

## Catalytic Properties of Transition Metal Carbides

### II. Activity of Bulk Mixed Carbides of Molybdenum and Tungsten in Hydrocarbon Conversion

L. LECLERCQ, M. PROVOST,\* H. PASTOR,† AND G. LECLERCQ

*Laboratoire de Catalyse Hétérogène et Homogène, UA CNRS No. 402, Université des Sciences et Techniques de Lille Flandres-Artois, 59655 Villeneuve d'Ascq Cédex, France; \*Laboratoire de Catalyse Organique, Université de Poitiers, France; and †Ugicarb Morgon, B.P. 65X, 38041 Grenoble, France*

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The dehydrogenation of cyclohexane and the hydrogenolysis of butane were studied on bulk tungsten-molybdenum mixed carbides as a function of their composition. Some analogies with noble metals have been confirmed for selectivity in hydrogenolysis. Tungsten carbide gives only single hydrogenolysis like platinum, while molybdenum carbide leads to multiple hydrogenolysis like ruthenium. When the activities in cyclohexane dehydrogenation and butane hydrogenolysis are plotted versus the relative surface composition  $\text{Mo}/(\text{Mo} + \text{W})$ , curves with a minimum are obtained. This change of the activities of the mixed carbide catalysts correlates with the molybdenum surface enrichment deduced from XPS results. © 1989 Academic Press, Inc.

#### INTRODUCTION

Since the early work of Gaziev *et al.* (1) on the activity of transition metal carbides in cyclohexane dehydrogenation, most catalytic studies have shown striking analogies between carbide activities and those of Group VIII metals like Pt and Ru towards such reactions as the isomerization and the hydrogenolysis of 1,1,3-trimethylcyclopentane (2), the hydrogenolysis of ethane (3), and the isomerization of neopentane (4). The carbides exhibited activities and selectivities that were much higher than those of the parent metals (3-5). The presence of interstitial carbon (6) favorably changes the catalytic properties of these metals by alloying them to a nonmetal element, leading to binary alloys.

In the first paper of this series (7), some bulk mixed W,Mo carbides have been synthesized and their structures have been studied in order to have well characterized reference compounds which could be compared with supported carbides. These latter are less easily characterized, but having higher specific surface areas are potentially

more interesting for catalysis. Among other results, it has been shown that during the preparation of the mixed carbides, molybdenum surface enrichment occurs. We have tried, using some assumptions, to estimate the surface compositions of these samples (7). In the present paper are reported the catalytic properties of these bulk carbides for two simple test reactions, namely the dehydrogenation of cyclohexane and the hydrogenolysis of butane, both of which are known to occur typically on metals.

The catalytic dehydrogenation of cyclohexane to benzene is important in the reforming process which uses predominantly multimetallic systems for the purpose of improved stability, activity, and selectivity, as demonstrated for Group VIII metals (8). As the dehydrogenation of cyclohexane is known to be a structure-insensitive reaction on noble metals (9, 10) and consequently to be less affected by intermediate bonding changes induced by alloying, we have added a reaction more suitable as test reaction for these new catalytic materials, i.e., the hydrogenolysis of butane. This re-

action is very sensitive to the surface composition and has already shown a synergy effect for bimetallic systems (11). Thus, by a complementary study (7) we have correlated the catalytic activities of these two reactions with their surface composition as determined by XPS.

#### EXPERIMENTAL

##### *Dehydrogenation of Cyclohexane*

The reaction was carried out in a flow reactor at atmospheric pressure at temperatures between 300 and 350°C. The experimental device and the kinetic measurement procedures have been described previously (11, 17, 20). The cyclohexane flow rate was  $1.85 \times 10^{-2}$  mol h<sup>-1</sup> ( $P_C = 0.1$  atm,  $P_H = 0.9$  atm) and the reaction products were analyzed by gas chromatography (column Reoplex 400, 2 m  $\times$   $\frac{1}{8}$  in.). The major product was benzene but trace amounts of products of hydrogenolysis were detected.

##### *Hydrogenolysis of Butane*

The same experimental conditions were used for the study of butane hydrogenolysis except for the analysis of the reaction products (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>10</sub>) which was performed on a column of Spherosil XOB 075 impregnated with 10 wt% squalane (2 m  $\times$   $\frac{1}{8}$  in.). The reaction temperature was between 340 and 380°C.

The activation energies were determined by experiments at varying temperatures (between 300 and 350°C for the dehydrogenation of cyclohexane and 340 and 380°C for the hydrogenolysis of butane) on the same sample of catalyst according to the procedure explained in detail in Ref. (20). The rates at varying temperatures were extrapolated to time zero in order to measure the rate on the "clean" original catalyst. Each energy of activation has been determined from at least five rate measurements at different temperatures. Under these conditions the accuracy of the activation energies is about 10%.

##### *Catalysts*

The catalysts are described in Part I (7).

#### RESULTS AND DISCUSSION

##### *Dehydrogenation of Cyclohexane*

*Activation treatments.* After the preparation and before transfer of the samples in air, the catalysts were passivated at room temperature in a flow of 2% O<sub>2</sub> in N<sub>2</sub> in order to avoid undue reoxidation, as indicated in Part I (7). Since passivation consists in a superficial oxidation, an activation treatment reducing the surface oxide is necessary before performing catalytic tests.

