Hydrogen Effect on Hydrocarbon Reactions over Bulk Tungsten Carbide

Yiping Zhuang[1] and Albert Frennet[2]

Catalyse Hétérogène, Université Libre de Bruxelles, CP243 Campus Plaine ULB, 1050 Brussels, Belgium

The reactions of five hydrocarbon molecules (*n*-hexane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, and methylcyclopentane) were studied as a function of hydrogen pressure ranging from 60 to 680 Torr over bulk tungsten carbide prepared by direct carburisation of WO_3 in a 20% CH_4/H_2 flow. The sample was activated in H_2 at 1073 K for 5 h before the reactions. No significant deactivation was observed during reactions. Olefins represent an important group of the products. Increasing hydrogen pressure leads to a decrease of isomerisation rate in *n*-hexane, 3-methylpentane, and 2,2-dimethylbutane reactions, while a maximum rate was observed in 2,3-dimethylbutane reactions. Irrespective of the hydrogen pressure, the isomerisation rate is always larger than the rate of methylcyclopentane ring opening. The formation rate of the products resulting from single hydrogenolysis exhibits a maximum on increasing hydrogen pressure; the deethylation rate is faster than the demethylation and depropylation rates by a factor of 3 to 10 at the hydrogen pressure corresponding to the maximum rate. The exposure of the catalyst to oxygen leads to a fast decrease of the hydrogenolysis rate and a high selectivity to the isomerisation products in *n*-hexane reactions. The results confirm that the hydrogenolysis takes place on a tungsten carbide phase and the isomerisation on a tungsten oxycarbide or a tungsten oxide phase through a bond-shift mechanism. © 1996 Academic Press, Inc.

1. INTRODUCTION

Transition metal carbides were reported to have catalytic properties similar to those of precious metals (1–4). Pure tungsten carbides catalyse alkane hydrogenolysis reactions (5–8) but deactivate rapidly in *n*-hexane and *n*-heptane reactions due to deposits of carbon fragments on the catalyst surface (6). The surface of tungsten carbide is easily contaminated by oxygen, even at room temperature. Chemisorbed oxygen leads to a dramatic change of product distribution in hydrocarbon reactions and the isomerisation becomes predominant (5–8). It was proposed that the chemisorbed oxygen introduces acid sites on the surface of bulk tungsten carbides and the catalysts are bifunctional for isomerisation reactions: hydrocarbon dehydrogenation

and hydrogenation are considered to occur on the tungsten carbide phase and skeletal rearrangement on an oxidised tungsten phase through a carbenium ion mechanism (5–8). Nevertheless, the observed activity and product distribution have also been explained by a bond shift mechanism involving a metallacyclobutane-like intermediate formed on an oxycarbide phase (9, 10), analogous to some metal catalysts (11, 12).

Although the catalytic properties of tungsten carbides, both contaminated and noncontaminated by oxygen, in hydrocarbon reactions have been extensively studied recently, the effect of the composition of reaction gases on the activity and selectivity has not yet been explored. On both monofunctional and bifunctional metal catalysts, it was found that the amount of hydrogen in the reaction gases considerably affects the activity and product distribution, even if the hydrogen does not appear in the stoichiometric equations in some cases (13–15). In this work, the reactions of *n*-hexane (nH), 3-methylpentane (3MP), 2,2-dimethylbutane (2,2DMB), 2,3-dimethylbutane (2,3DMB), and methylcyclopentane (MCP) have been studied on a tungsten carbide catalyst at 633 K and a remarkable effect of hydrogen will be reported.

2. EXPERIMENTAL

2.1. Reactants

Hydrogen was from UCAB (H_2 5.5) and helium from BOC (grade A). nH ($>99.5\%$), MCP ($>99\%$), 3MP ($>99\%$), 2,2DMB ($>99\%$), and 2,3DMB ($>98\%$) were purchased from Fluka. The major impurities are MCP (0.28%) and 3MP (0.06%) in nH, cyclopentane (0.20%) and nH (0.07%) in 3MP, *i*-pentane (0.10%) in 2,2DMB, *n*-pentane (0.13%) and 2,2DMB (0.69%) in 2,3DMB, and nH (0.64%) in MCP as measured by GC. All the reactants were used without further purification. The amount of impurities in the hydrocarbon reactants has been deducted from the products.

2.2. Catalysts

The tungsten carbide, named as FB, was supplied by Professor G. Leclercq of the Université des Sciences et

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Technologies de Lille, (Villeneure d'Ascq, France). It is used as a reference material in the frame of a stimulation contract (ST2J-0467-C(TT)) with the former EEC (now the European Union, EU) and was prepared by direct carburisation of WO_3 in a 20% CH_4/H_2 gas flow at atmospheric pressure and 1073 K. The sample was finally passivated by a flow of 2% O_2/N_2 at room temperature. The composition of the sample is $WC_{1.30}O_{0.05}$ and the specific area of N_2 adsorption is about 12 m^2/g (8).

