpentane (2MP), *n*-hexane (nC_6), and the methylcyclopentane (MCP).

In this first paper, the preparation, characterization, and catalytic reactivity of 2-methylpentane, *n*-hexane,

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and methylcyclopentane will be described for "fresh" samples of bulk tungsten carbide WC, without oxygen. The 2-methylpentane reaction has been tested in order to study the isomerization and formation of cracking products. The *n*-hexane reaction has been studied to follow the isomerization into branched hexanes, the cracking, and eventually the aromatization into benzene. Two mechanisms have been proposed for hexane isomerization on metals, the so-called bond shift and cyclic mechanisms. In order to choose between these two possibilities, the comparison of the activity and products formed in the methylcyclopentane, *n*-hexane and 2-methylpentane reactions is very interesting. If the cyclic mechanism is involved, methylcyclopentane must be an intermediary appearing during the *n*-hexane and 2-methylpentane isomerization reactions; moreover, methylcyclopentane must react faster than the two other hydrocarbons.

In a second and third paper, the influence of oxygen addition in several conditions, viz. exposure at $T = -65°C$, $T = 350°C$, and $T = 700°C$, on catalytic activity and selectivity will be presented. Finally, in a fourth paper, a general discussion of the results obtained on fresh catalyst without oxygen and with oxygen will be given. To account for the experimental results, several mechanisms will be proposed.

2. EXPERIMENTAL METHODS

2.1. Preparation of WC Samples

The tungsten carbide samples were prepared in situ in our laboratory by direct carburization of WO_3 powder from Johnson Matthey. The carburization was performed by a mixture of CH_4 20%, and H_2 80% flowing under atmospheric pressure at 45 cm^3/min with a temperature ramp of 5°C/min until $T = 850°C$; this temperature is maintained for about 1 h. The catalyst is maintained in the same atmosphere for passivation by amorphous carbon, resulting from methane decomposition. Before catalytic measurements, the passivation layer must be removed by heating at $T = 750°C$ in hydrogen atmosphere for about 15 min. The hydrogen used was purified from eventual oxygen impurities with a Mn–oxide trap. The oxygen content is estimated to be less than 1 ppm. After activation, the catalyst is cooled down to the reaction temperatures under a helium flow (50 cm^3/min).

2.2. Characterization

X-ray diffraction shows the presence of WC only. Chemical analysis has been performed (Service Central d'Analyse C.N.R.S., 69390 Vernaison, France) by pyrolysis at $T = 2800°C$ where oxygen is transformed into CO which is analyzed by infrared spectroscopy. The oxygen content is lower than the detection limit of the method (wt% < 0.2%). The surface area was determined by the classical BET method (N_2 physisorption at $T = -200°C$) and was around 12 m^2/g. It has been shown that the passivation procedure used does not change this area very much. The sample passivated by carbon leads to a reduction of less than 5% of the nitrogen adsorbed.

For the sample prepared in situ in our laboratory, the isotherm of nitrogen desorption (following physisorption at liquid nitrogen temperature, $T = -200°C$) can give the pore size distribution using the method proposed by Barrett *et al.* (18), assuming a cylindrical shape for the pores. The results show that 80% of the surface is due to pores having a diameter greater than 40 Å, and that there are no pores with a diameter lower than 15 Å. Reproducible surface states determined by thermodesorption profiles of chemisorbed hydrogen can be obtained (19).

2.3. Apparatus and Procedures

The experiments have been performed in a glass flow system already described (11), equipped with purification traps to remove oxygen traces, with about 300 mg of tungsten carbide powder. Reactions were carried out under 1 atm of hydrogen pressure at a flow rate of about 60 cm^3/min. Five microliters of reactant were injected into a U-tube maintained at −38°C, then the hydrocarbon partial pressure was maintained constant in the catalytic reactor (5 Torr of 2-methylpentane and *n*-hexane and 3.5 Torr of methylcyclopentane). The reaction temperature was varied from 150 to 350°C on "fresh" tungsten carbides. After reaction, the products were analyzed by gas chromatography (CPSIL5) with a flame ionization detector (CF.1.0) and 40 cm^3/min flow of helium as carrier gas.