Sample B<sub>1</sub> was selected to study the influence of the activation treatment under flowing hydrogen (5 liters/h) on the catalytic activity for cyclohexane dehydrogenation and to check the reproducibility of the measurements. The rates of cyclohexane dehydrogenation determined at 300°C and the apparent activation energies are reported in Table 1. The mixed carbide sample B<sub>1</sub> exhibits a low dehydrogenation activity after an activation treatment in flowing hydrogen for 12 h at 300°C. In the same way as in Ref. (12), a tenfold activity increase is observed when the activation temperature is raised to 400°C. Then the rate values remain within the same range of magnitude whatever the temperature and the time of pretreatment. The apparent activation energies becomes consequently constant and markedly lower than after the pretreatment at 300°C.

These observations corroborate the XPS results reported in Part I (7). Hydrogen pretreatment at 400 or 500°C is necessary to reduce the oxygen of the passivated layers. A treatment in hydrogen is more efficient than a thermal treatment under vacuum since Kojima *et al.* (13) reported that a thermal treatment at 1100°C *in vacuo*, resulting in the desorption of poisoning oxygen, was necessary to activate WC catalysts.

Let us mention here the high apparent energy of activation of 50 kcal mol<sup>-1</sup> observed after a pretreatment of 12 h at 300°C

TABLE I

Influence of the Activation Treatment on the Activity on a Sample of W,Mo Mixed Carbides (B<sub>1</sub>) in Cyclohexane Dehydrogenation

Sample weight (g)	Cyclohexane flow rate (mol h <sup>-1</sup> )	Temp. (°C) pretreatment	Time (h)	$r_D^a$ reaction rate ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )	Activation energy (kcal mol <sup>-1</sup> )
1.108	0.0185	300	12	5	50
1.108	0.0185	400	7	40	35
3.120	0.0347	400	7	41	34
3.120	0.0185	400	7	39	34
3.120	0.0185	500	12	50	35
3.2995	0.0185	400	7	48	33
3.2995	0.0185	500	20	58	33

<sup>a</sup> Experimental conditions of reaction:  $T = 300^\circ\text{C}$ ,  $P_H/P_C = 9$ ,  $P_T = 1 \text{ atm}$ .

compared to the value of 33–35 kcal mol<sup>-1</sup> after reduction at higher temperatures. Such a high energy of activation could be related to an insufficient reduction of the passivated layer at 300°C. When the reaction temperature is increased the degree of reduction increases, leading to higher catalyst activity. The presence of hydrocarbon could help the catalyst reduction. Such a better reducing effect of hydrocarbons than of hydrogen has already often been observed. This would result in a higher energy of activation than that on a well reduced surface. Such a high energy of activation could also be characteristic of a carbide surface which is partly oxidized.

In the following, all catalyst samples were activated in flowing hydrogen for 7 h at 400°C.

*Monometallic carbides.* The activities of the monometallic carbides, expressed per gram of catalyst ( $r_D$ ) and per square meter ( $r'_D$ ), together with the energies of activation, are reported in Table 2. In this table the stoichiometry of the samples and the amount of free carbon are recalled from Part I (7). Some results from Ref. (12) concerning chemical mixtures of WC and W<sub>2</sub>C prepared by carburization with mixtures of CO/CO<sub>2</sub> have also been included.

Since tungsten and molybdenum carbides have in some cases been compared to noble

metals, and particularly to platinum, some results obtained on Pt/SiO<sub>2</sub> and on Pt/Al<sub>2</sub>O<sub>3</sub> are reported from Refs. (14) and (15). The results of Table 2 first indicate clearly that the catalyst CC 1b-2 with a high content of free carbon exhibits very low activity (expressed per square meter) and high energy of activation as expected compared to other samples with lower contents of free carbon. This confirms that for the high area solids of the CC series prepared by carburization at lower temperature (method 2, Ref. (7)), the total surface area is mainly composed of carbon.

If, as emphasized in the following, the value of  $30 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  is assumed to be the characteristic rate of cyclohexane dehydrogenation on a "clean" stoichiometric WC, then the active specific surface area of sample CC 1b-2 would be 0.16 m<sup>2</sup> g<sup>-1</sup>. This indicates the extent of the surface pollution with free carbon. For the samples with higher loadings of free carbon, the high energies of activation are probably related to a better cleaning of the surface at higher temperatures.

Let us now consider the catalysts with low carbon contents. Only three samples (CWF-2, L-643-1, and L-643-2) from different sources lead to identical specific dehydrogenation rates (about  $30 \times 10^{15} \text{ mole s}^{-1} \text{ m}^{-2}$ ) and apparent energies of activation (20

TABLE 2  
 Activity of Monometallic Carbides in Cyclohexane Dehydrogenation

Sample designation (Ref. (7))	$C^a$ W or Mo	$C_F^b$ W or Mo	$S$ ( $m^2 g^{-1}$ )	$r_D^c$ ( $\mu mol h^{-1} g^{-1}$ )	$r_D'$ ( $10^{15} molec s^{-1} m^{-2}$ )	$E$ ( $kcal mol^{-1}$ )
WC						
CWF 2	0.992	0.005	1.3	230	29.6	20
L.643.1	0.990	0.005	1.4	250	29.9	20
L.643.2	0.992	0.016	2.4	410	28.6	19
L.643.3 (Wimet)	0.935	0.016	2.8	880	52.5	17
CC 1b-2 (Wimet)	0.997	0.284	12.1	27	0.4	43
F (Battelle)	0.981	0.023	2.8	160	9.5	25
Wh-WC-100 <sup>d</sup>	1.00	—	28	330	2.0	29
Wh-W <sub>2</sub> C-wc <sup>d</sup>	0.50	—	33	180	0.9	34
Wh-WC-55 <sup>d</sup>	0.69	—	30	400	2.2	27
Wh-WC-14 <sup>d</sup>	0.54	—	32	1880	9.8	26
Mo <sub>2</sub> C						
E <sub>1</sub>	0.496	0.027	0.4	110	46	23
Pt						
Pt/SiO <sub>2</sub> <sup>e,g</sup> (2.86 wt% Pt)	—	—	—	—	5500	—
Pt/Al <sub>2</sub> O <sub>3</sub> <sup>f,g</sup> (2 wt% Pt)	—	—	—	—	4900	—

<sup>a</sup> Metal-carbon stoichiometry of carbides.

