# Tungsten carbides as substitutes of platinoids in heterogeneous catalysis
# I. The effect of surface composition on the reactivity of methylcyclopentane on tungsten carbides

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Reactions of methylcyclopentane on tungsten carbides show that in presence of oxygen the extensive hydrogenolysis is inhibited in favour of ring enlargement and ring opening via a bifunctional mechanism due to the coexistence of surface acid-rearrangement and hydrogenation-dehydrogenation sites. The oxycarbidic materials are very active and selective in skeletal rearrangement of hydrocarbons.

**Keywords:** Methylcyclopentane reactivity; tungsten carbides; heterogeneous catalysis; surface composition; hydrogenolysis

## 1. Introduction

It has been well established that carbides or nitrides have interesting catalytic properties. In 1970, J.M. Muller et al. [1] studied the hydrogenolysis of trimethyl 1,1,3-cyclopentane on several metallic films deposited under vacuum (Ni, Rh, Pt, Pd, W). On tungsten films at 350 ° C, a very fast reaction occurred giving mainly extensive hydrogenolysis to methane and traces of pentanes. However with time, the product distribution changed and gemdimethylcyclopentane, benzene, toluene and xylenes were formed. As the reaction proceeds, the amounts of aromatic hydrocarbon increase due to a modification of the catalytic properties of the tungsten film and attributed by the authors to the formation of a 2D "surface carbide" [1]. R. Levy et al. [2] and M. Boudart et al. [3] showed that tungsten carbide has properties completely different from tungsten and comparable in some aspects to those of platinum. Tungsten carbide like platinum can isomerize 2,2-dimethylpropane to 2-methylbutane but the activity for isomerization is lower compared with platinum. The extent to which the catalytic properties of carbides or nitrides of some transition metals can compete with those of transition metals (Pt, Pd, Rh, Ru) is a subject which has attracted many scientists working in the field of catalysis.

Because of the important role Pt plays in the chemical industry and in electrocatalysis, it is not surprising that carbides or nitrides have received particular attention. J. Lemaitre et al. [4] and B. Vidick et al. [5,6] studied tungsten carbide activity for ethylene hydrogenation and cyclohexane dehydrogenation. The contamination of the catalyst surface by polymeric carbon and by oxygen can deeply reduce its activity. The surface contamination by carbon has also been clearly shown for ethylene hydrogenation on tantalum carbide by I. Kojima et al. [7]. Other reactions like hydrogenation of carbon monoxide on $W_2C$, WC and W powders and decomposition of methanol on several carbides (TiC, TaC, $MO_2C$, WC, $W_2C$) have been studied [8,9]. As for ethylene hydrogenation, carbon in polymeric form and oxygen can act as poisons for the hydrogenation of carbon monoxide on tungsten carbide. X-ray photoelectron spectroscopy (X.P.S.) measurements, on TaC have revealed that the catalytic activity for methanol decomposition depends on the removal of surface oxygen and on the subsequent formation of monocarbide surfaces. On the other hand, the main activities leading to the formation of methylformate on $W_2C$ and $MO_2C$ would be due to oxycarbide surfaces [9]. The scope of this paper is to present results obtained for the test reaction of methylcyclopentane plus hydrogen on tungsten carbides (bulk tungsten carbide $W_2C$ plus tungsten metal and model tungsten carbide produced by carburization of a tungsten ribbon). The catalytic results are correlated to the surface species of the catalysts observed by X-Ray Photoelectron Spectroscopy (X.P.S.) and Auger Electron Spectroscopy (A.E.S.). On such catalysts new mechanisms are involved in the processes in comparaison with transition metal surface.

## 2. Experimental

### 1. MATERIALS

Two catalysts have been used:

– A powder catalyst, bulk mixture of $W_2C$ and W, was supplied by G. and L. Leclercq from the "Laboratoire de Catalyse de Lille". It was prepared by reduction and carburization of $WO_3$ in a stream of $CH_4/H_2$ between 500–600 °C during 10 hours [10]. Characterization by X-ray diffraction before and after catalytic reactions revealed the coexistence of W and $W_2C$ phases without any trace of tungsten oxide. The specific surface area in 8 $m^2/g$. After preparation, the catalyst is passivated by oxygen following a standard recipe [10]. Before catalytic measurements, the passivation layer must be removed by heating at 350 °C in a hydrogen atmosphere during 10 hours.