3. REACTIVITY OF HYDROCARBONS

During the catalytic process, several reactions can occur. The conversion (or activity) is defined as the percentage of reactant transformed. The selectivity, S, of a product is given as the percentage of this product among all the products formed. The yield percentage of a product represents the amount of this product, calculated from the selectivity multiplied by the conversion. As the hydrocarbon molecule can undergo one or several carbon–carbon bond cleavages, these processes will be called single or extensive (or multiple) cracking (or hydrogenolysis in presence of hydrogen). The importance of the extensive cracking can be estimated by the average carbon atom number ($\bar{n}$) in the hydrogenolysis products (20). For hexanes, it is given by

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

TABLE 1

Distribution of the Reaction Product Percentages of 2-Methylpentane on "Fresh" Tungsten Carbide versus Temperature

Temp. (°C)	Conv. α(%)	Cracking (%)							Isomerization (%)		
		C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	23DB	3MP	nC_6
350	100	100	0	0	0	0	0	0	0	0	0
300	80.9	38.9	33.8	14.6	3.5	1.8	4.5	2.9	0	0	0
250	54.7	21.9	34.7	19.3	5.8	2.1	7.7	6.7	0.3	1.2	0.3
200	26.5	16.8	18.9	25.0	8.9	0.9	9.9	10.9	0.4	6.6	1.5
150	11.5	18.0	18.3	17.3	7.5	1.0	12.4	14.8	0.7	6.6	3.4

where S_c and c are respectively the selectivity and the carbon atom number of each cracked product.

The mean number of carbon–carbon bonds broken, $\overline{X}$, (20) is given by

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

For a simple reaction

$$(1 - \alpha)\, A \xrightarrow{k} (\alpha)\, B,$$

where α is the fractional conversion of A of k the rate constant; the reaction rate r is given by the classical relation: $r = d\alpha/dt = k(1 - \alpha)^n$, with n being the reaction order. In the present case this reaction order is assumed to be equal to 1; i.e., the reaction coefficient k is zero order with the hydrocarbon pressure, in agreement with the results of many authors, namely Frennet *et al.* (21, 22) and Boudart *et al.* (23) for hydrocarbon decomposition on a tungsten surface; Leclercq *et al.* (24) for hydrocarbon reaction on tungsten carbide; Vidick *et al.* (25) and Suarez *et al.* (26) for ethylene reaction on tungsten carbide.

From the mass balance and by integration the following relationship is obtained

$$\frac{k}{\rho} = k' = \frac{F}{\omega} \times \ln\left(\frac{1}{1 - \alpha}\right), \qquad [3]$$

where ω and ρ are respectively the weight and the mass density of the catalyst.

3.1. Reactivity of 2-Methylpentane (2MP)

The catalytic activities of "fresh" WC powder for 2-methylpentane are given in Table 1, where the five working temperatures appear in the first column. In the second column, the conversion α is shown. In the following columns the selectivity for cracking and isomerization are given. The 2-methylpentane reaction leads to the formation of cracked products (methane (C_1), ethane (C_2), propane (C_3), isobutane (iC_4), n-butane (n-C_4), isopentane (iC_5) and n-pentane (n-C_5)) and of isomerized products (2,3-dimethylbutane (23DB), 3-methylpentane (3MP), and n-hexane (nC_6)). In Figure 1a the total yield variations of cracked and isomerized products with temperature are shown. Figures 1b and 1c give respectively the yield percentage variation of each isomerized and