<sup>b</sup> Number of free carbon atoms over the total number of metal atoms.

<sup>c</sup> Reaction rate determined at  $T = 300^\circ C$ ,  $P_H/P_C = 9$ ,  $P_T = 1 atm$ .

<sup>d</sup> From Ref. (12).

<sup>e</sup> From Ref. (14).

<sup>f</sup> From Ref. (15).

<sup>g</sup> Experimental conditions of reaction:  $T = 270^\circ C$ ,  $P_C = 0.023 atm$ ,  $P_H = 0.0997 atm$ .

$kcal mol^{-1}$ ). These three samples are WC with a stoichiometry C/W very close to 1; hence this activity seems to be characteristic of a carbon-free surface of stoichiometric WC and the "active" surface area of a tungsten carbide with a stoichiometry WC could be estimated knowing the rate of dehydrogenation of cyclohexane. On the other hand, sample L-643-3 with lower C/W ratio (0.935) exhibits a significantly higher activity and has a slightly lower energy of activation ( $17 kcal mol^{-1}$ ). Hence a decrease in the stoichiometry of tungsten carbide seems to be beneficial to its activity in the dehydrogenation of cyclohexane. Such a result has already been obtained by Kharlamov *et al.* (16) for the hydrogenation of propene on  $TiC_x$  catalysts with carbon deficiency. The activity and the energy of

activation measured with sample F (Battelle) seem, at first glance, to contradict these observations. However, one can tentatively rationalize all these results. This sample contains only a slightly higher amount of free carbon than samples L-643-2 and L-642-3, but this excess of carbon could be at the surface, explaining the decreased activity and the increased energy of activation counteracting the slight carbon deficiency effect.

A more extended study of the influence of the stoichiometry of tungsten carbide is not easy, since when substoichiometric carbides are prepared, it seems practically impossible to avoid excess free carbon. However, the results in Table 2 recalled from Ref. (12) can help us. Unfortunately these tungsten carbides seem to have surfaces

loaded with free carbon, since the activity of Wh-WC-100 with a stoichiometry C/W of 1 is very low ( $2 \times 10^{15} \text{ mol s}^{-1} \text{ m}^{-2}$ ) compared to "clean" WC. The "free" carbide surface area of Wh-WC-100 should be of the order of  $2 \text{ m}^2 \text{ g}^{-1}$ . The other tungsten carbides of this series having similar total surface areas (about  $30 \text{ m}^2 \text{ g}^{-1}$ ) have probably a "free" carbide surface area of the same order of magnitude as Wh-WC-100. Hence the changes in activity in cyclohexane dehydrogenation are probably mainly a consequence of changes in the carbide stoichiometry as assumed in Ref. (12).

This illustrates that the use of a catalytic reaction as a chemical probe of the active surface could be very helpful.

The activity of  $\text{Mo}_2\text{C}$  with low free carbon content is not very different from those of tungsten carbides.

*Mixed W, Mo carbides.* A first series of model catalysts ( $A_1$ ,  $B_1$ ,  $C_1$ ,  $D_1$ ) well defined and with low free carbon contents has been prepared by a metallurgical method as reported in Part I (7). X-ray diffraction patterns have shown that the hexagonal crystal structure of WC is retained and that W has progressively been substituted by Mo. XPS experiments have revealed molybdenum surface enrichment (7).

The activities of these catalysts and the energies of activation in the dehydrogenation of cyclohexane are reported in Table 3, where their main physicochemical characteristics are recalled. Results with catalyst  $E_1$  ( $\text{Mo}_2\text{C}$ ) and L.643.1 (WC) have been included in this table for comparison.

A striking feature is that the apparent energies of activation in cyclohexane dehydrogenation are significantly higher (from 10 to  $20 \text{ kcal mol}^{-1}$  higher) for mixed carbides than for pure tungsten carbides. This points out an important qualitative modification of the catalytic sites. This increase does not seem to be due to carbon contamination because of their low free carbon content, except maybe for sample  $B_1$  which exhibits a somewhat higher free carbon content than the others. The fact that for  $B_1$  the energy of activation is significantly higher than that of the other mixed carbides arises probably from some partial carbon poisoning. Hence its activity could be somewhat underestimated.

The activities of mixed carbides are affected by the composition of the carbides. The changes of these activities versus the ratio  $\text{Mo}/(\text{Mo} + \text{W})$  of the surface composition as calculated in Part I (7) are in Fig. 1, where it can be seen that the rate first de-

TABLE 3  
Characteristics and Activities of Mixed W and Mo Carbides in Cyclohexane Dehydrogenation  
( $P_{\text{H}} = 0.9 \text{ atm}$ ,  $P_{\text{C}_6\text{H}_{12}} = 0.1 \text{ atm}$ ,  $T = 300^\circ\text{C}$ )

Catalyst designation (Ref. (7))	Mo Mo + W (%)		C <sup>c</sup> Mo + W	C <sub>F</sub> <sup>d</sup> Mo + W	S ( $\text{m}^2 \text{ g}^{-1}$ )	$r_{\text{D}}$ ( $\mu\text{mol h}^{-1} \text{ g}^{-1}$ )	$r'_{\text{D}}$ ( $10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$ )	E ( $\text{kcal mol}^{-1}$ )	
	Bulk	Surface <sup>a</sup>							Composition <sup>b</sup>
WC									
L.643.1 (W,Mo)C	0	0	0	0.992	0.005	1.3	250	30.0	20
$A_1$	5.7	7.5	19	0.997	0.002	1.5	100	11.2	35
$B_1$	17.9	23.5	58	0.988	0.028	1.2	40	5.5	40
$C_1$	25.1	34.7	94	0.990	0.013	1.7	510	50.1	30
$D_1$	26.4	33.0	74	0.996	0.001	0.4	63	26.4	32
$\text{Mo}_2\text{C}_{1-x}$									
$E_1$	100	100	100	0.496	0.027	0.4	110	46.0	23

<sup>a</sup> Surface composition obtained from XPS experiments using the ratios of corrected intensities.

