JOURNAL OF CATALYSIS **134**, 383–398 (1992)

# Compared Activities of Platinum and High Specific Surface Area $Mo_2C$ and WC Catalysts for Reforming Reactions

## I. Catalyst Activation and Stabilization: Reaction of *n*-Hexane

MARC J. LEDOUX[1], CUONG PHAM HUU, JEAN GUILLE*, AND HUGH DUNLOP†

*Laboratoire de Catalyse et Chimie des Surfaces, URA432 du CNRS, Université Louis Pasteur,*
*4 rue Blaise Pascal, 67000 Strasbourg, France;*
**Groupe des Matériaux Inorganiques, IPCMS, EHICS, 1 rue Blaise Pascal, 67000 Strasbourg, France;*
*†Centre de Recherche de Voreppe–Pechiney, BP27, 38340 Voreppe, France*

Received May 6, 1991, revised July 16, 1991

The catalytic properties of high specific surface area (>150 $m^2/g$) molybdenum and tungsten carbides are studied in hydrocarbon-reforming reactions and compared to conventional platinum supported on alumina. The isomerization of *n*-hexane is used as a test reaction. TPR and XPS analyses show that the raw materials are contaminated by oxygen and need an activation process to become reactive. These analyses also show that $Mo_2C$ is decomposed by pure hydrogen at 800°C to form methane and metallic molybdenum. Different methods of reductive activation are tested: high-temperature reduction (800°C) by hydrogen leads to metallic Mo and W on the surface (catalytically unreactive for reforming); coreduction by a mixture of pentane and hydrogen (700°C) gives active catalysts but less so than conventional platinum, probably because of the presence of carboneous residues formed by decomposition of the *n*-pentane. Trace amounts of different group VIII transition metals (≤500 ppm) can catalyze the activation process, probably by preventing the formation of the carboneous residues. $Mo_2C$ activated by 500 ppm of Pt, Ir, or Ru can reach total specific activities 6 to 7 times higher than the conventional Pt catalyst. However in terms of yield, the best carbide, activated by Ir, only doubles the performance of conventional platinum, with a high amount of cracked molecules formed in parallel. Clean surfaces of $Mo_2C$ or WC can be much more reactive than conventional Pt catalysts in terms of specific activity, isomerization, plus cracking; however, the best selectivity in isomers never exceeds 30% while selectivity on Pt is usually in the range 75 to 85%.

## INTRODUCTION

In the petroleum refining industry, catalytic reforming transforms low-octane-number naphta to higher-octane motor fuel. Two reactions are desirable: isomerization of linear to branched alkanes, and aromatization. Hydrocracking into light hydrocarbons must be avoided. The catalyst used in most of the industrial units is platinum supported on alumina (~0.2% weight), doped with different additives, ranging from chlorine to metals such as Sn, Ir, Re, with different objectives: control of acidity and dispersion, resistance to sulfur and coke, etc. The mechanisms of the different reactions occurring on these catalysts have been extensively studied; one school supports the unique role of the metal (*1*) while general agreement seems to consider a bifunctional mechanism in industrial conditions where the metal hydrogenates/dehydrogenates and the support with chlorine performs the acidic isomerization. This article does not deal with any of these mechanistic aspects even if some new ideas emerge from such a consideration, but the aim is to compare the reforming activity of high specific surface area $Mo_2C$ and WC to conventional platinum on alumina.

During the isomerization of trimethyl-1,1,3-cyclopentane on tungsten films, Muller and Gault (*2*) observed the formation of xylene after a period of activation, this formation being characteristic of Pt and Pd. The authors introduced the idea of the for-

---

[1] To whom correspondence should be addressed.

0021-9517/92 $3.00

mation of a surface carbide to explain this phenomenon. Sinfelt and Yates (*3, 4*) found that qualitatively $Mo_2C$ behaves like Ru for the hydrogenolysis of ethane. These first observations and their own experiments when comparing tungsten carbide and Pt for the isomerization of dimethyl-2,2-propane led Boudart and Levy (*5*) to conclude that heavy metal carbides could replace the precious metals in their catalytic applications. This idea was largely illustrated in a review by Leclercq (*6*) in which the catalytic performances of the carbides and nitrides for hydrogenation and oxidation reactions were compared to the performances of their parent metals; the results led Leclercq to conclude that these materials behave similarly to the group VIII transition metals.

An explanation of the reason for such behavior of the carbides is still not clear, although many sophisticated studies have been made on the electronic properties and the nature of the bonding (*7*). The very well-documented review by Oyama and Haller (*7*) presents most of the results obtained with carbides for catalysis.

Another important point investigated in the literature was the role of adsorbed atoms such as O, C, and S on the catalytic properties of the carbides surfaces. Most of the authors (*8–10*) share the idea, as shown by their different tests, that chemisorbed oxygen, surface oxides, or even intercalated oxygen atoms are poison for most of the reactions.

Finally another problem that must be seriously considered in using carbides as catalysts is the fact that these materials usually present a very low surface area (0.1 to 1 $m^2/g$), which is a serious handicap in catalytic applications. Many authors have used new synthetic routes to improve this surface area (*11–16*). Although these routes are sometimes difficult to apply industrially, some authors have obtained very satisfactory results (100–200 $m^2/g$).

The object of this article is to test, for the reforming reaction, Mo and W carbides which were obtained by a new synthetic route (*17*), derived from the same concept applied to the synthesis of high specific surface silicon carbide (*18*); here we describe a new activation procedure of these carbides (*19*) while a subsequent article (*20*) will be directly devoted to the reforming reactions.

## CATALYSTS

$Mo_2C$ and WC were prepared by reacting $MoO_3$ or $WO_2$ vapors with activated carbon (Fluka Puriss), 1150 $m^2/g$, under vacuum (*18, 19*). The low residual pressure was composed of the oxidic vapors and CO as one of the products of the reaction. The surface area of the two carbides used in this study are respectively 147 and 168 $m^2/g$. A double elemental analysis on $Mo_2C$ samples gave the stoichiometry of $Mo_2C$ and the amount of remaining unreacted carbon. The X-ray diffraction patterns of the two carbides are shown in Figs. 1 and 2. They show the very high purity of the products; only trace amounts of $W_2C$ were observed in WC. The very narrow peaks seem to contradict the high specific surface area; a theoretical calculation of the specific surface obtained from the expected particle size measured by the Scherrer equation based on the peak broadening gives 15 to 20 $m^2/g$! This phenomenon was also observed on SiC and may be explained either by the existence of a porous structure obtained by a specific arrangement of micro-single crystals forming pores and channels (this arrangement would be reminiscent of the starting activated carbon) or by an undetected disordered or highly dispersed phase.

To show the existence of a highly dispersed phase, samples were treated at very high temperature (1400°C) under vacuum for different times in order to recrystallize the dispersed phase. By using an internal crystalline standard added after each treatment, the diffraction peak intensities were used to evaluate the relative amount of the crystalline phase. It was found that the sharp crystalline peaks diminished in intensity while at the same time increased in breadth! The elemental analysis still gave the $Mo_2C$ stoichiome-

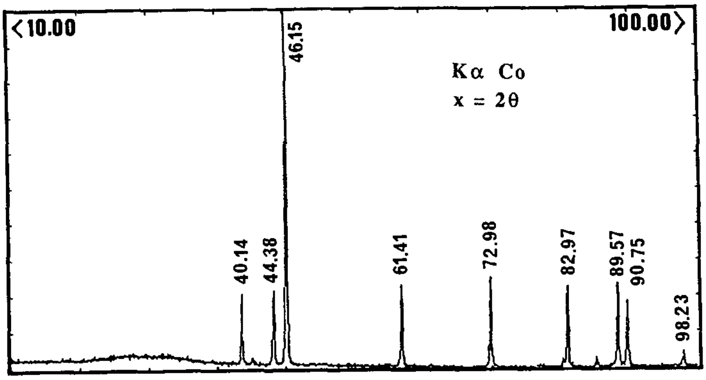

FIG. 1. X-ray diffraction patterns of pure $Mo_2C$ (147 $m^2/g$).

try. This is consistent with the formation of small $Mo_2C$ crystallites from the highly dispersed precursor invisible to XRD.