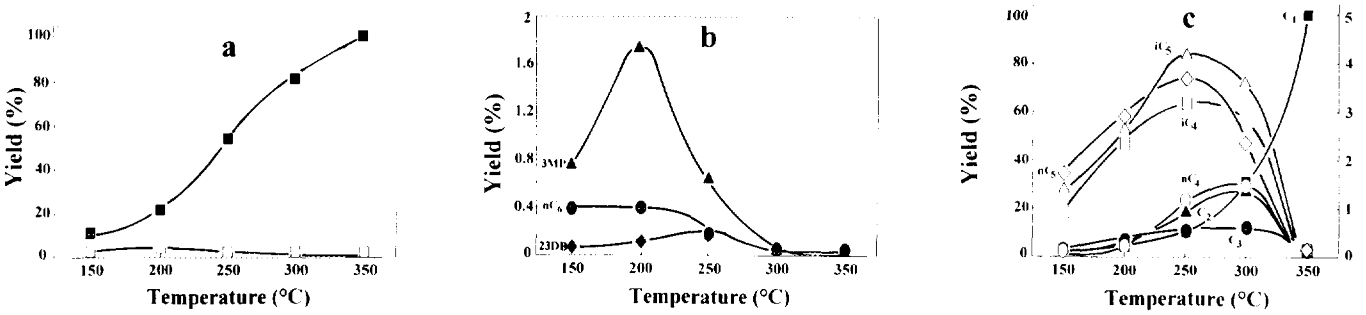


FIG. 1. (a) 2MP total hydrogenolysis and isomerization yield percentages versus temperature. ■, hydrogenolysis; □, isomerization. (b) 2MP isomerization yield percentages versus temperature. ◆, 23DB; ▲, 3MP; ●, nC_6. (c) 2MP hydrogenolysis yield percentages versus temperature. Left Y-axis: ■, C_1; ▲, C_2; ●, C_3. Right Y-axis: □, iC_4; ○, nC_4; △, iC_5; ◇, nC_5.

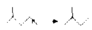
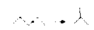
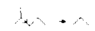
TABLE 2

Average Number of Carbon Atoms in the Cracking Products of 2-Methylpentane ($\bar{n}$) and Average Number of Carbon–Carbon Bonds Cleaved ($\bar{X}$)

Temperature (°C)	$\bar{n}$	$\bar{X}$
350	1	5
300	2.08	1.88
250	2.57	1.33
200	2.99	1.07
150	3.1	0.95

TABLE 3

Demethylation, Deethylation, and Depropylation Ratios of 2-Methylpentane at 250, 200, and 150°C, in Comparison with Statistical Values

Temperature (°C)	 C_I–C_{III}	 C_I–C_{II}	 C_{II}–C_{II}	 C_{II}–C_{III}
250	0.22	0.26	0.20	0.32
200	0.26	0.25	0.20	0.30
150	0.23	0.33	0.20	0.23
Statistical	0.40	0.20	0.20	0.20

cracked product. At T = 350°C, the total activity is very high and the whole of the reactant has been transformed into methane. This activity decreases with temperature, as shown Table 1. At T = 150°C, its value is about 10%. In Table 1 and in Fig. 1a, we may notice that the cracking reactions are the most important and that their rates increase with the temperature, while isomerization remains at a very low level. The yield percentage of cracked product goes through a maximum at T = 250°C, except methane (Fig. 1c). At T = 350°C, 2-methylpentane leads only and totally to extensive cracking, as shown in Table 1 and in Fig. 1a. At temperatures below T = 350°C, we observe the formation of the other cracked products (ethane, propane, butanes and pentanes). By lowering the temperature, we have simple hydrogenolysis instead of an extensive one, which means an increase of the average of the number of carbon atoms in the cracked products, and a decrease of the average of the number of broken carbon–carbon bonds, as shown in Table 2, where $\bar{n}$ and $\bar{X}$, previously defined, are given. n-Butane, which is not an initial product of the reaction, is present in small amounts at T = 150°C and T = 200°C (Table 1) and becomes more important at T = 250°C. As it could not result from only one carbon–carbon bond breaking off the starting molecule (2-methylpentane), its presence must be accounted for either by a repetitive process or by the cracking of an isomerized product. This last assumption is highly improbable for 2-methylpentane which does not produce isomers in a significant amount whatever the temperature range. The different ways of single carbon–carbon bond cleavage (demethylations, deethylation and depropylation) are given in Table 3. The values reported represent the ratios of single carbon–carbon bond breaking to the total bond breaking resulting from all the single carbon–carbon bond cleavages. We observe that, at T = 150°C, all the ratios for demethylations, deethylation, or depropylation are close to the statistical ones. Concerning the depropylation reaction by C_{II}–C_{III} bond breaking, this is favored by increasing the temperature, although demethylations and deethylation ratios are not modified.

Under T = 250°C, the presence of isomerized products is detected, as shown in Fig. 1b. 3-Methylpentane is formed predominantly in comparison with 2,3-dimethylbutane or n-hexane. As the reaction temperature increases, the isomerization selectivity does not exceed 10% (Table 1). The isomerization product yield percentage versus temperature (Fig. 1b) goes through a maximum at around T = 200°C, which is a little lower than the maximum observed for the cracked products, as shown in Fig. 1c.