<sup>b</sup> From XPS, surface composition calculated according to Ref. (33).

<sup>c</sup> Stoichiometry of the mixed carbides.

<sup>d</sup> Free carbon content.

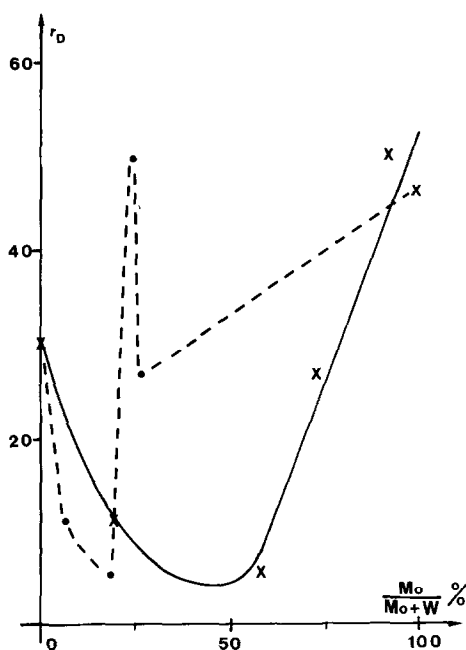


FIG. 1. Rates of cyclohexane dehydrogenation ( $10^{15}$  molec  $s^{-1} m^{-2}$ ,  $300^{\circ}C$ ,  $P_H/P_C = 9$ ,  $P_T = 1$  atm) as a function of the bulk Mo/(Mo + W)% (●) and as a function of surface composition for molybdenum and tungsten from XPS (7) (X).

increases when the relative Mo percentage increases, goes through a minimum for a ratio Mo/(Mo + W) of about 0.4, and then increases up to molybdenum carbide. These results of activity in the dehydrogenation of cyclohexane corroborate the calculation of the surface composition since for sample C<sub>1</sub> with a bulk Mo/(Mo + W) ratio of only 25%, but with a surface Mo/(Mo + W) of 94%, the activity is about the same as that of pure molybdenum carbide. This confirms the molybdenum surface enrichment of mixed W<sub>1</sub>Mo carbides and underlines the importance of catalytic test chemical reactions in the characterization of catalyst surfaces.

The crystallographic structure of the carbides does not seem to have any influence on their catalytic activity in cyclohexane dehydrogenation since Mo<sub>2</sub>C (close-packed hexagonal) and C<sub>1</sub> (simple hexagonal) with

approximately the same surface composition have the same activity for this reason.

#### Hydrogenolysis and Isomerization of *n*-Butane

The reactions of butane in the presence of hydrogen are simple hydrogenolysis to propane (C<sub>3</sub>) and methane (C<sub>1</sub>) or to ethane (C<sub>2</sub>), successive demethylations (multiple hydrogenolysis) to 4C<sub>1</sub> or to C<sub>2</sub> + 2C<sub>1</sub>, and isomerization to isobutane (*i*-C<sub>4</sub>). The formalism used to characterize activities and selectivities is explained in detail in Ref. (20).

The rates of transformation of *n*-butane into products will be referred to as  $r_{C_1}$ ,  $r_{C_2}$ ,  $r_{C_3}$ ,  $r_{i-C_4}$ . Several selectivity ratios are used (Table 5):

$\alpha = 3r_{C_1}/r_{C_3}$  is a measure of the extent of multiple hydrogenolysis; when  $\alpha = 1$  only single hydrogenolysis occurs; when  $\alpha > 1$ , multiple hydrogenolysis occurs.

$\beta = (r_{C_1} + r_{C_2})/r_{C_2}$  characterizes the cleavage of terminal bonds of butane compared to the internal bond.  $\beta = 2$  means an equal probability of bond cleavage.

$\gamma = r_H/r_{i-C_4}$ ;  $r_H$  is the global rate of hydrogenolysis.

*Monometallic carbides.* The reaction rates of *n*-butane hydrogenolysis and isomerization are reported in Table 4 where they can be compared with the cyclohexane dehydrogenation rates ( $r_D$ ) calculated at  $350^{\circ}C$  from Arrhenius plots. For all samples of tungsten carbide, whatever their stoichiometry and their free carbon content, the ratio of the rates of dehydrogenation of cyclohexane and of hydrogenolysis of butane is of the same order of magnitude (between 15 and 22). This ratio is quite different on Mo<sub>2</sub>C (about 30) and it indicates that hydrogenolysis is less favored on molybdenum carbide than on tungsten carbides. The activities of tungsten and molybdenum carbides ranging between 6 and  $10 \times 10^{15}$  molec  $s^{-1} m^{-2}$  at  $350^{\circ}C$  are much lower than those obtained for Pt (11). Betizeau *et al.* (11b) reported a rate of butane hydrogenolysis

TABLE 4  
Activity of Monometallic Carbides in *n*-Butane Hydrogenolysis and Isomerization