After synthesis both carbides were handled in air without precaution and were thus quickly covered by oxygen atoms, probably as metal oxides or carboxides as is revealed by the high-resolution TPR (*21*) performed on them (Figs. 3 and 4). In these figures the reduction patterns of the most common oxides $MoO_3$, $WO_2$, and $WO_3$ under pure $H_2$ are reported together with the reduction patterns of the two carbides (the water emitted was detected by TCD and the other gas by chromatography). The three oxides were reduced in the same range of temperatures, i.e., 500 to 700°C. The reduction of the two carbides showed multi-peaks of water in the same range; this indicated that oxygen was in a structure similar to that in the oxides, at least in its reducibility properties.

Three routes of activation were tested on these carbides in order to eliminate the surface oxidic layer. The three treatments carried out *in situ* before the catalytic reaction itself. The reasons for these different tests are explained in the discussion of this article. The first treatment was a simple hydrogen reduction at 800°C and normal pressure for 2 h; the second treatment consisted of adding Puriss *n*-pentane (20 Torr) to hydrogen and reacting the mixture at 700°C; and the third treatment was identical to the second but trace amounts of a group VIII transition metal were preliminarily deposited on the carbide using a water solution of a salt

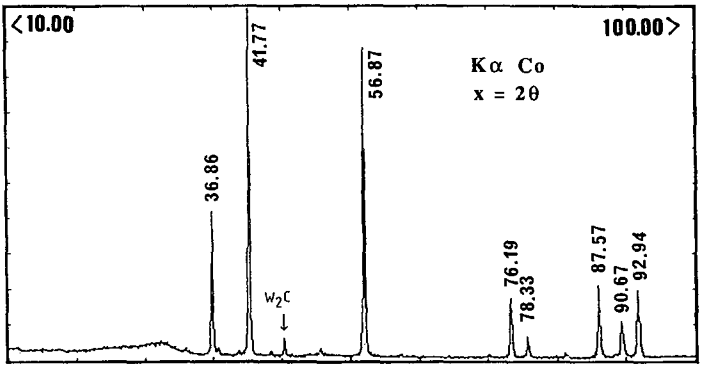

FIG. 2. X-ray diffraction patterns of pure WC (168 $m^2/g$).

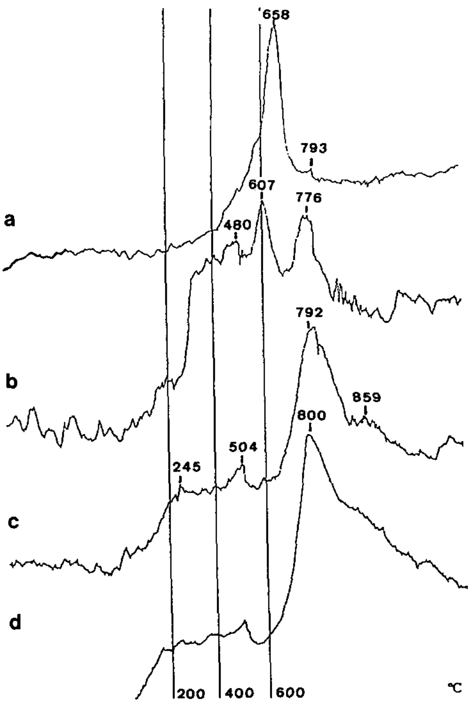

FIG. 3. TPR spectra under pure $H_2$ flow (0.5°C/s). (a) $MoO_3$. (b) $Mo_2C$ before activation. (c) $Mo_2C$ after activation (*n*-pentane + $H_2$). (d) Pt (500 ppm)/$Mo_2C$ after the same activation. The peaks are proportional to the amount of the water emitted by oxygen reduction (to the amount of $CH_4$ in c and d).

of the chosen metal. The TPR of the two carbides after the second treatment are also shown in Fig. 3 and 4. For tungsten (Fig. 4) all reducible oxygen atoms had disappeared and no other gas was detected by the TCD cell.

For molybdenum with or without traces of Pt (Fig. 3), in the absence of reducible oxygen, a peak of methane was detected at 790°C, showing that hydrogen during the TPR either reduced some surface polymeric carbon formed by the activation process or decomposed the carbide itself to form metallic molybdenum. Lee *et al.* (*28*) observed in a TPR reaction a methane peak at a slightly lower temperature range than the 790°C observed here and suggested that $Mo_2C$ was a catalyst for surface polymeric carbon hydrogenation. Ranhotra *et al.* (*10*) did a very careful study of such treatments and concluded that pure $H_2$ decomposes $Mo_2C$ to form methane and metallic Mo on the surface. This decomposition was confirmed by XPS (see below).

XPS analyses were performed on a Cameca Nanoscan 50 using the Mg*K*α band at 1253.6 eV. The C 1*s* at 284.5 eV of C–C was used for reference; the resolution in energy was 0.7 eV and the vacuum was maintained below $5.10^{-9}$ Torr. The samples were treated in the catalytic reactor, then pressed on an indium foil in a glove box under pure argon atmosphere. The transfer into the XPS preparation cell was effected under argon flow but some contamination by air could not be totally excluded during this operation. The deconvolution of the different XPS spectra were obtained using "Kernel" soft provided by Cameca (FWHM for

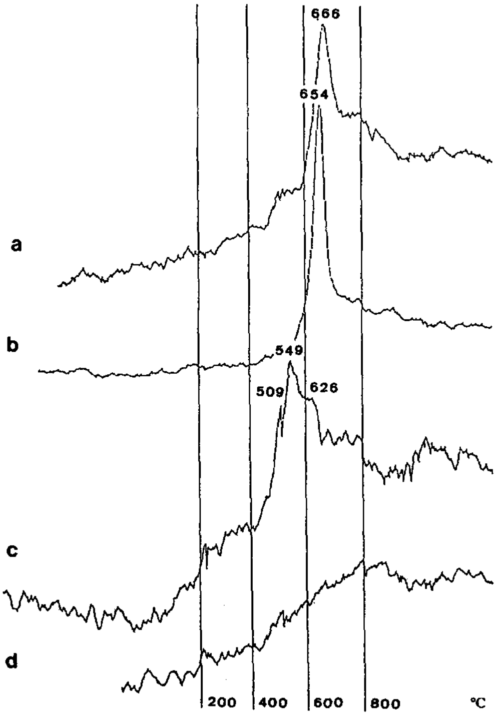

FIG. 4. TPR spectra under pure $H_2$ flow (0.5°C/s). (a) $WO_2$. (b) $WO_3$. (c) WC before activation. (d) WC after activation (pentane + $H_2$). The peaks are proportional to the amount of water emitted by oxygen reduction.

metal and carbide = 1.0 and for oxide = 1.6; ratio $3d_{5/2}/3d_{3/2}$ = 1.5 and distance $3d_{5/2} - 3d_{3/2}$ = 3.2 eV for Mo; ratio $4f_{7/2}/4f_{5/2}$ = 1.33 and distance $4f_{7/2} - 4f_{5/2}$ = 2.15 eV for W).

Figure 5 gives the high-resolution Mo spectra for five samples.

(a) $Mo_2C$ after synthesis and left under air atmosphere for 6 months: The deconvolution (see Table 1) gave 55% of surface Mo atoms engaged in $Mo_2C$ with a shift of +0.5 eV from the metallic bonding energy, which corresponds to values given in the literature (*22, 23*); 8% of surface Mo at the degree $IV^+$, $MoO_2$, or oxicarbide; and 37% of surface Mo at the degree $VI^+$, corresponding clearly to $MoO_3$ (*22, 24*). This analysis totally confirms the TPR analysis shown in Fig. 3.