TABLE 4

Distribution of the Reaction Product Percentages of n-Hexane on "Fresh" Tungsten Carbide versus Temperature

Temp. (°C)	Conv. (%)	Cracking (%)							Isomerization (%)		$\bar{n}$	$\bar{X}$
		C_1	C_2	C_3	iC_4	nC$_4$	iC_5	nC$_5$	2MP	3MP		
350	100	100	0	0	0	0	0	0	0	0	1	5
300	97.0	100	0	0	0	0	0	0	0	0	1.03	4.83
250	81.8	29.8	34.8	16.6	0.2	11.2	0.2	6.7	0.31	0.16	2.30	1.61
200	47.7	19.9	27.6	20.0	0.2	16.3	0.3	13.4	1.4	0.9	2.76	1.17
150	20.2	15.0	26.0	19.5	0.05	15.2	0.3	18.0	3.7	2.3	2.96	1.03

Note. $\bar{n}$: Average number of carbon atoms in the cracking products. $\bar{X}$: Average number of carbon-carbon bonds cleaved.

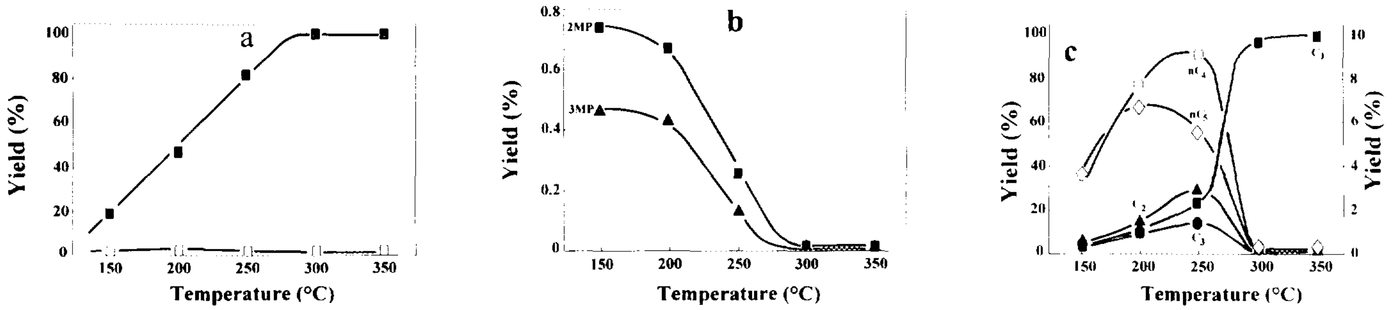


FIG. 2. (a) nC_6 total hydrogenolysis and isomerization yield percentages versus temperature. ■ Hydrogenolysis, □ isomerization. (b) nC_6 isomerization yield percentages versus temperature. ■, 2MP; ▲, 3MP. (c) nC_6 hydrogenolysis yield percentages versus temperature. Left Y-axis: ■, C_1; ▲, C_2; ●, C_3. Right Y-axis: ○ nC_4; ◇, nC_5.

3.2. *Reactivity of n-Hexane (nC_6)*

The distributions of the products are given in Table 4 for different temperatures ($T = 150°C$ to $T = 350°C$) and are expressed as the selectivity of each product formed. The evolutions of total cracking and isomerization yield percentages as a function of temperature are given in Figure 2a. The variations of isomerization and cracking yield percentages are shown respectively in Figs. 2b and 2c. As for 2-methylpentane, *n*-hexane undergoes predominantly cracking instead of isomerization and the activity is very high at $T = 350°C$ (Fig. 2a). By comparison with the results given in Tables 1 and 4, it appears that the conversion is more important for *n*-hexane (linear) than for 2-methylpentane (branched) from $T = 150°C$ up to $T = 300°C$. At $T = 300°C$, only extensive cracking into methane is observed for *n*-hexane, while at this temperature, 2-methylpentane gives all the other cracked products. If the temperature of reaction is lowered, simple hydrogenolysis is favored. As for 2-methylpentane, the cracked product yield percentages, except for C_1, go through a maximum at about $T = 250°C$.

From a linear reactant, like *n*-hexane, isobutane (iC_4) and isopentane (iC_5) cannot result from a single or multiple carbon–carbon bond cleavage, but must do so from the cracking of isomerized products. Their amounts are very low as shown in Table 4. *n*-Hexane, like 2-methylpentane, does not undergo extensive cracking below $T = 250°C$; $\bar{X}$ varies from 1 to 1.6 for both hydrocarbons, as shown in Tables 2 and 4. The percentages of single hydrogenolysis (demethylation, deethylation, and depropylation) are given in Table 5. By lowering the temperature, terminal cleavage (demethylation) is favored, in comparison to deethylation and depropylation.