Sample	Reaction rates <sup>a</sup> ( $\mu\text{mol h}^{-1} \text{g}^{-1}$ )							
	$r_{C_1}$	$r_{C_2}$	$r_{C_3}$	$r_{C_4}$	$r_H$	$r_T$	$r_D^b$	$\frac{r_D}{r_T}$
WC								
CWF-2	8.7	23.5	22.5	8.2	54.7	62.9	933	15
L.643.1	5.5	22	16	4.7	43.5	48.2	1014	21
L.643.2	12.5	38	38	6.2	88.5	94.7	1550	16
L.643.3 (Wimet)	17.5	61	56.5	40	135	175	2893	16
F (Battelle)	4.5	19	12	6.8	35.5	42.3	921	22
Mo <sub>2</sub> C								
E <sub>1</sub>	3.5	5.3	7.2	1.4	16	17.4	550	31

<sup>a</sup> Experimental conditions of *n*-butane conversion:  $T = 350^\circ\text{C}$ ,  $P_H/P_C = 9$ ,  $P_T = 1$  atm.

<sup>b</sup> Calculated rate of cyclohexane dehydrogenation at  $350^\circ\text{C}$  from Arrhenius plot.

lysis on Pt/Al<sub>2</sub>O<sub>3</sub> (2 wt% Pt,  $D_{Pt} = 0.53$  (11a)) of  $0.046 \times 10^{-4} \text{ mol h}^{-1} \text{ m}^{-2}$  ( $7.7 \times 10^{14} \text{ molec s}^{-1} \text{ m}^{-2}$ ) at  $240^\circ\text{C}$ ,  $P_H = 0.9$  atm,  $P_{C_4H_{10}} = 0.1$  atm, which using  $E = 34 \text{ kcal mol}^{-1}$  makes  $270 \cdot 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  at  $350^\circ\text{C}$ . In other experiments we obtained rates of butane hydrogenolysis of  $240 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  on Pt/Al<sub>2</sub>O<sub>3</sub> (2 wt% Pt assuming 100% Pt dispersion) (17) at  $330^\circ\text{C}$  ( $600 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  at  $350^\circ\text{C}$  with  $E = 36 \text{ kcal mol}^{-1}$ ) and  $30 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  at  $300^\circ\text{C}$  on Pt/SiO<sub>2</sub> ( $D_{Pt} = 0.59$ ) (14) which makes  $200 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$  at  $350^\circ\text{C}$ .

Hence on various Pt samples the rates of butane hydrogenolysis are between 200 and  $600 \times 10^{15} \text{ molec s}^{-1} \text{ m}^{-2}$ , taking into account the uncertainties in the rate measurements and in the determination of energies of activation.

Concerning the selectivities, it is clear that tungsten carbide catalysts whatever their sources and preparation methods lead to "single" hydrogenolysis ( $\alpha$  close to 1 in Table 5). On the contrary molybdenum carbide induces some multiple hydrogenolysis ( $\alpha = 1.5$ ).

TABLE 5  
Selectivity of Monometallic Carbides in *n*-Butane Hydrogenolysis and Isomerization ( $T = 350^\circ\text{C}$ ,  $P_H/P_C = 9$ ,  $P_T = 1$  atm)

Sample	$\alpha = \frac{3r_{C_1}}{r_{C_3}}$	$\beta = \frac{r_{C_1} + r_{C_3}}{r_{C_2}}$	$\gamma = \frac{r_H}{r_{C_4}}$	$\frac{r_D}{r_{C_1} + r_{C_3}}$	$\frac{r_D}{r_{C_2}}$
WC					
CWF.2	1.1	1.25	7	30	40
L.643.1	1.0	1.0	9	47	46
L.643.2	1.0	1.25	14	31	41
L.643.3	1.0	1.25	3	39	47
F (Battelle)	1.1	0.83	5	56	49
CC-1b-2	1.4	0.66	2	—	—
Mo <sub>2</sub> C					
E <sub>1</sub>	1.5	2.0	11.4	52	104

TABLE 6

Selectivity of Platinum in the Bond Splitting of *n*-Butane as a Function of Reaction Temperature (from Ref. (17)) ( $P_H/P_C = 9$ ,  $P_T = 1$  atm)

$T$ (°C)	245	264	278	288	299	312	321.5	330.5
$\beta = \frac{r_{C_1} + r_{C_3}}{r_{C_2}}$	3.40	2.80	2.10	1.83	1.62	1.20	1.18	1.12

The selectivity  $\alpha$  of tungsten carbide confirms the analogies between platinum, which is well known for leading to only "single hydrogenolysis" (Pt and Pd being the only two Group VIII metals in this category) (17–23), and tungsten carbide, as already mentioned by Levy and Boudart (4), while molybdenum carbide resembles more the second group of metals, such as ruthenium (or Ni, Co, . . .), as observed by Sinfelt and Yates, (3) for the hydrogenolysis of ethane.

Considering now the selectivity  $\beta$  in the splitting of the two C–C bonds in butane, it is clear that the ratio  $\beta$  is not very different for all tungsten carbides and it is close to 1 taking into account the uncertainty due to the occurrence of secondary hydrogenolysis of the primary products of reaction. Here again the analogy with Pt is obvious when, these results are compared with those in Table 6 (from Ref. (17)). At 350°C, molybdenum carbide (sample E<sub>1</sub>) gives a statistical splitting ( $\beta = 2$ ) with equal probability for each bond breaking.