(b) $Mo_2C$ after reduction under pure $H_2$ at 800°C: Trace amounts of Mo(IV) and Mo(VI) (6 and 7%), probably due to oxidation during the transfer, were detected, but the main observation was the appearance of a large amount of metallic Mo (29% of surface Mo atoms) with a binding energy (227.9 eV) corresponding exactly to the value in the literature (*22, 25*). 58% of surface Mo atoms, were engaged in $Mo_2C$, showing that most of the oxidized Mo atoms on the raw sample were only reduced to Mo metal by the reduction treatment adopted.

(c) $Mo_2C$ after reduction by a mixture pentane/$H_2$ at 700°C: Trace amounts of Mo(IV) and Mo(VI) were observed (4 and 4%) probably due to pollution and most of the Mo surface atoms (92%) appeared as $Mo_2C$ without any trace of metallic Mo.

(d) The same sample containing 500 ppm of Pt and treated as in (c): The same partition of surface Mo atoms as that on sample (c) was observed. The three spectra of samples (b), (c), and (d) are superposed in Fig. 6. The bands for sample (b), wider than those of samples (c) and (d), show without ambiguity the presence of metallic Mo on the surface of sample (b).

(e) Sample reexposed to air: A distribution of Mo in carbide and Mo(IV) and Mo(VI) almost identical to that in sample (a) was observed. Instead of 37% in (a), 25% of MoVI can easily be attributed to the fact that sample (e) was exposed to air for only a few seconds.

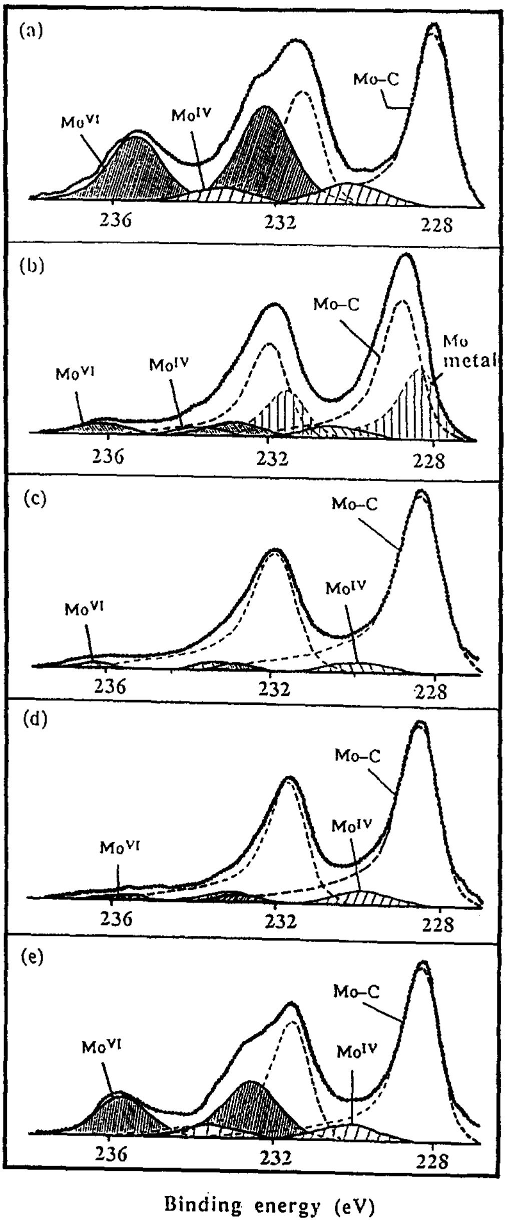

FIG. 5. XPS analysis of the different $Mo_2C$ samples (see text). The binding energies are not corrected of the charge shift.

The same study was performed on tung-

TABLE 1

Binding Energies in eV Measured from XPS for $Mo_2C$ and WC Samples (Corrected from Charge Shift Using C 1*s* at 284.5 as Reference)

| Samples | Binding energies and concentrations | | | | | | |
|---|---|---|---|---|---|---|---|
| | C 1*s* | | Mo $3d_{5/2}$ | | | | O 1*s* |
| | C–C | C–Mo | Mo metal | Mo–C | MoIV | MoVI | |
| (a) | 284.5 | 283.3 | — | 228.4 | 230.0 | 232.5 | 531.0 |
| | | | | 55% | 8% | 37% | |
| (b) | 284.5 | — | 227.9 | 228.3 | 230.0 | 232.1 | 531.0 |
| | | | 29% | 58% | 6% | 7% | |
| (c) | 284.5 | — | — | 228.1 | 229.5 | 232.1 | 530.7 |
| | | | | 92% | 4% | 4% | |
| (d) | 284.5 | — | — | 228.2 | 229.6 | 232.2 | 531.0 |
| | | | | 90% | 7% | 3% | |
| (e) | 284.5 | — | — | 228.3 | 230.2 | 232.5 | 530.9 |
| | | | | 68% | 7% | 25% | |
| Ref. (*22*) | | | 227.9 | 228.6 | 229.6 | 232.8 | |
| Ref. (*25*) | | | | 228.3 | 229.4 | 232.6 | ** |
| | C 1*s* | | W $4f_{7/2}$ | | | | O 1*s* |
| | C–C | C–W | W metal | W–C | W IV | W VI | |
| (a) | 284.5 | 282.4 | — | 31.3 | — | 35.4 | 530.8 |
| | | | | 84% | | 16% | |
| (c) | 284.5 | 282.7 | — | 31.4 | — | 34.9 | 531.3 |
| | | | | 92% | | 8% | |
| (d) | 284.5 | 282.8 | — | 31.4 | — | 34.9 | 531.5 |
| | | | | 90% | | 10% | |
| (e) | 284.5 | 282.6 | — | 31.3 | — | 35.2 | 531.2 |
| | | | | 84% | | 16% | |
| Ref. (*26*) | | 282.6 | 30.6 | 31.6 | 32.5 | 35.5 | |
| Ref. (*27*) | | 282.4 | | 31.3 | | 35.2 | |
| Ref. (*22*) | | | | 31.5 | 32.7 | 35.7 | |

*The energy scale of the instrument was calibrated using Ag $3d_{5/2}$ = 368.0 eV and Au $4f_{7/2}$ = 84.0 eV.

sten carbide (Fig. 7 and Table 1). Some differences were observed clearly when compared to the molybdenum carbide analyses. On sample (a) the only oxidized W surface atoms were $W^{(VI)}$; no $W^{(IV)}$ was ever detected. In addition 84% of surface W atoms appeared as WC, meaning that the tungsten carbide was less oxidized by air than the molybdenum carbide. In sample (b), reduction by pure $H_2$ was not studied in the case of WC. In samples (c) and (d), reduction by pentane/$H_2$ on pure or Pt-activated WC contained about 90 to 92% of W in the form of WC. The reexposure of (d) to air (sample (e)) oxidized it and features similar to those in sample (a) appeared. The binding energy for W in WC and $W^{(VI)}$ corresponds strictly to the literature data (*22, 26, 27*).

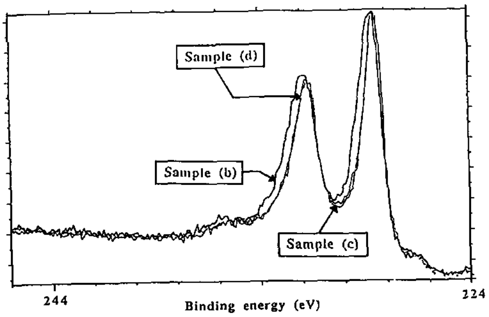

FIG. 6. Superposition of the XPS spectra of samples (b), (c), and (d) of $Mo_2c$. The binding energies are corrected from the charge shift.