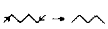
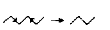
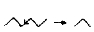
Concerning isomerization (less than 6% of the total products formed), 2-methylpentane and 3-methylpentane are the only detected molecules (and no 2,3-dimethylbutane as for 2-methylpentane below $T = 250°C$).

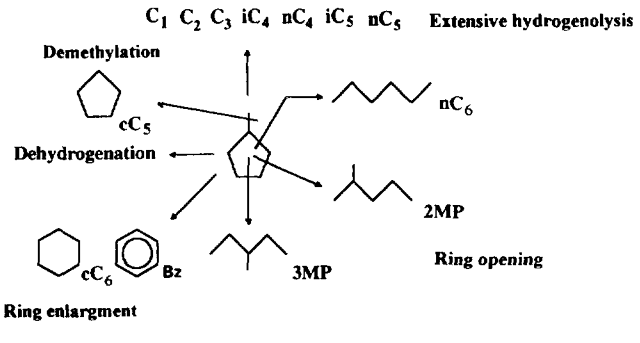
3.3. *Reactivity of Methylcyclopentane (MCP)*

The results are given in Table 6. The reactions have been performed at the same temperatures as for 2-methylpentane and *n*-hexane. As previously mentioned for the results obtained with 2-methylpentane and *n*-hexane, the activity given in the second column is expressed as a percentage of methylcyclopentane transformed. In the other columns, the selectivities for the corresponding molecules are given. In Figure 3a, extensive hydrogenolysis leading to C_1, C_2, C_3, iC_4, nC_4, iC_5, and nC_5 and single hydrogenolysis leading to cyclopentane by demethylation and to 2-methylpentane, 3-methylpentane, and *n*-hexane by ring opening as illustrated in Scheme 1, are given for the different reaction temperatures.

TABLE 5

Demethylation, Deethylation, and Depropylation Ratios of *n*-Hexane at 250, 200, and 150°C, in Comparison with Statistical Values

Temperature (°C)	 C_I–C_{II}	 C_{II}–C_{II}	 C_{II}–C_{II}
250	0.26	0.42	0.32
200	0.34	0.41	0.25
150	0.42	0.35	0.23
Statistical	0.40	0.40	0.20



SCHEME 1.

TABLE 6

Distribution of the Reaction Product Percentages of Methylcyclopentane on "Fresh" Tungsten Carbide versus Temperature

Temp. (°C)	Conv. (%)	Extensive hydrogenolysis (%)							Single hydrogenolysis (%)				
		C_1	C_2	C_3	iC_4	nC_4	iC_5	nC_5	cC_5	2MP	3MP	nC_6	MCP^{2-}
350	100	100	0	0	0	0	0	0	0	0	0	0	0
300	98.9	95.0	3.0	0.9	0	0	0	0	0	0	0	0	0
250	49.9	39.4	33.8	9.2	2.1	3.5	3.2	1.6	1.6	2.8	2.0	0.5	0.06
200	10.12	28.7	22.1	5.7	2.4	4.7	6.3	3.3	3.3	10.1	7.5	2.6	0.2
150	8.00	21.4	16.9	2.9	1.5	3.9	7.3	3.9	3.9	13.0	9.7	4.2	0.2

Note. MCP^2 = methylcyclopentenes.

Figures 3b and 3c show the yield percentage for each product, resulting from single hydrogenolysis and extensive hydrogenolysis, respectively. As observed for 2-methylpentane and *n*-hexane, at temperature higher than $T = 300°C$, extensive hydrogenolysis is predominant; its importance decreases on lowering the temperature. The variations of the yield percentage of each extensive hydrogenolysis product except methane (Fig. 3c) and each single hydrogenolysis product (Fig. 3b) versus temperature, show a maximum at around $T = 250°C$. These results are very similar to those obtained with 2-methylpentane and *n*-hexane. In Table 7 the percentage of single hydrogenolysis products resulting from demethylation and ring opening at $T = 150°C$, $T = 200°C$, $T = 250°C$ are compared with the percentages which would be obtained for statistical bond cleavages. It can be observed that *n*-hexane amounts are far lower than the statistical predictions at the three temperatures considered, while 2-methylpentane and 3-methylpentane amounts are higher than the statistical predictions. Concerning the *n*-hexane results, the difference between the experimental results and the statistical model could be due either to the steric difficulty of C_{II}–C_{III} bond cleavage, compared to the other carbon–carbon bond cleavages of the methylcyclopentane molecule, or to the faster cracking process of the *n*-hexane molecule. This latter hypothesis seems less reasonable than the former one, because of the similar cracking activity of *n*-hexane and 2-methylpentane.