Hence tungsten and molybdenum carbides are nonselective toward C<sub>I</sub>–C<sub>II</sub> and C<sub>II</sub>–C<sub>II</sub> bonds (C<sub>I</sub> and C<sub>II</sub> are respectively for primary and secondary carbon atoms) like Pt (21, 24) and Ru (25, 26), while other group VIII metals such as Ni and Co lead to selective demethylations (21, 27–29) or such as Rh and Ir which split preferably C<sub>II</sub>–C<sub>II</sub> bonds. Of course one must be cautious when comparing unsupported carbides and noble metals since some parameters other than the intrinsic properties of

the metals could have an influence on the selectivities. For platinum (Table 7) the selectivity factor  $\beta$  is enhanced on a highly dispersed platinum catalyst on silica like Eurocat ( $D_{Pt} = 100\%$ ) and to a larger extent on activated carbon support where carbon poisoning is involved. This last effect is also included in the increase of  $\beta$  for molybdenum oxycarbide, molybdenum carbide (Mo<sub>2</sub>C-1) prepared by methane decomposition in hydrogen which gives uncontrollable free carbon deposit. Interestingly, for the sample WC-AEG (carbon deficient, C/W ~ 0.6), with a structure close to W<sub>2</sub>C as shown by the proximity of the shape parameters of the carbon KLL Auger transition of this sample to those of W<sub>2</sub>C (30), the selectivity factor  $\beta$  is between WC and Mo<sub>2</sub>C values, indicating a different array of surface metal atoms involved in reaction intermediates.

The variations of selectivity between hydrogenolysis and isomerization (Table 5) are more difficult to interpret but it is also the case for metals like platinum ( $6 < \gamma < 34$ ) where metal–support interaction plays an important role. Under our experimental conditions, tungsten carbide and molybdenum carbide with low free carbon contents favor hydrogenolysis against isomerization, the rate of hydrogenolysis being about 10 times higher than that of isomerization. However, when nonstoichiometry (as for sample L643-3 and WC-AEG) or excess of polymeric carbon occur (Mo<sub>2</sub>C-1, Table 7, and CC-1b-2, Table 5) the selectivity  $\gamma$  strongly decreases.



TABLE 7  
Comparison of Selectivity of Supported Platinum Catalysts and Bulk Monometallic Carbides for *n*-Butane Hydrogenolysis and Isomerization ( $T = 300^\circ\text{C}$ ,  $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm)

Sample	Temperature of reduction ( $^\circ\text{C}$ )	$\alpha$	$\beta$	$\gamma$
6.3% Pt/SiO <sub>2</sub> (Eurocat.)	500	1.1	2.5	5.6
2% Pt/Al <sub>2</sub> O <sub>3</sub> (CBL <sub>1</sub> ) <sup>a</sup>	300	1.2	1	40.2
2% Pt/Al <sub>2</sub> O <sub>3</sub> (CBL <sub>1</sub> ) <sup>a</sup> calcined at 1040°C	300	1	1.3	8.9
10% Pt/C <sup>a</sup>	300	0.9	7.3	33.7
WC				
L.643.2 <sup>b</sup>	400	1.0	1.25	10.4
WC-AEG (Telefunken) <sup>b</sup>	300	1.0	1.55	0.28
MoO <sub>x</sub> C <sub>y</sub> <sup>d</sup>				
Before carburization	350	4.4	5.6	1
After carburization	350	3.5	2.6	15.3
Mo <sub>2</sub> C				
Mo <sub>2</sub> C-1 <sup>d</sup>	350	3.3	5.3	3.4
E <sub>1</sub> <sup>b</sup>	400	1.4	2.1	17.9

<sup>a</sup> From Ref. (34).

<sup>b</sup> This study.

<sup>c</sup> From Ref. (5a).

<sup>d</sup> From Ref. (5b).

*Mixed W, Mo carbides (Tables 8 and 9).* When cyclohexane dehydrogenation and butane hydrogenolysis are compared (Table 8) the three samples B<sub>1</sub>, C<sub>1</sub>, D<sub>1</sub> with a large molybdenum surface enrichment as seen by

XPS, behave differently from WC and Mo<sub>2</sub>C (ratios  $r_{\text{D}}/r_{\text{H}} \sim 40$ ); sample A<sub>1</sub> resembles closely WC. Thus on these catalysts, dehydrogenation is favored against hydrogenolysis to a larger extent than for mono-

TABLE 8  
Activity of Mixed W,Mo Carbides in Reactions of Butane and Hydrogen ( $T = 350^\circ\text{C}$ ,  $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm)

Sample	Reaction rates ( $10^{15}$ molec s <sup>-1</sup> m <sup>-2</sup> )							$\frac{r_{\text{D}}}{r_{\text{T}}}$
	$r_{\text{C}_1}$	$r_{\text{C}_2}$	$r_{\text{C}_3}$	$r_{\text{C}_4}$	$r_{\text{H}}$	$r_{\text{T}}$	$r_{\text{D}}^a$	
WC								
L.643.1	0.66	2.64	1.92	0.56	6.56	7.1	122	17
(W,Mo)C								
A <sub>1</sub>	1.1	2.25	2.7	0.7	6.05	6.75	130	19
B <sub>1</sub>	0.33	0.73	0.82	0.32	1.92	2.24	91	40
C <sub>1</sub>	1.4	3.6	4.0	1.2	8.9	10.1	410	40
D <sub>1</sub>	0.9	1.8	2.05	1.0	4.6	5.6	247	44
Mo <sub>2</sub> C								
E <sub>1</sub>	1.5	2.2	3.0	0.6	6.7	7.3	230	31

<sup>a</sup> Rate of cyclohexane dehydrogenation ( $T = 350^\circ\text{C}$ ,  $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm).