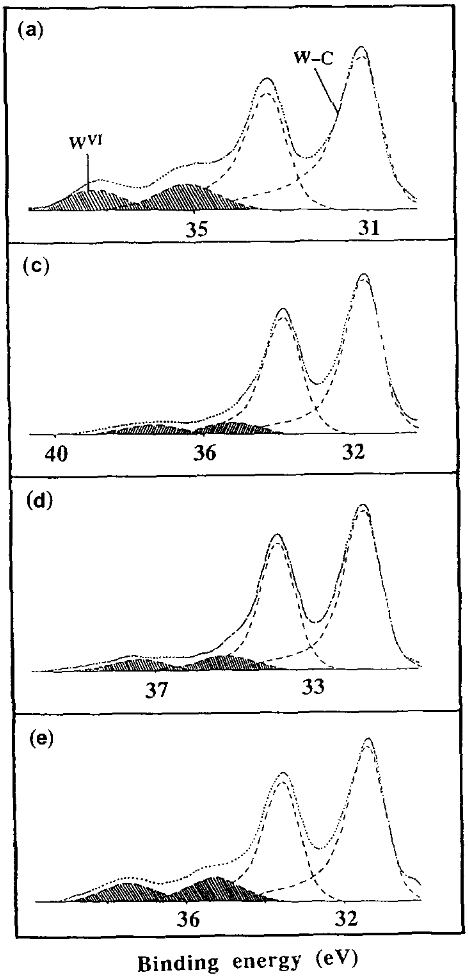

FIG. 7. XPS analysis of the different WC samples (see text). The binding energies are not corrected for the charge shift.

The C 1*s* peaks for $Mo_2C$ and WC are compared on Fig. 8. The general features of both the $Mo_2C$ and WC samples are identical. A difference exists between the two carbides: on WC the peak corresponding to the C–W bonding energy (between 282.4 and 282.8 eV) was better resolved than that on $Mo_2C$ (283.3 eV). We do not have a clear explanation for this difference. (The large amount of C–C was due to charcoal present in the samples).

X-ray diffraction and BET measurements were performed after the sequence of catalytic reactions and no significant change was observed with the same analyses made before activation and reaction.

Conventional $Pt/Al_2O_3$ catalyst containing 0.18 wt%. Pt was prepared by impregnation of a water solution of $H_2PtCl_6$ on $\gamma$-alumina (Rhône-Poulenc), 240 $m^2/g$.

### REACTION CONDITIONS

All reactions were run in the same lab test all glass microreactor. The system was equipped with greaseless valves, a flow meter, a U-shaped silica reactor, a double TCD system recording the constant pressure of reactant (provided by a saturator) before the reactor and the pressure of the products after the reaction, a system to extract the products for gas chromatography analysis, and a needle valve to regulate the gas flow. The catalyst was kept on a silica fritted disc and the reactor was working on a fixed bed, isotherm, isobar, and at low conversion to guarantee a differential behavior.

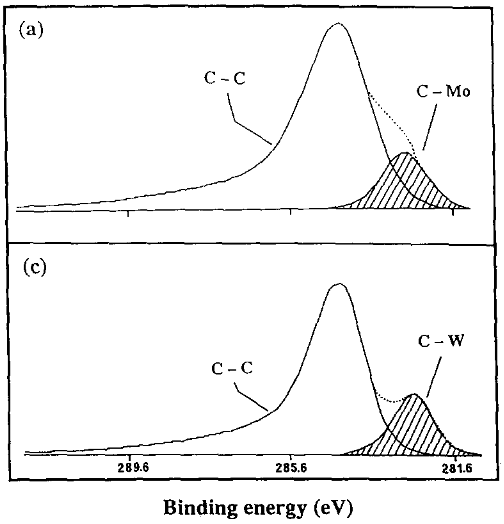

FIG. 8. C 1*s* peaks for $Mo_2C$ samples (a) and WC (c).

Five C6 molecules (Puriss Fluka) were systematically used for the test: cyclohexane (CYC), methyl-cyclopentane (MCP), methyl-2 (M2P) and methyl-3-pentane (M3P), and *n*-hexane (HEX). In order to avoid any problem of "memory" in the product distributions from desorption of molecules used previously, the pilot was systematically "cleaned" by heating the walls between 70 and 140°C under $H_2$ for $\frac{1}{2}$ h, then pumped off under vacuum for $\frac{1}{4}$ h, the catalyst being maintained at the working temperature. Obviously, in order to evaluate the performance of each catalyst in terms of yield, all the measurements were made on stabilized catalysts. This point will be discussed during the presentation of the results.

The five tested molecules were introduced at the same partial pressure, 5 Torr (with $H_2$ as complement to the atmospheric pressure), on the catalyst. Analysis of the products was performed in a gas chromatograph equipped with a 5-m long, $\frac{1}{8}$-in. column, filled with SE30 silicon on firebrick, and a FID detector, allowing the accurate analysis of C1 to C7 hydrocarbons. The conversion $\alpha$ of the reaction was calculated in percentage of C6-transformed molecules by adding the C6 isomers and the cracked molecules expressed in equivalent C6 as (C5 + C1), (C4 + C2), (2C3), (3C2), and (6C1). The rate $r$ of the reaction was measured in mole $\cdot$ g of catalyst$^{-1} \cdot s^{-1}$ assuming a first-order rate toward the hydrocarbon concentration by using the reduced equation $r = \alpha \cdot F/\omega$ because of the low conversion ($r$, rate; $\alpha$, conversion; $F$, hydrocarbon flow in mole $\cdot s^{-1}$; and $\omega$, mass of catalyst in g). We could not evaluate a turnover frequency per active site because we did not know if any chemisorbed molecule ($H_2$, CO, . . .) could

TABLE 2

Pt Catalyst Deactivation with Time

Catalyst: Pt (0.18%)/alumina
Tested molecule: *n*-Hexane

| Time (min): | 0 | 50 | 1450 | 1750 | 2350 | 4350 |
|---|---|---|---|---|---|---|
| Conversion $\alpha$ (%) | 50.66 | 38.44 | 12.42 | 6.01 | 4.11 | 0.76 |
| $r \times 10^{-10}$ mole/s · g | 3144 | 3009 | 1131 | 632 | 446 | 82 |
| $S_i$ | 79 | 81 | 84 | 79 | 79 | 79 |
| Yield $y_i$ | 2484 | 2437 | 950 | 499 | 325 | 65 |
| $\sum$ cracking | 21 | 19 | 16 | 21 | 21 | 21 |
| Selectivity of the reaction products | | | | | | |
| Isomers C6 (%) | | | | | | |
| DM-2,2B | — | — | — | — | — | — |
| M2P | 47 | 47 | 40 | 31 | 20 | 11 |
| M3P | 25 | 24 | 19 | 15 | 10 | 14 |
| HEX | — | — | — | — | — | — |
| MCP | 8 | 11 | 26 | 43 | 62 | 66 |
| BEN | 7 | 11 | 10 | 7 | 8 | 8 |
| CYC | 13 | 7 | 5 | 4 | — | 1 |
| Cracked products (%) | | | | | | |
| C5 + C1 | 46 | 42 | 40 | 33 | 29 | 32 |
| C4 + C2 | 28 | 28 | 29 | 31 | 31 | 32 |
| 2C3 | 24 | 25 | 29 | 36 | 37 | 36 |
| 3C2 | 1 | 2 | 1 | — | 2 | — |
| 6C1 | 1 | 3 | 1 | — | 1 | — |

*Note*. Reaction: *n*-Hexane, 5 Torr, 350°C, 1 atm $H_2$. Conventional treatment.

be used to titrate the site of the studied reactions. For the reaction of the cyclohexane the aim of the test was to compare the catalysts' capacities for maximum conversion into aromatic benzene; only the conversion and the selectivity in benzene were evaluated. For all the other reactions, the selectivity $S_i$ was given by the percentage of isomer molecules on the total converted molecules expressed in C6 equivalent. Thus the yield in isomerication, $y_i$, is the product of the rate $r$ by the selectivity $S_i$.