Finally, it is important to notice that no ring enlargement process, leading to benzene and cyclohexane, is observed. Only a few percent of dehydrogenation (methylcyclopentenes) are obtained.

4. DISCUSSION

From the conversion percentage α of each hydrocarbon, it is possible to calculate the rate constant k, as defined by Eq. [3]. The corresponding k values, versus $1/T$, are given for *n*-hexane, 2-methylpentane, and methylcyclopentane in Figure 4. Activation energies can be deduced for the conversion process between $T = 300°C$ and $T = 150°C$. The k values for $T = 350°C$ are not accurate, because the conversion is around 100% and will not be taken into account for the activation energy determinations. These energies are around 8, 9, and 12 kcal/mol for 2-methylpentane, *n*-hexane, and methylcyclopentane, respectively. The disappearance of hydrocarbon results from several processes: cracking leading to smaller molecules (C_1, C_2, C_3, ...) and isomerization which, in this case, is of low importance. These activation energies are

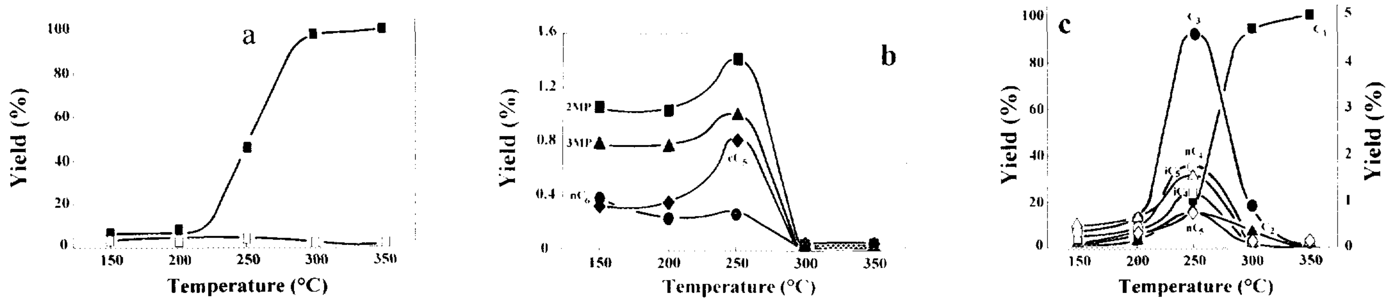
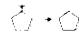
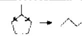
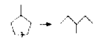


FIG. 3. (a) MCP total single and extensive hydrogenolysis yield percentages versus temperature. ■, extensive hydrogenolysis; □, single hydrogenolysis. (b) MCP single hydrogenolysis yield percentages versus temperature. ◆, cC_5; ■, 2MP; ▲; 3MP; ●, nC_6. (c) MCP extensive hydrogenolysis yield percentages versus temperature. Left *Y*-axis: ■, C_1; ▲ C_2. Right *Y*-axis: ●, C_3; □, iC_4; ○, nC_4; △, iC_5; ◇, nC_5.

TABLE 7

Single Hydrogenolysis Ratios by Demethylation and Ring Opening for Methylcyclopentane at 250, 200, and 150°C, in Comparison with Statistical Values

Temperature (°C)	 C_I–C_{III}	 C_{II}–C_{III}	 C_{II}–C_{II}	 C_{II}–C_{II}
250	0.23	0.07	0.40	0.29
200	0.14	0.11	0.43	0.31
150	0.13	0.13	0.42	0.31
Statistical	0.17	0.3	0.3	0.17

rather low in comparison with those obtained on metals like platinum and ruthenium, which are around 50 kcal/mol (27).