– A model tungsten carbide $W_2C$, was prepared by ethylene decomposition (at 600 ° C–5 mm–$10^{-7}$ Torr $C_2H_4$) on a tungsten ribbon supplied by Heraeüs Company (purity 4 N) and heated at 600 ° C during 5 min in $10^{-7}$ Torr ethylene pressure. The ribbon has been previously cleaned by oxygen treatment at high temperature to remove carbon which is the main impurity, the cleanliness of the surface has been controlled by A.E.S.

– Reactants

The hydrocarbons used as reactants or references were: 2-methylpentane (2 MP), 3-methylpentane (3 MP), n-hexane (n-HX), methylcyclopentane (MCP), cyclopentane (CP), benzene (BZ) and cyclohexane (CH) Fluka purissgrade. They were purified if necessary before each use by G.L.C. Ethylene (purity 99.95%), oxygen (purity 99.98%), hydrogen (purity 99%) were purchased from the Air Liquide Company.

## 2. APPARATUS AND PROCEDURE

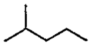
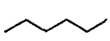
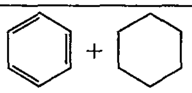
The experiments have been performed in a flow system and in a static system.

*Experiments in a flow system.* The experiments were carried out with 250 mg of powder in all glass system already described [11]. Reactions were performed at 350 ° C and under 1 atm of hydrogen at a flow rate of 65 cc/min. A small amount, 5 mg, of (MCP) was injected into the reactor at constant pressure (3.5 Torr). When the pulse of (MCP) had passed the reactor, a sample was taken with a syringe and the product distribution was recorded by simple G.C. analysis over a 500 cm × 0.2 cm column of DC 200 (silicon 5%) firebrick with a flame ionization detector CF.1,0, and 40 cc/min flux of helium as gas carrier.

*Experiments in a static system.* The experiments were carried out in a U.H.V. chamber with X.P.S. and A.E.S. facilities. An isolation cell housed within the main chamber allows catalytic reaction up to atmospheric pressure with the rest of the chamber in U.H.V. conditions. More details of the apparatus are given elsewhere [12]. The catalytic reaction cell is connected to a gas inlet system which also allows the sampling of the reaction products.

– For the powder catalyst $W_2C + W$ experiments, the sample was 250 mg of powder pressed in a disk of 8 mm diameter and 1 mm thick under a pressure of 15 $kg/cm^2$ and placed on a tantalum holder heated by direct Joule effect. The temperature was measured by a chromel-alumel thermocouple spotwelded on the holder. In each run, 5 Torr of hydrocarbon were introduced with 755 Torr of pure hydrogen and then the desired catalyst temperature was achieved. This temperature was usually 350 ° C and the reaction time varied between 15 mn and 60 mn. The catalytic properties of the tantalum holder was undetectable as tested by blank experiments for hydrogenolysis of (MCP) under the same experimental conditions. The surface species of the catalyst were determined by X.P.S. before and after an experiment. Before the catalytic activity and selectivity measurements, the passivation layer was removed by heating under hydrogen

Table 1
Product distribution of methylcyclopentane reaction at 350 ° C on tungsten carbides

| $\alpha_t$ (%) | $\Sigma$ (acyclic cracking) (%) |  |  |  |  |  | $S$ (%) | |
|---|---|---|---|---|---|---|---|---|
| 10.4 | 29.0 | 3.1 | 6.3 | 3.4 | 5.3 | 53.0 | 68.0 | I |
| 10.5 | 39.0 | 5.7 | 6.3 | 3.5 | 4.3 | 40.5 | 54.6 | II |
| 19.0 | 100.0 | 0 | 0 | 0 | 0 | 0 | 0 | III |
| 5.8 | 0 | 0 | 48.4 | 16.6 | 30.3 | 4.7 | 100.0 | IV |

I Catalytic flow experiments } on tungsten carbide
II Catalytic static experiments } powder ($W_2C+W$).
III Catalytic static experiments on a model tungsten carbide $W_2C$.
IV Catalytic flow experiments on $Pt/Al_2O_3$ 0.2% [6].