## RESULTS AND DISCUSSION

### (*1*) *Reactions of the Reference Catalyst Pt/Al$_2$O$_3$–0.18 wt%*

The catalyst was prepared as described above, then calcined in air at 400°C for 2 h. In a first experiment 68 mg of catalyst was placed in the reactor and reduced in hydrogen flow for 2 h at 400°C. The activity and selectivities were followed with time; the values are reported in Table 2. The rate $r$ is plotted versus time in Fig. 9.

Two regimes of deactivation were clearly observed in our conditions of reaction; the first regime lasted ~1750 min with a rapid deactivation from 3144 to 632 × $10^{-10}$ mole/g · s; the second regime was slower, the rate decreasing from 632 to 82 × $10^{-10}$ mole/g · s in 2600 min. The same deactivation process has already been observed by Margitfalvi *et al.* (*29*). The selectivity $S_i$ remained constant (~80%), thus the yield followed the rate. However, the selectivity inside the C6 isomers showed a clear evolution with time: the relative amount of the branched molecules, M2P and M3P, decreased with time to the advantage of the MCP while the C6 rings, BEN (benzene) and CYC, remained more or less constant. On such a Pt catalyst the main mechanism of isomerization is the cyclic mechanism discovered by Gault (*1*); if the conversion diminishes, the relative amount of MCP, the intermediate of reaction, increases.

In order to compare the activities of different catalysts, it is necessary to measure these activities on a stabilized catalyst, in other words, on catalysts that present a weak slope of deactivation. However, the weak slope on Pt catalysts was reached only after 30 h; to accelerate the process, the catalysts were treated at higher temperature (700°C instead of 350°C) and at higher partial pressure of the hydrocarbon (20 Torr instead of 5 Torr). In addition, *n*-pentane was used instead of *n*-hexane because traces of the C5 molecule were easier to eliminate than the C6 after the treatment. After 2 h of treatment the catalyst was left for 12 h at 400°C and 2 h at 600°C under pure $H_2$; the temperature was then dropped to the reaction temperature and the first C6 molecule for testing was introduced under 5 Torr of constant partial pressure.

The second advantage of such a treatment was in that it was the same treatment used to activate the carbidic catalysts. Thus the two families of catalysts, i.e., Pt and carbides, were tested under the same conditions.

Table 3 reports of the reaction of *n*-hexane

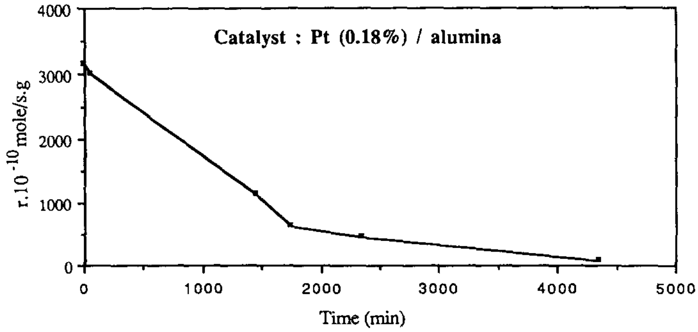

FIG. 9. Evidence for two regimes of deactivation on Pt/alumina catalyst

on the Pt catalyst after this "rapid" treatment. The activity was found well within the range of the second slope of deactivation: $r = 120 \times 10^{-10}$, $y_i = 108 \times 10^{-10}$ mole/s · g. The selectivities were, however, slightly different: $S_i$ was 90% instead of 80% and the selectivity inside the C6 isomers was identical to the fresh catalyst, i.e., large amount of M2P and M3P. The activity is probably mainly dependent on the coking of the surface while the selectivity depends also on the shape of the platinum particles, which can be modified by the thermal treatment.

TABLE 3

Pt Catalyst Activity after Treatment at 700°C and 20 Torr of *n*-Pentane in 740 Torr of $H_2$ for 2h; followed by 12h of pure $H_2$ at 400°C and 2h at 600°C.

Catalyst: Pt (0.18%)/alumina
Tested molecule: *n*-Hexane

| Time (min): | 0 | 1420 | 0 | 10 | 20 | 30 |
|---|---|---|---|---|---|---|
| Conversion $\alpha$ (%) | 2.88 | 0.45 | 27.38 | 5.43 | 4.03 | 3.34 |
| $r \times 10^{-10}$ mole/s · g | 120 | 21 | 976 | 229 | 183 | 146 |
| $S_i$ | 90 | 82 | 87 | 74 | 76 | 75 |
| Yield $y_i$ | 108 | 17 | 849 | 169 | 139 | 109 |
| $\sum$ cracking | 10 | 18 | 13 | 26 | 24 | 25 |
| Selectivity of the reaction products | | | | | | |
| Isomers C6 (%) | | | | | | |
| DM-2,2B | 0 | 0 | 3 | 0 | 0 | 0 |
| M2P | 54 | 38 | 47 | 31 | 31 | 32 |
| M3P | 38 | 52 | 33 | 22 | 24 | 25 |
| HEX | — | — | — | — | — | — |
| MCP | 8 | 10 | 12 | 37 | 36 | 35 |
| BEN | 0 | 0 | 5 | 10 | 9 | 8 |
| CYC | 0 | 0 | 0 | 0 | 0 | 0 |
| Cracked products (%) | | | | | | |
| C5 + C1 | 71 | 80 | 47 | 37 | 38 | 36 |
| C4 + C2 | 18 | 14 | 32 | 29 | 31 | 30 |
| 2C3 | 11 | 6 | 20 | 26 | 25 | 24 |
| 3C2 | 0 | 0 | 0 | 1 | 0 | 0 |
| 6C1 | 0 | 0 | 1 | 7 | 6 | 10 |

*Note*. Reaction: *n*-Hexane, 5 Torr, 350°C, 1 atm hydrogen.

In the same table, deactivation and reactivation experiments were also reported showing a relatively stable activity ($y_i$ between 108 and 169) even after a strong reactivation by pure $H_2$ at 600°C and 1 h under dynamic vacuum at 350°C. It is interesting to note that after this reactivation the two selectivities, $S_i$ and inside C6 isomers, were identical to the selectivities observed on the Pt catalyst conventionally treated by the "slow" treatment described before. For all these reasons the test effected 20 min after the reactivation was the most representative of a conventional stabilized Pt catalyst and is used as reference for comparison with carbide catalysts (Table 5).

### (2) *Reactions of Carbide Catalysts Reduced at 800°C under Pure $H_2$*

In order to clean the oxygen atoms from the surface 0.106 g of $Mo_2C$ and 0.099 g of WC were reduced directly *in situ* at 800°C for 2 h. These catalysts did not show any significant activity in the usual range of temperature 350 to 450°C. From the XPS analyses one can see that the surface of $Mo_2C$ contained an important amount of metallic

TABLE 4

*n*-Hexane Reforming Reaction on Molybdenum Metallic Powder

| Catalyst | Mo metal powder | Mo metal powder | Mo metal powder reoxidized | Mo metal powder reoxidized |
|---|---|---|---|---|
| Tested molecule | HEX | HEX | HEX | HEX |
| Temp. of reaction in °C | 350 | 450 | 350 | 450 |
| Conversion | 0.03 | 11.86 | 0.39 | 20.09 |
| $r \times 10^{-10}$ | 0.3 | 118 | 4 | 185 |
| $S_i$ | 0 | 11 | 13 | 9 |
| $y_i$ | 0 | 13 | 0.5 | 17 |
| $\sum_{\text{cracking}}$ | 100 | 89 | 87 | 91 |
| Selectivity of the reaction products | | | | |
| C6 isomers (%) | | | | |
| M2P | 0 | 3.5 | 43 | 3 |
| M3P | 0 | 5.0 | 43 | 2 |
| HEX | — | — | — | — |
| MCP | 0 | 0.4 | 0 | 0 |
| BEN | 0 | 91 | 14 | 95 |
| CYC | 0 | 0 | 0 | 0 |
| Cracking products (%) | | | | |
| C5 + C1 | 32 | 2 | 45 | 2 |
| C4 + C2 | 25 | 7 | 28 | 6 |
| 2C3 | 13 | 11 | 16 | 10 |
| 3C2 | 4 | 33 | 4 | 31 |
| 6C1 | 25 | 47 | 6 | 51 |

Mo, as also observed by Ranhotra *et al.* (*10*), because of the reduction of the quite large amount of oxidic phases and the decomposition of $Mo_2C$. The surface of WC probably contained much less metallic W because only the oxidic phases were reduced and this oxide phase was much smaller than on $Mo_2C$; no sign of methane formation was ever observed by TPR (the catalytic reforming reactions of these catalysts at 600°C are reported in a future article (*20*).