With a simple model, the hydrocarbon disappearance from the gas phase can be assumed to result from adsorption on free surface sites $1 - \theta_c$, with θ_c being the surface fraction occupied by hydrocarbon residues. The hydrocarbon disappearance rate is given by

$$\frac{d_{HC}}{dt} = \frac{P_{HC}}{\sqrt{2\pi mkT}} \times (1 - \theta_c) \times k_{(ads\text{-}react.)} \qquad [4]$$

θ_c can be determined by assuming a stationary state due to the equilibrium between adsorption rate and reaction rate (which are not distinguished) for the hydrocarbons on the free surface sites, on the one hand, and desorption of hydrocarbon species, on the other hand.

$$\frac{d\theta_c}{dt} = \frac{P_{HC}}{\sqrt{2\pi mkT}} \times (1 - \theta_c) \times k_{(ads\text{-}react.)} - \theta_c \times k_{des} = 0. \qquad [5]$$

with $k_{(ads\text{-}react.)}$ and k_{des} being respectively the rate constant for adsorption and reaction of the adsorbed hydrocarbon and desorption processes. In the case where the adsorption and reaction processes are the most important, and where the desorption rate is negligible in comparison with reaction rate, the reaction rate of the hydrocarbon can be approximated by

$$\frac{d_{HC}}{dt} \approx k_{des} \qquad [6]$$

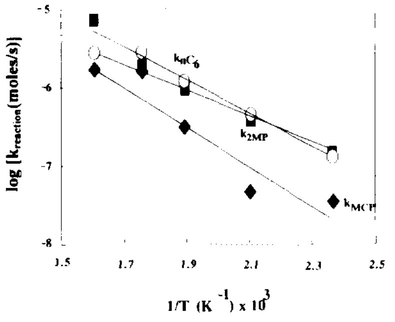


FIG. 4. 2MP, nC_6, and MCP rate constants versus $1/T$ (K) × 10^3.

The observed activation energy values, around 9 and 12 kcal/mol, are comparable with desorption energies usually found for hydrocarbons adsorbed on metals (28). As tungsten carbide shows cracking properties close to those observed on metals, like Ir and Ru, it is reasonable to assume that the binding energies are of the same order than those found on these metals. The reaction process of hydrocarbons on tungsten carbide WC would be limited by the desorption of hydrocarbon residues from the surface. This is confirmed by results obtained in our laboratory, showing that tungsten carbide surface deactivation by hydrocarbon residues is a process occurring rapidly. After 20 minutes under the reaction mixture HC + H_2 at $T = 200$°C on bulk WC tungsten carbide, the hydrocarbon conversion is reduced to around 50% of its initial value; this result shows clearly that the hydrocarbon species are strongly adsorbed on the surface.

The presence of maxima in the curves giving the yield percentage for all the molecules (except methane) appearing during the reactions studied, is explained by the competition between the kinetics of production and cracking of the same molecule. The cracking of these molecules, becoming more and more important as the experimental temperature increases, leads ultimately to the formation of methane, which is the only molecule stable at high temperature. The competition of these different molecular processes (formation and cracking) will also be discussed in the fourth paper, of this series.

Finally, tungsten carbide exhibits catalytic properties close to those of transition metals like Ru, Ir, and Ni for hydrocarbon cracking (29). For example, on 10% Ru/Al_2O_3 at $T = 160$°C (30), carbon–carbon bonds with a tertiary carbon are unaffected. The authors assumed that this could be explained by carbene species. These species are favored at low temperature. On 25% Ni/SiO_2, bond breaking including a tertiary carbon is favored. In this case, the authors have assumed that metallacyclobutane could be a reaction intermediate, such a species being favored at high temperature. On "fresh" tungsten carbide, an increase of the cleavage of the C_{II}–C_{III} 2-methylpentane bond with the temperature is observed.

Concerning the reaction of methylcyclopentane, it is observed in the literature that on Ir/SiO_2 (30), methylcyclopentane undergoes exclusively extensive hydrogenolysis. Hydrogenolysis of methylcyclopentane at $T = 200$°C on Ru/Al_2O_3 (31) shows that the ring opening is very selective (32). There is mainly a breaking of the C_{II}–

C_{II} bonds, and the 3-methylpentane/*n*-hexane ratio is high. In the same way, Ni is very selective for ring opening with very high ratio of 3-methylpentane/*n*-hexane as the temperature varies from T = 150°C to T = 220°C.