$\alpha_t$ (%) (moles) = overall conversion.
$S$ (%) = selectivity for ring opening and ring enlargement.

at atmospheric pressure following the same procedure as for the experiments conducted in the flow system.

– For the model $W_2C$ catalyst experiments, the ribbon 7 cm length, 2 mm wide and 30 $\mu$m width was spotwelded at the ends of the sample holder, its temperature was given by a W-Re 5%–W-Re 75% thermocouple spotwelded on its central part. As for the previous experiments the reaction temperature chosen was 350 ° C and the contact time between the gases and the surface lasted 60 mn. The total area of the sample was 2.8 $cm^2$.

## 3. Results

### CATALYTIC RESULTS

The distribution of the products obtained for the reaction of (MCP) for both sets of experiments (in the flow and in the static systems) are presented in table 1, where column 1, $\alpha_t$% is the percentage overall conversion of (MCP); column 2, $\Sigma$ (acyclic cracking) (%) is the percentage of the total acyclic cracking ($CH_4$, $C_2H_6$, $C_3H_8$, $nC_4H_{10}$, iso $C_4H_{10}$, $nC_5H_{12}$ and iso $C_5H_{12}$) among the whole products of the reaction; columns 3,4,5,6, and 7 are respectively the percentage of (CP), (2MP), (3MP), ($n$-HX), (BZ) + (CH); column 8, $S$ (%), is the selectivity defined as the sum of the percentages of the $C_6$ isomers produced by ring opening plus the (BZ) and (CH) formed by ring enlargement.

The results obtained at 350 ° C and given in table 1 are divided in four groups which respectively correspond to: I: Experiments done on the tungsten carbide powder ($W_2C$ + W) in the flow system; II: Experiments done on the tungsten carbide powder ($W_2C$ + W) in the static system for 30 mn contact time. III:

Experiments done on the model tungsten carbide in the static system; IV: Experiments previously performed in this laboratory on platinum reference catalyst (0.2%-$PtAl_2O_3$-$D = 100$) cf. [12].

The analysis of the results presented in table 1 shows clearly that on the tungsten carbide powder ($W_2C + W$), the formation of benzene and cyclohexane by ring enlargement is the major contribution at a conversion of around 10% for the experiments done in the flow and in the static systems and the product distributions are quite the same.

It is very important to outline the total absence of olefins in the acyclic hydrocarbons. Another interesting result concerning the experiments in the flow system on the powder catalyst in the very good resistance to poisoning by hydrocarbon as illustrated in fig. 1, where the selectivity $S$ (%), the sum of (BZ) + (CH), and the overall conversion $\alpha_t$% are plotted versus time at constant pressure (3.5 Torr of MCP in $H_2$ atmosphere for more than two hours). There is no change at all in the product distribution and only a very low decrease in $\alpha_t$ (%) from 8 to 6%. The constancy of the selectivity was also observed in the static experiments in agreement with the results obtained in the flow experiments. At this stage, we can first conclude that the experiments done in the flow and in the static systems are very complementary and indicate the same behaviour on the tungsten carbide powder ($W_2C + W$).

On the model tungsten carbide ($W_2C$), the product distribution is totally different as shown by the experiment of group III in table 1. Only extensive cracking reactions giving $CH_4 + C_2H_6$ are observed even at $\alpha_t = 19\%$.

The experiment of group IV in table 1 shows the classical product distribution on platinum leading almost to the hydrogenolysis of the $C_5$ ring by a non-selective mechanism as already known on small particles [12]. The main differences in selectivity on tungsten carbide catalysts compared to platinum are a very enhanced ring enlargement on the $W_2C + W$ powder catalyst and a selective extensive cracking on the $W_2C$ model catalyst.