To prove that the inertness of metallic Mo toward the reforming reaction caused the lack of activity of the carbides reduced under pure hydrogen at high temperature, a series of test reactions were performed on Mo metallic powder.

The results of *n*-hexane reforming reactions on Mo metal are reported in Table 4. Half a gram of high-purity metal powder of Mo was reduced in a flow of hydrogen at 835°C for 2 h; it was checked by TPR that most of the oxidic layer was reduced above 800°C, which was consistent with the TPR of $MoO_3$ in Fig. 3. The reaction of *n*-hexane on this powder at 350°C showed that only very few molecules reacted (conversion = 0.03%), as already observed by Burch and Mitchell (*30*), to give exclusively cracked products with a typical distribution decreasing from (C5 + C1) to (3C2) together with a rather large amount of extensive cracking in (6C1), 25%.

When the temperature was increased to 450°C the extensive cracking in (3C2) and (6C1) became largely predominent. However, at this temperature, we observed some C6 isomers ($S_i$ = 11%) in which benzene amounted to 91%. This ability to crack was already reported by Nakamura *et al.* (*31*) and did not fit with the results reported by Holl *et al.* (*32*). That could be explained by an incomplete reduction of the Mo catalysts studied by Holl *et al.*, as shown when the powder was reoxidized in air at room temperature for 12 h. At 350°C the activity of the powder in terms of rate increased by a factor of 13 and, inside the cracking distribution, the (6C1) diminished strongly; the selectivity in C6 isomers became significant (13% instead of 0%). At 450°C, the rate *r* also seriously increased when compared to the rate on well-reduced powder.

### (*3*) *Reactions of Carbide Catalysts Reduced at 700°C under 20 Torr of Pentane and $H_2$*

The lack of activity when the carbides were reduced under pure $H_2$ was attributed to the presence of reduced Mo metal on the surface. To avoid this reduction, it was decided to transform the superficial oxides directly into epitaxial carbides without going through the metallic intermediate. This treatment was based on the synthesis treatment developed by Lee *et al.* (*28*), in which Mo oxide was directly transformed into Mo carbide by temperature-programmed reaction between $MoO_3$ and a mixture of $CH_4$/$H_2$.

The activation treatment with Pt/alumina catalysts is described above: 700°C, 2 h under 20 Torr of *n*-pentane and 740 Torr of $H_2$ at 50 cc/min, followed by 12 h under pure $H_2$ at 400°C and 2 h at 600°C. The temperature was then dropped to the reaction temperature and *n*-hexane (HEX) was introduced at a constant pressure of 5 Torr.

At 350°C $Mo_2C$ then had a higher total rate r than the conventional Pt/alumina–0.18% catalyst, 362 against 183 $\times 10^{-10}$ mole/s · g (see Table 5). However, because of its rather poor selectivity $S_i$, 9 against 76%, the yield in C6 isomers only attained 33 $\times 10^{-10}$ instead of 139 $\times 10^{-10}$ mole/s · g for platinum. In addition, two important differences were observed in the selectivity in products. First benzene amounted to 19% of the C6 isomers on $Mo_2C$ and only 9% of benzene was formed on the platinum catalyst, and second more extensive cracking was found on $Mo_2C$.

At the same temperature, 350°C, WC exhibited a very low activity, probably because it is a poor catalyst for carbon residues hydrogenation as shown in the TPR reaction. No $CH_4$ was ever detected below 850°C on this carbide. In order to measure its reforming activity, the reaction of HEX was made at 450°C. The rate, 314 $\times 10^{-10}$ mole/s · g, was equivalent to the rate found on $Mo_2C$ at 350°C, but as the selectivity $S_i$ was much higher (35%), the yield in C6 isomers reached 110 $\times 10^{-10}$ mole/s · g.

It was quite obvious after these tests that the adopted activation procedure was not as efficient as expected, especially when the yield was compared to the activities of conventional Pt catalysts. We thought that this lack of performance was due to carbonaceous deposit on the surface during activation with pentane, as many authors had already reported. This carbonaceous residue blocks the access of the reacting molecules to the surface.

### (*4*) *Reactions of Carbide Catalysts Activated by Trace Amounts of Platinum*

In a recent publication (*33*) Lee *et al.* proposed a new direct route for synthetizing Mo

TABLE 5

Comparison between the Different Activation Procedures and Effect on *n*-Hexane Reaction

| Catalyst: | $Mo_2C$ | $Mo_2C$ + 480 ppm Pt | WC + 560 ppm Pt | Pt/Alumina 1800 ppm (0.18%) | WC | WC + 560 ppm Pt | WC + 0.25% Pt | WC + 0.25% Ni |
|---|---|---|---|---|---|---|---|---|
| Tested molecule: | HEX | HEX | HEX | HEX | HEX | HEX | HEX | HEX |
| Temp. of reaction in °C | 350 | 350 | 350 | 350 | 450 | 450 | 400 | 400 |
| Conversion $\alpha$ (%) | 4.16 | 14.93 | 15.82 | 4.03 | 3.78 | 16.05 | 9.56 | 2.97 |
| $r \times 10^{-10}$ | 362 | 1283 | 1317 | 183 | 314 | 3510 | 759 | 199 |
| $S_i$ | 9 | 14 | 17 | 76 | 35 | 18 | 89 | 18 |
| $y_i$ | 33 | 180 | 224 | 139 | 110 | 632 | 675 | 36 |
| Σ cracking | 91 | 86 | 83 | 24 | 65 | 82 | 11 | 82 |
| Selectivity of the reaction products | | | | | | | | |
| C6 isomers (%) | | | | | | | | |
| M2P | 44 | 43 | 46 | 31 | 28 | 23 | 25 | 11 |
| M3P | 25 | 23 | 19 | 24 | 19 | 14 | 12 | 11 |
| HEX | — | — | — | — | — | — | — | — |
| MCP | 12 | 17 | 25 | 36 | 30 | 14 | 58 | 75 |
| BEN | 19 | 17 | 10 | 9 | 3 | 49 | 3 | 3 |
| CYC | 0 | 0 | 0 | 0 | 20 | 0 | 2 | 0 |
| Cracking products (%) | | | | | | | | |
| C5 + C1 | 30 | 29 | 27 | 38 | 27 | 17 | 36 | 10 |
| C4 + C2 | 36 | 32 | 25 | 31 | 31 | 24 | 29 | 8 |
| 2C3 | 24 | 26 | 22 | 25 | 21 | 21 | 29 | 5 |
| 3C2 | 5 | 7 | 6 | 0 | 9 | 13 | 3 | 2 |
| 6C1 | 5 | 6 | 20 | 6 | 12 | 25 | 3 | 75 |

carbide starting from $MoO_3$ by impregnating the oxide with 0.25% of Pt and treating the solid with a flow of methane in hydrogen. In this synthesis Pt was a catalyst for the carburation. Obviously this technique is not interesting industrially if one desires to substitute precious platinum for Mo carbide for catalytic applications, but this property of Pt gave us a new idea for activating the poorly active high specific surface carbides. It was shown above that activation by pure $H_2$ led to inactive catalysts and that activation by pentane + $H_2$ led to better catalysts but partially poisoned by carbon deposit due to the activation; *addition of trace amounts of Pt* ($\leq$ *500 ppm) could be sufficient to catalyze the carburation of the small amount of oxidic layer poisoning the surface and could give clean surfaces with far less carbonaceous residue because Pt is also a hydrogenating catalyst.*

In Table 5 the results of such activated catalysts are reported. The same gaseous and temperature treatments were applied to $Mo_2C$ and WC impregnated with 480 and 560 ppm of Pt, respectively.