In conclusion, the reforming reactions of 2-methylpentane, *n*-hexane, and methylcyclopentane are mainly cracking reactions leading to hydrocarbons of lower molecular mass. At T = 350°C, all the carbon-carbon bonds are broken and only methane is observed. At lower temperatures, molecules containing several carbon atoms are stable; their concentrations go through a maximum as reaction temperature is lowered and become zero at temperatures lower than T = 150°C. At the lowest reaction temperature (T = 150–200°C), isomerization reactions are observed but the corresponding products represent only a few percent of the total reaction products.

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. Colton, R. J., Huang, J. T. J., and Rabalais, J. W., *Chem. Phys. Lett.* **34,** 337 (1975).
4. Kojima, I., and Miyazaki, E., J. Catal., **89,** 168 (1984).
5. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *Bull. Chem. Soc. Jpn.* **56,** 611 (1985).
6. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59,** 472 (1979).
7. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **73,** 128 (1982).
8. Yang, R. T., and Wong, Ch., *J. Catal.* **85,** 154 (1984).
9. Schultz-Ekloff, G., Barasel D., and Sarholz, W., *J. Catal.* **43,** 353 (1976).
10. Keller, V., Cheval, M., Vayer, M., Ducros, R., and Maire, G., *Catal. Lett.* **10,** 137 (1991).
11. Keller, V., Cheval, M., Maire, F., Wehrer, P., Ducros, R., and Maire, G., *Catal. Today* **17,** 493 (1993).
12. Boudart, M., Lee, J. S., Imura, K., and Yoshida, S., *J. Catal.* **103,** 30 (1987).
13. Ribeiro, F. H., Della-Betta, R. A., Boudart, M., Baumgartner, J., and Iglesia, E., *J. Catal.* **130,** 86 (1991).
14. Ribeiro, F. H., Boudart, M., Dalla-Betta, R. A., and Iglesia, E., *J. Catal.* **130,** 498 (1991).
15. Iglesia, E., Baumgartner, J. E., Ribeiro, F. H., and Boudart, M., *J. Catal.* **131,** 523 (1991).
16. Iglesia, E., Ribeiro, F. H., Boudart, M., and Baumgartner, J. E., *Catal. Today* **15,** 307 (1992).
17. Frennet, A., *et al.*, Proc. Int. Congr. Catal., 10th (Budapest 1992) (L. Guczi, F. Solymosi and P. Tétényi, Eds.), p. 927, Elsevier, Amsterdam, 1993
18. Barrett, E. P., Joyner, L. G., and Halenda, P. P., *J. Am. Chem. Soc.* **73,** 373 (1951).
19. Wehrer, P., Vennegues, P., Bastin J. M., and Maire, G., *Ann. Chim. Fr.* **18,** 128 (1993).
20. Paál, Z., and Tétényi, P., in Spec. Per. Rep. Vol 5, p. 80 "Catalysis", Roy. Soc. Chem., London, 1982.
21. Frennet, A., and Lienard, G., *J. Chim. Phys.* **68,** 1526 (1971).
22. Frennet, A., Lienard, G., Crucq, A., and Degols, L., *J. Catal.* **53,** 150 (1978).
23. Boudart M., Ollis, D. F., and Harris, G. W., *Trans. Faraday Soc.* **65,** 519 (1969).
24. Leclercq, L., Provost, M., Pastor, H., and Leclercq, G., *J. Catal.* **117,** 384 (1989).
25. Vidick, B., Lemaitre, J., and Leclercq, L., *J. Catal.* **99,** 439 (1986).
26. Suarez, M. P., Cechini, J. O., and Löffler, *J. Catal.* **89,** 527 (1984).
27. Garin, F., and Gault, F. G., *J. Am. Chem. Soc.* **97,** 4466 (1975).
28. Rideal, E. K., *in* "Concepts in Catalysis," p. 60. Academic Press, London, 1968.
29. Carter, J. L., Cusumano, J. A., and Sinfelt, J. H., *J. Catal.* **20,** 223 (1971).
30. Diaz, G., Garin, F., and Maire, G., *J. Catal.* **82,** 13 (1983).
31. Weisang, F., and Gault, F. G., *J. Chem. Soc. Chem. Commun.* **S19** (1989).
32. Gault, F. G., *Adv. Catal.* **30,** 81 (1981).