## SURFACE RESULTS

The surface characterization of the carbide tungsten powder has been performed by X.P.S. measurements after removing the passivation layer by the procedure previously mentioned [10] and after hydrogen treatment at atmospheric pressure at 350 ° C during several hours to stabilize the surface composition The corresponding $W_{4f}$, $C_{1s}$ and $O_{1s}$ levels are given in figs. 2A, 2B, and 2C respectively. All the spectra have been decomposed assuming several contributions each of them having a Doniach-Sunjic shape [13]. With this procedure three contributions for these $W_{4f}$ states are given in fig. 2A: one for the tungsten metal (peak 1 (4f 7/2), peak 2 (4f 5/2)), one for the tungsten carbide (peak 3 (4f 7/2), peak 4 (4f 5/2)), and another for the "oxide" (peak 5 (4f 7/2), peak 6 (4f 5/2)). The last peak labelled 7 corresponds to the 5p 3/2 level of the tungsten

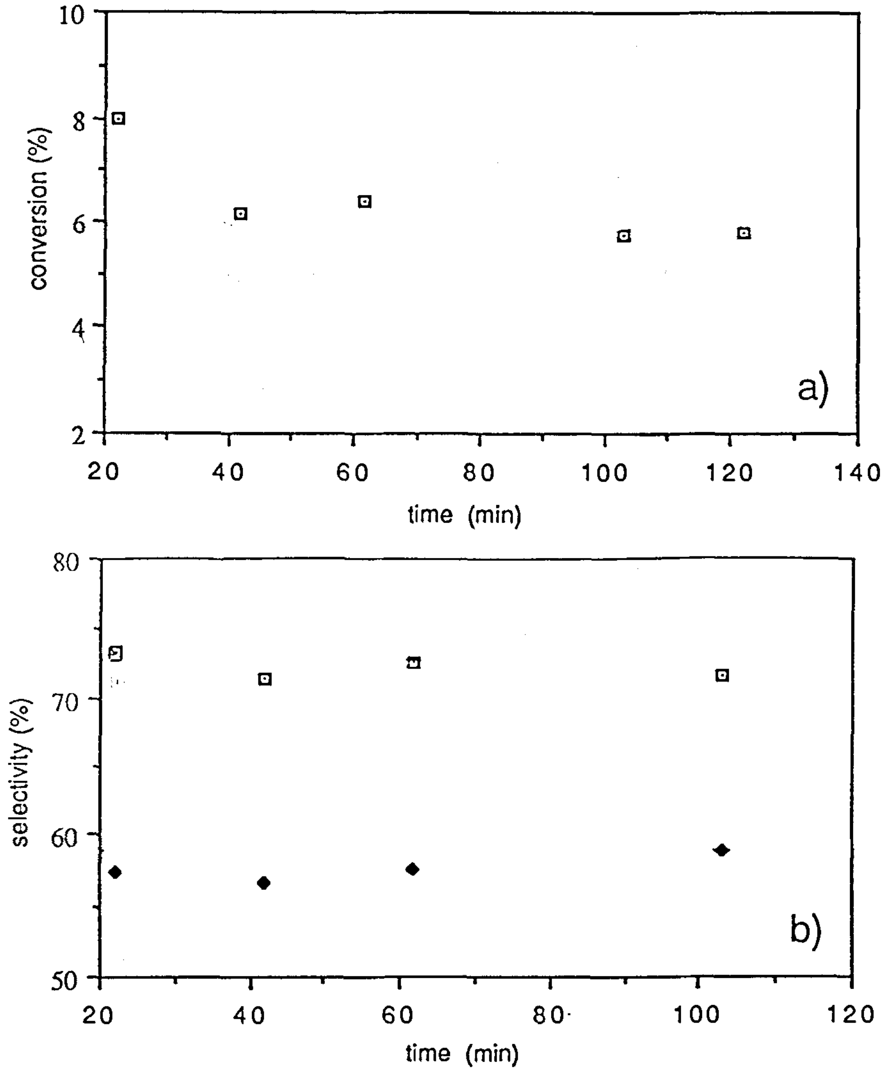


Fig. 1. a. Variation of the conversion $\alpha_t$% against time; b. Variation of the selectivity $S$% against time; benzene + cyclohexane ♦; benzene + cyclohexane + 2 methyl pentane + 3 methyl pentane + n-hexane.

metal. The 3.1 eV shift between the 4f 7/2 peak of tungsten metal and the 4f 7/2 peak of the oxide, leads us to assume that the corresponding "oxide" would have a composition close to $WO_3$ [14] The $C_{1s}$ spectrum given in fig. 2B clearly shows two contributions: one for the amorphous carbon at 284.8 eV which represents the most important part of the signal, and the second at 283.1 eV for the carbon bonded to W. The $O_{1s}$ spectrum of fig. 2C shows two contributions: the first one at 530.6 eV is the finger-print of atomic oxygen or of oxide. The