The rate of reaction rose from 362 to $1283 \times 10^{-10}$ on $Mo_2C$ and from $<10$ to $1317 \times 10^{-10}$ mole/g · s at 350°C on WC; at 450°C on WC, the rate rose from 314 to $3510 \times 10^{-10}$ mole/g · s. The selectivity $S_i$ was not greatly improved from 9 to 14% on $Mo_2C$ at 350°C and even deteriorated on WC at 450°C from 35 to 18%. However, as the rate was so high (factor 4 on $Mo_2C$ and $>10$ on WC), the yield rose to 180 and $224 \times 10^{-10}$ mole/g · s, respectively, and became better than on a conventional Pt catalyst, $139 \times 10^{-10}$ mole/g · s. Figure 11 shows the improvement of the activity in function of the nature of the activating traces of group VIII metal.

One could attribute this increase in activity to the activity of the Pt traces added to the carbides. Two strong arguments will show that it was not the case.

The selectivity $S_i$ as the selectivity in the reaction products, C6 isomers and cracking distribution were strictly identical on pure $Mo_2C$ and on $Mo_2C$ + 480 ppm Pt (see Fig. 10 or on pure WC and WC + 560 ppm Pt, and were very different than the selectivities found on Pt/alumina. This was particularly true for $S_i$, which ranged between 9 and 35% depending on the temperature and the nature of the carbide (WC being always better than $Mo_2C$) and always above 75% on Pt/alumina whatever the state of deactivation.

One could imagine that Pt on carbide support could react differently than on alumina and for this reason 0.25% of Pt on WC was also tested (Table 5), and at 400°C, a temperature between the two temperatures used previously, the catalyst was typically of platinum character, $S_i$ = 89%, and a small amount of C6 rings, BEN + CYC. WC impregnated with 0.25% of Ni was tested under the same conditions, and the typical character of Ni supported on alumina was also found which was extensive cracking where 61.5% of the transformed HEX gave methane.

The second argument, which confirmed that the strong increase in activity of the carbides was not due to the addition of the platinum activity, was that we found other metals capable of activating the carbide catalysts, without changing their selectivity.

### (5) *Reactions of Carbide Catalysts Activated by Trace Amounts of Different Group VIII Transition Metals*

$Mo_2C$ was impregnated with water solutions containing the salt of the group VIII transition metal: Co nitrate, Rh and Ru chloride, Pd tetramine, Pt hexachloric acid, and Ir hexachloric acid. The catalyst was then dried at 130°C for 12 h. Activation of the catalyst proceeded in the same way as in the absence of trace amounts of metal.

The reaction of *n*-hexane on $Mo_2C$ activated by these different transition metals is reported in Table 6 and compared to pure $Mo_2C$. Three groups of activating metals were produced: Co and Rh deactivated the

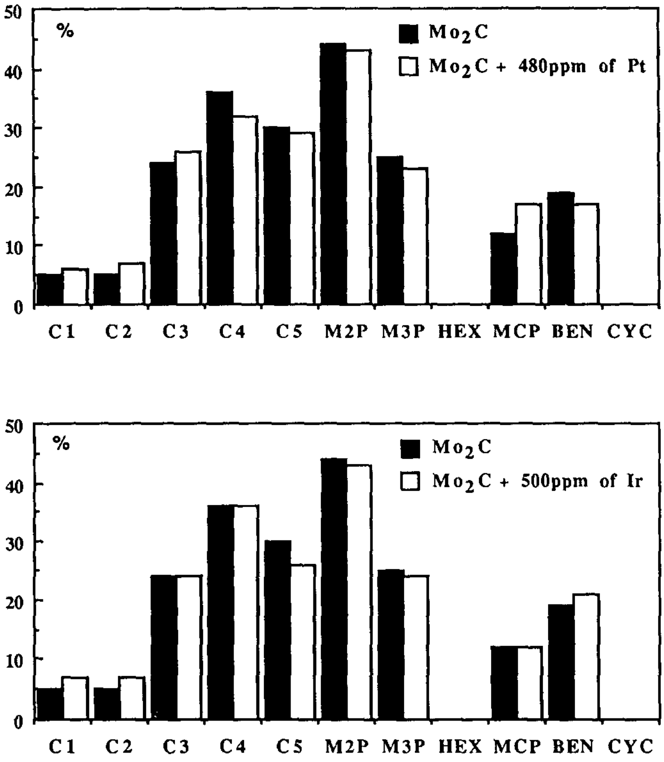

FIG. 10. Identical selectivities between $Mo_2C$ pure and $Mo_2C$ with trace amounts of Pt or Ir. (C1 = 6C1; C2 = 3C2; C3 = 2C3; C4 = C4 + C2; C5 = C5 + C1; M2P = methyl-2-pentane; M3P = methyl-3-pentane; HEX = *n*-hexane; MCP = methylcyclopentane; BEN = benzene and CYC = cyclohexane).

carbide, Pd was neutral, and Ru, Pt, and Ir were strong activating metals. The rate and the yield $y_i$ are compared in Fig. 11 with conventional Pt/alumina catalyst.

The deactivating effect of the first group can be easily explained. The distributions of the cracked molecules were found strickly identical to the distribution found on metallic Mo at 350°C (Table 4), i.e., decreasing from (C5 + C1) to (3C2) and a relatively large amount of (6C1). Co and Rh, instead of transforming the oxidic passivating layer into carbide during the hydrocarbon/hydrogen treatment, probably catalyzed the reduction to the metallic state. And as previously shown, Mo metal was a very poor catalyst for reforming reaction. Pd seemed to be neutral and did not catalyze the carbide formation or the reduction. The selectivities and the activities were identical on pure $Mo_2C$ and on $Mo_2C$ + 500 ppm of Pd.

Only Pt, as already shown, and Ir have been found, up to now, to be good catalysts for the formation of the superficial carbide. Ru exhibited an intermediate action. The hypothesis suggested by the article of Lee *et al.* (*3*), where Pt was used as catalyst for the carburization of Mo oxide, can probably be extended to Ir and Ru and explains the high effectiveness of traces of these three metals for the activation of $Mo_2C$. Ir was even better than Pt because if the total rate $r$ was $1119 \times 10^{-10}$ instead of $1283 \times 10^{-10}$ mole/g · s, the selectivity $S_i$ was doubled (28% versus 14%). In consequence, the yield in C6 isomers was also almost multiplied by two, 313 versus $180 \times 10^{-10}$ mole/g · s. In addition, as for Pt, the selectiv-