TABLE 9

Selectivity of Mixed W,Mo Carbides in *n*-Butane Hydrogenolysis and Isomerization ( $T = 350^\circ\text{C}$ ,  $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm)

Sample	$\alpha$	$\beta$	$\gamma$	$\frac{r_{\text{D}}}{r_{\text{C}_1} + r_{\text{C}_3}}$	$\frac{r_{\text{D}}}{r_{\text{C}_2}}$
WC					
L.643.1	1.0	1.0	9.0	47	46
(W,Mo)C					
A <sub>1</sub>	1.25	1.7	9.0	34	58
B <sub>1</sub>	1.21	1.6	5.8	79	125
C <sub>1</sub>	1.02	1.5	6.8	76	112
D <sub>1</sub>	1.28	1.7	4.7	84	141
Mo <sub>2</sub> C					
E <sub>1</sub>	1.5	2.0	11.4	52	104

metallic carbides; this property has been applied for supported mixed carbides as reforming catalysts and will be the subject of further papers. Qualitatively the changes of the rate of butane hydrogenolysis are similar to those of cyclohexane dehydrogenation (Table 8). However, Fig. 2 shows that unlike what was observed for cyclohexane

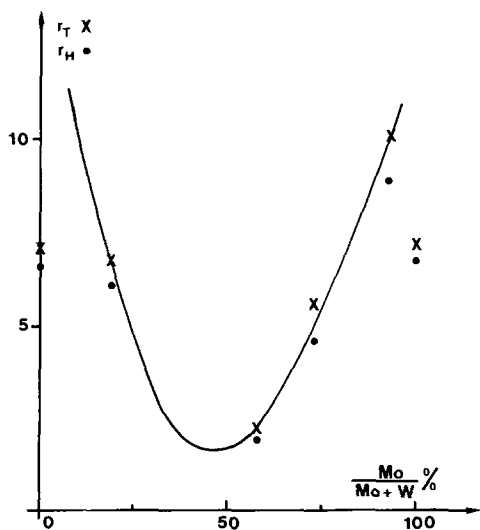


FIG. 2. Rates of *n*-butane conversion ( $10^{15}$  molec  $\text{s}^{-1}$   $\text{m}^{-2}$ ,  $350^\circ\text{C}$ ,  $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm) as a function of surface composition for molybdenum and tungsten from XPS (7).  $r_{\text{H}}$ , rate of butane hydrogenolysis;  $r_{\text{i}}$ , rate of butane isomerization;  $r_{\text{T}} = r_{\text{H}} + r_{\text{i}}$ .

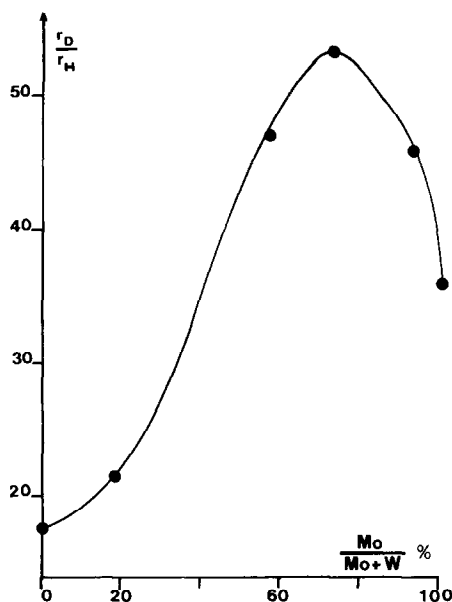


FIG. 3. Ratios of the rates of cyclohexane dehydrogenation and *n*-butane hydrogenolysis ( $r_{\text{D}}/R_{\text{H}}$ ) determined at  $350^\circ\text{C}$  ( $P_{\text{H}}/P_{\text{C}} = 9$ ,  $P_{\text{T}} = 1$  atm) versus surface composition of molybdenum and tungsten by XPS (7).

dehydrogenation, only the points relative to mixed carbides lie on the same curve; monometallic carbides have activities lower than those obtained by extrapolation of the curve relative to mixed carbides. This phenomenon is probably related to the well-known demanding character of hydrogenolysis (31) or to its structure sensitivity (32). Moreover, we have compared cyclohexane dehydrogenation and butane hydrogenolysis at the same temperature ( $350^\circ\text{C}$ ) and same partial pressures. By plotting the ratio of the rates of these reactions against the surface composition determined by XPS according to Ref. (33), a curve with a maximum is obtained for an optimal composition of 73 at.% of molybdenum (Fig. 3). From this result, we can forecast that the selectivity in the reforming of saturated hydrocarbons toward high octane number products from dehydrogenation reactions will be higher on mixed carbides than on monometallic ones. Indeed this has been verified and results will be published later.

Concerning the selectivity factors in butane hydrogenolysis except for  $A_1$ , mixed W,Mo carbides exhibit their own values, which means that  $\alpha$ ,  $\beta$ ,  $\gamma$  are characteristic of an intrinsic property of mixed active sites different from those of monometallic carbides as evidenced in Table 9. Mixed W,Mo carbides lead to more multiple hydrogenolysis than W carbides and slightly favor the rupture of terminal C-C bonds. They all exhibit roughly the same selectivities (the low value of  $\alpha$  observed for  $C_1$  is probably erroneous).

#### CONCLUSIONS

After an activation treatment in hydrogen at 400 or 500°C, following their passivation after preparation, bulk W and Mo carbides are active in model reactions such as cyclohexane dehydrogenation and butane hydrogenolysis which typically take place on Group VIII metals. However, their specific activities are two to three orders of magnitude lower than those of platinum, taken as an example of Group VIII metals.