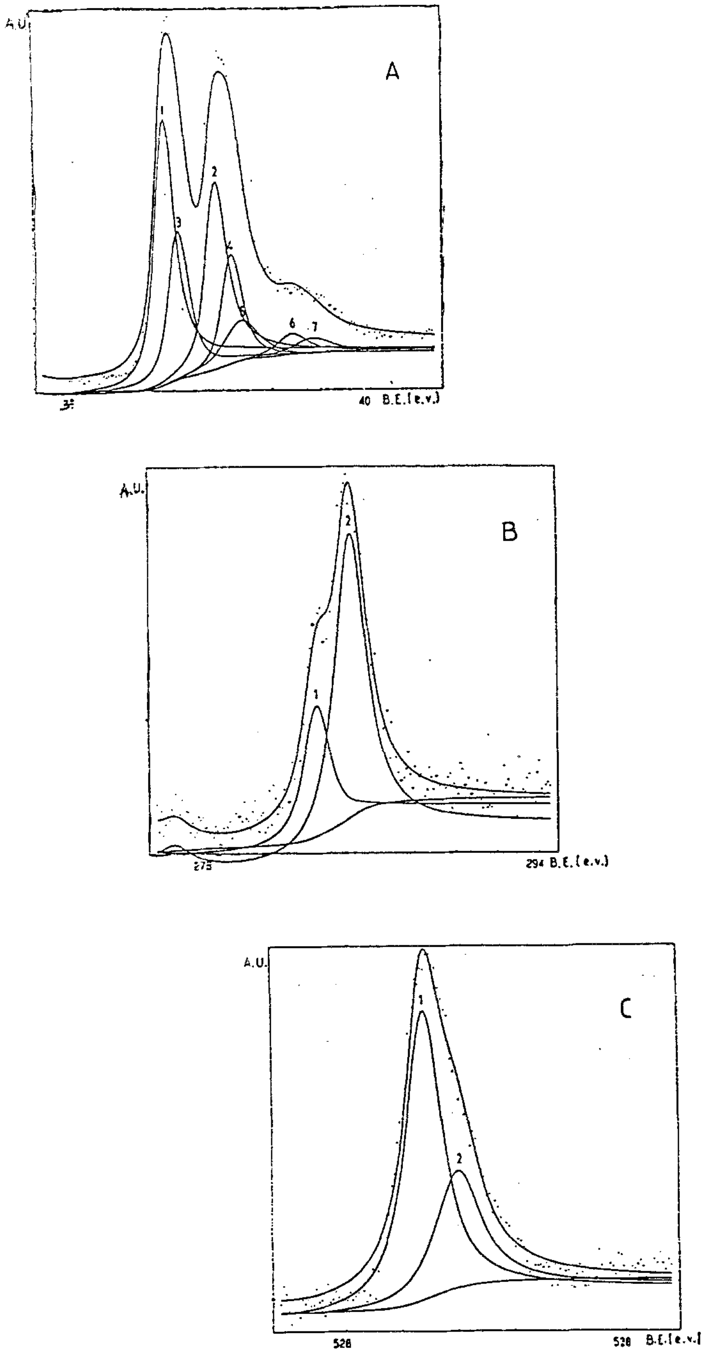


Fig. 2. X.P.S. spectra of the tungsten carbide powder ($W_2C+W$). A. W4f levels; B. C1s levels; C. O1s levels.

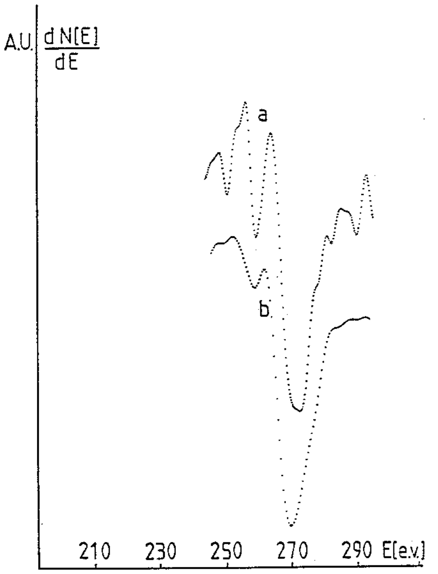


Fig. 3. Carbon Auger spectra of the model carbide $W_2C$. a. After carburization and before catalytic reaction; b. After catalytic reaction.

origin of the second peak at 531.8 eV is not completely elucidated but it could be attributed to OH radicals as already observed by A.F. Careley et al. on Zn(0001) [15].