TABLE 6

Comparison between the Different "Activating" Group VIII Transition Metals and Effect on *n*-Hexane Reaction

| Catalyst | $Mo_2C$ | $Mo_2C$ + 500 ppm Co | $Mo_2C$ + 670 ppm Rh | $Mo_2C$ + 500 ppm Pd | $Mo_2C$ + 500 ppm Ru | $Mo_2C$ + 480 ppm Pt | $Mo_2C$ + 500 ppm Ir |
|---|---|---|---|---|---|---|---|
| Tested molecule | HEX | HEX | HEX | HEX | HEX | HEX | HEX |
| Conversion (%) | 4.16 | 2.07 | 0.71 | 5.02 | 14.13 | 14.93 | 30.15 |
| $r \times 10^{-10}$ | 362 | 84 | 25 | 274 | 569 | 1283 | 1119 |
| $S_i$ | 9 | 10 | 11 | 8 | 25 | 14 | 28 |
| $y_i$ | 33 | 8 | 3 | 22 | 142 | 180 | 313 |
| Σ cracking | 91 | 90 | 89 | 92 | 75 | 86 | 72 |
| Selectivity of the reaction products | | | | | | | |
| C6 isomers (%) | | | | | | | |
| M2P | 44 | 47 | 32 | 45 | 36 | 43 | 43 |
| M3P | 25 | 36 | 42 | 31 | 20 | 23 | 24 |
| HEX | — | — | — | — | — | — | — |
| MCP | 12 | 13 | 16 | 9 | 13 | 17 | 12 |
| BEN | 19 | 4 | 10 | 9 | 31 | 17 | 21 |
| CYC | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cracking products (%) | | | | | | | |
| C5 + C1 | 30 | 36 | 25 | 23 | 27 | 29 | 26 |
| C4 + C2 | 36 | 25 | 25 | 40 | 32 | 32 | 36 |
| 2C3 | 24 | 16 | 21 | 30 | 20 | 26 | 24 |
| 3C2 | 5 | 2 | 7 | 4 | 9 | 7 | 7 |
| 6C1 | 5 | 22 | 22 | 3 | 12 | 6 | 7 |

ities of $Mo_2C$ activated by Ir were strictly identical to the selectivities of pure $Mo_2C$ (Fig. 10), confirming that the extra activity was not due to the addition of the Ir particular activity, although it was difficult in the case of Ir to distinguish its activity from the $Mo_2C$ activity, because, taken individually, their selectivities are very similar (*34*).

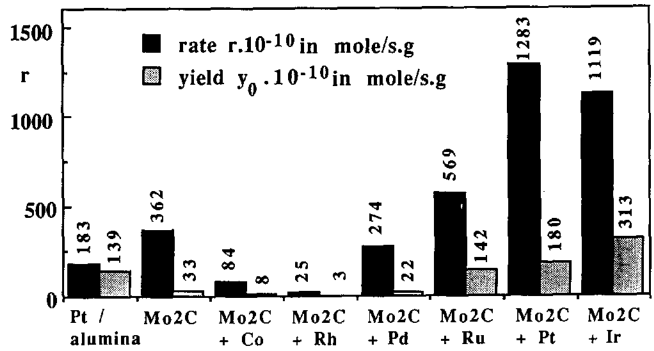

FIG. 11. Rate and yield of the reforming reactions of n-hexane on Mo carbide activated by different group VIII transition metals.

## CONCLUSION

High specific surface Mo and W carbides can be unreactive for reforming reactions when polluted by uncontrolled oxygen.

A strong reduction by hydrogen only leads to metallic Mo or W on the surface. Clean surfaces of Mo are not reactive for reforming.

Coreduction by a flow of mixed hydrocarbon and hydrogen needs the presence of trace amounts of Pt, Ir, or Ru ($\leq$ 500 ppm) to avoid the formation of carbonaceous poisoning residues. The process probably leads to the transformation of the surface oxidic species into carbidic species. Pd is ineffective while Co and Rh lead to the formation of Mo metal on the surface.

Clean activated carbide surfaces are more reactive than Pt catalysts for reforming reactions (isomerization and cracking) in terms of specific activity but the selectivities in isomers are always below 50% while these selectivities can reach 80% on Pt.

New ways of activation to increase the selectivity will be published later.

## ACKNOWLEDGMENTS

This research was supported by a contract with Pechiney. We thank all the people of this company who have helped us.

## REFERENCES

1. Gault, F. G., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.) Vol. 30, p. 1. Academic Press, San Diego, 1981.
2. Muller, J. M., and Gault, F. G., *Bull. Soc. Chim. France* **2,** 416 (1970).
3. Sinfelt, J. H., and Yates, D. C. J., *Nature Phys. Sci.* **229,** 27 (1971).
4. Sinfelt, J. H., and Yates, D. C. J., *J. Catal.* **8,** 82 (1967).
5. Boudart, M., and Levy, R., *Science* **181,** 547 (1973).
6. Leclercq, L., "Surface Properties and Catalysis by Non-metals" (J. P. Bonnelle, B. Delmon, and E. Derouane, Eds.) p. 433. NATO ASI Series, 1983.
7. Oyama, S. T., and Haller, G. L., "Catalysis," Vol. 5, p. 333, Specialist Periodical Reports. The Chemical Society, London, 1982.
8. Ko, E. I., and Madix, R. J., *J. Phys. Chem* **85,** 4919 (1981).
9. Kojima, I., Miyazaki, E., Inoue, Y., and Yasomori, I., *J. Catal.,* **59,** 472 (1979).
10. Ranhotra, G. S., Bell, A. T., and Reimer, J. A., *J. Catal.* **108,** 40 (1987).
11. Svatá, M., and Zabransky, Z., *Collect, Czech. Chem. Commun.* **39,** 1015 (1974).
12. Ross, P. N., and Stonehart, P., *J. Catal.* **48,** 42 (1977).
13. Mazulevskii, E. A., Palanker, V. S., Baibatyrov, E. N., Khisametdinov, A. M., and Domanovskaya, E. I., *Kinet. Katal.* **18,** 767 (1977).
14. Fornwalt, D. E., Felten, E. J., and Stonehart, P., *Micron* **6,** 147 (1975).
15. Imura, K., Yoshida, S., Barbee, T., and Boudart, M., "Preparation of Catalyst II," Vol. 3, p. 627. Elsevier, Amsterdam, New York, 1979.
16. Volpe, L., and Boudart, M., *J. Solid State Chem.* **59,** 348 (1985).
17. Ledoux, M. J., Pham Huu, C., Marin, S., and Guille, J., Eur. Pat. 89-04433.
18. Ledoux, M. J., Hantzer, S., Pham Huu, C., Desaneaux, M. P., and Guille, J., *J. Catal.* **114,** 176 (1988).
19. Ledoux, M. J., Pham Huu, C., Marin, S., Guille, J., and Weibel, M., *C.R. Acad. Sci. Ser. II,* 707 (1990).
20. Ledoux, M. J., Pham Huu, C., and Guille, J., to appear.
21. Ledoux, M. J., Hantzer, S., and Guille, J., *Bull. Soc. Chim. Belges* **96,** 855 (1987).
22. Briggs, D., and Seah, M. P., "Practical Surface Analysis," 2nd ed., Vol. 1. Wiley, New York, 1990.
23. Moshier, W. C., Davis, G. D., and Cote, G. O., *J. Electrochem. Soc.* **136,** 356 (1989).
24. Olefjord, I., Brox, B., and Jelvestam, U., *J. Electrochem. Soc.* **132,** 2854 (1985).
25. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E., "Handbook of X-Ray Photoelectron Spectroscopy." Perkin–Elmer, Eden Prairie, MN, 1979.
26. Ramqvist, L., Hamrin, K., Johansson, G., Fahlman, A., and Nordling, C., *J. Phys. Chem. Solid* **30,** 1835 (1969).
27. Nakazawa, M., and Okamoto, H., *Appl. Surf. Sci* **24,** 75 (1985).
28. Lee, J. S., Oyama, S. T., and Boudart, M., *J. Catal.* **106,** 125 (1987).
29. Margitfalvi, J., Göbölös, S., Talas, E., Hegedös, M., and Szedlacsek, P., *in* "Catalyst Deactivation 1987" B. Delmon and G. F. Froment Eds., p. 147. Elsevier Amsterdam, 1987.

*30.* Burch, R., and Mitchell, P. C. H., *J. Less Common Met.* **54,** 363 (1977).

*31.* Nakamura, R., Poich, D., Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **93,** 338 (1985).

*32.* Holl, Y., Garin, F., Maire, G., Muller, A., Engelhard, P. A., and Grosmangin, J., *J. Catal.* **104,** 225 1987).

*33.* Lee, J. S., Volpe, L., Ribeiro, F. H., and Boudart, M., *J. Catal.* **112,** 44 (1988).

*34.* Weisang, F., and Gault, F. G., *J. Chem. Soc. Chem. Commun.*, 519 (1979).