Surprisingly, the selectivities of W carbides in the hydrogenolysis of butane are similar to those observed on Pt catalysts, which gives another example of analogy between tungsten and molybdenum carbides and noble metals already mentioned by other authors (3, 4).

Several parameters influence the activities of carbides: their stoichiometry (C/Metal), their free carbon content, and the relative composition in molybdenum and tungsten for mixed carbides. A slight defect of carbon in tungsten carbides seems to be beneficial. On the contrary, mixed W,Mo carbides are less active than monometallic W or Mo carbides for the two test reactions studied here. However, they favor dehydrogenation (a desired reaction in the reforming of naphthas) by comparison to hydrogenolysis as indicated by the increase of the ratios  $r_D/r_H$  (Table 9).

For these mixed bulk carbides, a substantial molybdenum surface enrichment suggested by XPS studies (7) has been con-

firmed using the dehydrogenation of cyclohexane as a chemical probe.

#### REFERENCES

1. Gaziev, G. A., Samsonov, G. V., Kylon, O. V., Roginsky, S. Z., Forika, E. A., and Yanovskii, I. F., *Dokl. Akad. Nauk. SSSR* **140**, 863 (1961).
2. Muller, J. M., and Gault, F. G., *Bull. Soc. Chim. Fr.* **2**, 416 (1970).
3. Sinfelt, J. H., and Yates, D. J. C., *Nature (London) Phys. Sci.* **229**, 27 (1971).
4. Levy, R. B., and Boudart, M., *Science* **181**, 547 (1973).
5. (a) Leclercq, L., Imura, K., Yoshida, S., Barbee, T., and Boudart, M., in "Preparation of Catalysts II," Stud. Surf. Sci. Catal., Vol. 3, p. 627. Elsevier, Amsterdam, 1979; (b) Boudart, M., Oyama, S. T., and Leclercq, L., in "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 578. Elsevier, Amsterdam, 1981.
6. Toth, L. E., "Transition Metal Carbides and Nitrides," p. 8, Academic Press, New York, 1971.
7. Leclercq, L., Provost, M., Pastor, H., Grimblot, J., Hardy, A. M., Gengembre, L., and Leclercq, G., *J. Catal.* **117**, 371 (1989).
8. (a) Sinfelt, J. H., *J. Catal.* **29**, 308 (1973); (b) Sinfelt, J. H., in "Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 1, p. 257. Springer-Verlag, Berlin, 1981.
9. Sinfelt, J. H., *Catal. Rev. Sci. Eng.* **9**, 147 (1974).
10. Marecot, P., Thesis, University of Poitiers, 1985.
11. (a) Bolivar, C., Charcosset, H., Frety, R., Primet, M., Tournayan, L., Betizeau, C., Leclercq, G., and Maurel, R., *J. Catal.* **45**, 163 (1976); (b) Betizeau, C., Leclercq, G., Maurel, R., Bolivar, C., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **45**, 179 (1976).
12. Vidick, B., Lemaitre, J., and Leclercq, L., *J. Catal.* **99**, 439 (1986).
13. Kojima, I., Miyazaki, E., Inoue, Y., and Yasumori, I., *J. Catal.* **59**, 472 (1979).
14. Leclercq, G., Romero, T., Pietrzyk, S., Grimblot, J., and Leclercq, L., *J. Mol. Catal.* **25**, 67 (1984).
15. Leclercq, G., Charcosset, H., Maurel, R., Betizeau, C., Bolivar, C., Frety, R., Jaunay, D., Mendez, H., and Tournayan, L., *Bull. Soc. Chim. Belg.* **88**, 7-8 (1979).
16. Kharlamov, A. I., Krivitskii, V. P., and Lemershko, N. D., *React. Kinet. Catal. Lett.* **17**, 63 (1981).
17. Leclercq, G., Leclercq, L., and Maurel, R., *Bull. Soc. Chim. Fr.* **11**, 2329 (1974).
18. Sinfelt, J. H., *Catal. Rev.* **3**, 157 (1970); *Adv. Catal.* **23**, 91 (1973).
19. Anderson, J. R., *Adv. Catal.* **23**, 1 (1973).
20. Maurel, R., and Leclercq, G., *Bull. Soc. Chim. Fr.* 1234 (1971).

21. Matsumoto, H., Saito, Y., and Yoneda, Y., *J. Catal.* **19**, 101 (1970); *J. Catal.* **22**, 182 (1971).
22. Ponec, V., *Adv. Catal.* **32**, 149 (1983).
23. Van Broekhoven, E. H., and Ponec, V., *Prog. Surf. Sci.* **19**, 351 (1985).
24. Leclercq, G., Leclercq, L., and Maurel, R., *J. Catal.* **44**, 68 (1976); *J. Catal.* **50**, 87 (1977).
25. Machiels, C. J., and Anderson, R. B., *J. Catal.* **58**, 253, 260, 268 (1979).
26. Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem. Process. Res. Dev.* **9**, 116; **11**, 141 (1972).
27. Kikuchi, E., and Morita, Y., *J. Catal.* **15**, 217 (1969).
28. Kochloeff, K., and Bazant, B., *J. Catal.* **10**, 140 (1968).
29. Leclercq, G., Pietrzyk, S., Peyrovi, M., and Karroua, M., *J. Catal.* **99**, 1 (1986).
30. Boudart, M., Lee, J. S., Imura, K., and Yoshida, S., *J. Catal.* **103**, 30 (1987).
31. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).
32. Boudart, M., "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 1. The Chemical Society, London, 1977.
33. van Langeveld, A. D., and Ponec, V., *Appl. Surf. Sci.* **16**, 405 (1983).
34. Leclercq, L., Thesis, University of Poitiers, 1976.