The two main important results on the surface characterization which must be outlined at this point is first the presence of oxygen, mainly in the oxide form and the constancy of the surface composition during the catalytic experiments; no more carbon deposit has been observed. This result is in good agreement with the stability of the conversion and the selectivity observed during the catalytic flow experiments as shown in fig. 1.

Surface characterization of the model carbide has been performed by A.E.S. and the corresponding spectra are given in fig. 3. The spectrum labelled a) is the spectrum after carburization of the ribbon by ethylene decomposition ($P_{C_2H_4} \sim 5 \cdot 10^{-7}$ Torr) during 5 mn at 600 ° C and before the catalytic reaction. This spectrum is characteristic of carbon under the carbidic form [16–19]. However from this spectrum it is difficult to decide if it is WC, $W_2C$, or even the solid solution C–W, for these three compounds exhibit the same characteristic carbon Auger spectrum [16–19]. However the carbon flux due to ethylene decomposition and the total amount of carbon deposit assuming that all ethylene molecules impinging onto the surface are decomposed into carbon and hydrogen are respectively $3.7 \times 10^{14}$ carbon At/cm$^2 \times$ sec and $10^{17}$ carbon At/cm$^2$. The solubility limit of carbon into tungsten before the formation of $W_2C$ being very low, $1.5 \times 10^{-3}$ At% and the experimental temperature rather low, $T = 600$ ° C, which means low carbon diffusion rate [20], it appears reasonable to assume that this carbon given the formation of several layers of $W_2C$ at the ribbon surface.

The spectrum labelled b) in fig. 3 is the Auger spectrum after the catalytic test. The change observed in comparison with spectrum a) shows that carbon in the amorphous form has been deposited onto the surface during the catalytic reaction.

Another very important result is that no element like oxygen or sulfur have been detected on the surface of this model catalyst. The main difference between the model carbide catalyst and the tungsten carbide powder is the presence of oxygen on this last catalyst.

## 4. Discussion

No chemisorption measurements of CO, $H_2$ or $O_2$ were made in this work and this does not allow us to discuss the intrinsic activity of these carbidic or oxycarbidic catalysts in comparison with Pt, Ir, Ru. As the specific surface for the 0.2% $Pt/Al_2O_3$ reference catalyst [12] and for the $(W_2C + W)$ carbide catalyst are known, the number $N$ of MCP moles decomposed per $cm^2$ and per second are respectively: $1.6 \times 10^{-10}$ and $5.8 \times 10^{-13}$ for the platinum and the carbide catalyst. Despite a difference of two orders of magnitude, the activity of the carbide catalyst must be outlined.

The main results obtained for the reactivity of MCP on the tungsten carbides (powder catalyst $W_2C + W$ and model carbide $W_2C$ grown on a W ribbon) to be emphazised and discussed here are:

- Methylcyclopentane leads mainly to the formation of benzene plus cyclohexane by ring enlargement, hexanes (2MP, 3MP, *n*HX) plus cyclopentane by ring opening and selective demethylation, when oxygen is associated with tungsten carbides.
- On such catalyst the overall activity is not poisoned by carbon deposit as controlled by surface measurements which is different from what is observed on the model carbide catalyst $W_2C$ free of oxygen where amorphous carbon deposit builts up.
- No olefins are formed during the course of the hydrogenolysis of the cyclopentanic ring.
- Oxygen plays an important role by its contribution to the nature of the active sites and consequently on the selectivity in ring enlargement and ring opening.
- The active and selective "oxycarbidic" catalyst produced by the interaction of $W_2C$ with oxygen reveals by X.P.S. measurements the presence of metallic tungsten, carbidic tungsten, oxidic tungsten, carbidic and amorphous carbon, oxidic and probably OH radicals making the identification of the active sites very difficult.

– On the model carbide $W_2C$ without any trace of oxygen, only extensive cracking is occurring.

A careful analysis of the literature on the catalytic properties of tungsten or its combinations with oxygen or carbon indicates very extensive research in the field of skeletal rearrangement of hydrocarbons which can be classified in three categories depending on whether the emphasis is placed on the catalytic properties of the metal, of the oxides or of the carbides:

– J.M. Muller et al. [1] observed during the reaction of polymethyl substituted cyclopentanes on tungsten films, a change in the mechanisms from the extensive cracking to aromatization in xylenes attributed to the formation of "surface carbide", no activity being detected on a bulk tungsten carbide WC. M. Boudart et al. [2] verified that the catalytic activity is low on WC for neopentane isomerization, a parent reaction to the aromatization of the trimethylcyclopentane.

– G. Travert and D. Cornet [21,22] studied the skeletal isomerization of hexenes on various tungsten suboxides, and showed that the activity markedly depended upon the degree of reduction. The solid $WO_{2.98}$ obtained by reducing $WO_3$ by hydrogen at 400 ° C had low and unstable activity, while the $\beta$-oxide $WO_{2.90}$ obtained by reacting $WO_3$ with W at 900 ° C was both active and stable. Reaction rates were $0.8 \times 10^{-3}$ mole $\cdot$ $h^{-1}$ $\cdot$ $kg^{-1}$ for the isomerization of cyclohexane into methylcyclopentene at 335 ° C, and $0.7 \times 10^{-5}$ for the transformation of 1-hexene into isohexenes at 350 ° C.

– M. Molière and F. Gault [23] studied the isomerization of labelled $^{13}C$ hexanes on bulk and supported $WO_3$ catalysts treated at various temperatures in hydrogen. They concluded that the W-$WO_x$ systems are bifunctional catalysts.

Let us consider our results on the powder catalyst ($W_2C + W$) and on the model catalyst $W_2C$. It is clear that the formation of benzene plus cyclohexane and hexanes (2MP, 3MP, *n*-HX) plus cyclopentane (CP) by ring opening and demethylation is mainly linked to the presence of oxygen on the powder catalyst surface which inhibits extensive hydrogenolysis reaction appearing on the model catalyst free of oxygen, (even if the great texture difference of the surface of these catalysts can play an important role). It suggests a significant contribution of acid catalyzed mechanisms assuming olefin intermediates (methylcyclopentenes, cyclohexenes) related to carbonium ions or acidic surfaces sites [24].

But the absence of olefins in the product distribution formed by ring opening and in the hydrocarbons of lower weight due to extensive cracking suggests the presence of very active sites for hydrogenation. Recent data obtained with (MCP) in our laboratory [25] on a pure WC bulk show exactly the same catalytic behaviour at 350 ° C as for the tungsten carbide powder ($W_2C + W$) which excludes any contribution of the tungsten metal in the reaction. The results obtained on the model carbide $W_2C$, free of oxygen, suggest on the other hand an identification of the extensive cracking sites to tungsten carbide itself and the data from the literature [3–6] indicate that the tungsten carbide sites are also responsible for hydrogenation-dehydrogenation reactions, but the reactivity is decreased by polymeric carbon [26].

The last important question about the nature of the sites responsible for the MCP ring enlargement is: do we have $WO_x$ and $W_2C$ entities on the catalyst surface, $W_2C$ responsible for the hydrogenation-dehydrogenation steps, $WO_x$($x \leqslant 3$) responsible for the carbonium ion reaction, or $WO_xC_y$ oxycarbidic sites, or even "bronze like" superficial sites $H_x$ $WO_{3-y}$ [22,27–29] responsible for the whole bifunctional mechanism? We have no straight answer to this question yet, and experiments are conducted presently on $WO_x$ model catalyst.

## 5. Conclusion

In conclusion both experiments in flow and in static conditions show that the presence of oxygen on tungsten carbides inhibits the extensive hydrogenolysis in favour of ring enlargement and ring opening via a bifunctional mechanism due to the coexistence of acid-rearrangement sites and hydrogenating-dehydrogenating extensive cracking sites. The important parameter is the activation of the passivated carbides, thus these oxicarbidic materials or tungsten bronzes, are very active and selective in hydrogenation dehydrogenation, carbonium ion reactions in skeletal rearrangements of hydrocarbons. They resist surprisingly well to coke deactivation.

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