The sample as received is inactive due to the presence of excess carbon and oxygen on the sample surface (8). To remove these contaminants, 2.5 g of the received sample, placed in a U-type quartz glass reactor with an inside diameter of 10 mm, was *in situ* pretreated in a 30 ml/min hydrogen flow before the reactions. The temperature was first raised from room temperature to 1073 K at 10 K/min and maintained at this value for 5 h and then decreased to room temperature. This pretreatment was previously used and is called the standard activation procedure; the resulting material is a WC stoichiometric carbide (8).

The physical characterisations have been previously performed after such a standard activation. H_2 and CO chemisorptions were measured at room temperature and the adsorption amount for both the molecules is about 100 μmol/g, while on the fresh sample it is 0.1–0.5 μmol/g, indicating that the most of free carbon and oxygen was removed (8). The surface area from N_2 adsorption is about 10 m^2/g and does not change significantly after the activation. However, about two-thirds of the surface is contained in micropores, of size comparable to that of CF_4 (5.4 Å) (16).

2.3. Apparatus and Activity Measurements

The reactions were performed in a flow reaction apparatus. The reaction stream could be composed of three gas streams: hydrogen, helium, and either hydrogen or helium. By switching a four-way valve, the final gas stream could pass through or pass by a saturator filled with a liquid hydrocarbon at 274 K. The partial pressure of hydrogen and hydrocarbon was then adjusted by the flow rate of each gas stream. A multiposition valve (ST16P, Valco) with 16 loops of 0.5 ml was placed just after the reactor, 15 loops of which can be used to store the effluent gases. The product analysis was performed by a gas chromatograph (HP5890) fitted with a 50-m fused silica PLOT Al_2O_3/KCl column. Both the multiposition valve and GC were controlled by an IBM compatible personal computer using the HP chemstation program.

The flow rate of the reaction stream was kept at about 50 ml/min. The effluent gases were sampled twice in each reaction run, at 4 and 6 min after introducing a hydrocarbon reactant into the reaction system. The time on stream in one reaction rus was less than 8 min and the hydrogen was always flowing through the catalyst bed between two

successive runs for at least 5 min. The experiments were carried out in a sequence of hydrogen pressure changes from about 60, 680, 450, to 320 Torr and then to 60 Torr. The final run showed that no significant deactivation was taking place during the operation procedure.

The effect of hydrogen pressure on the hydrocarbon reactions was measured at 633 K on the catalyst as treated by the standard activation procedure. After this, oxygen was introduced into the reactor and its effect on *n*-hexane reactions was measured according to the following procedure:

(1) Measure the reaction rates at 653 K (the exposure time to oxygen is here defined as zero).

(2) Decrease the temperature to 633 K in a 10 ml/min H_2 flow and then replace this flow by a 10 ml/min flow of 10% O_2/Ar for 5 min. After this, raise the temperature to 653 K at 8 K/min in a 10 ml/min He flow; about 5 min later, replace this flow by a hydrogen flow and measure the reaction rates again (the exposure time is now 5 min; i.e., $0 + 5 = 5$ min).

(3) Repeat step (2) for the other measurements.

For all the hydrocarbon reactants studied here, the products were classified into three groups: small molecules ($<C_6$) resulting from hydrogenolysis, isomerisation products, and dehydrogenative C_6 products. However, due to the high concentration of helium contained in the reaction stream, a separation of C_1 and C_2 with helium was not achieved. The hydrogenolysis rate was then calculated only according to the concentration of $0.5C_3 + C_4 + C_5$ in the effluent gases.

Although the tungsten carbide sites can be estimated by H_2 or CO adsorption, according to our knowledge there are no methods available for measuring tungsten oxycarbide or oxide sites which are believed to be the active ones for isomerisation reactions (5–12). Thus the specific rate, expressed in terms of moles per gram catalyst and per second, was used in this work as in the literature for hydrocarbon reactions on tungsten carbides (8–10, 17–19). It should be noted that as the dehydrogenation is fast and may be at quasi-equilibrium, its rate given below may represent only the net one.

3. RESULTS

3.1. Hydrogen Effect on Activity

The following reactions were carried out at 633 K on 2.5 g sample activated in hydrogen at 1073 K for 5 h without exposure to oxygen. The results are presented for each hydrocarbon reactant independently. In all the tested reactions, the conversion of hydrocarbon reactant was always lower than 7%.

3.1.1. Reactions of 2,2DMB. The detected isomerisation product is 2,3DMB; its selectivity decreases with increasing hydrogen pressure, the value estimated according to Fig. 1 being about 65% at 60 Torr hydrogen and around
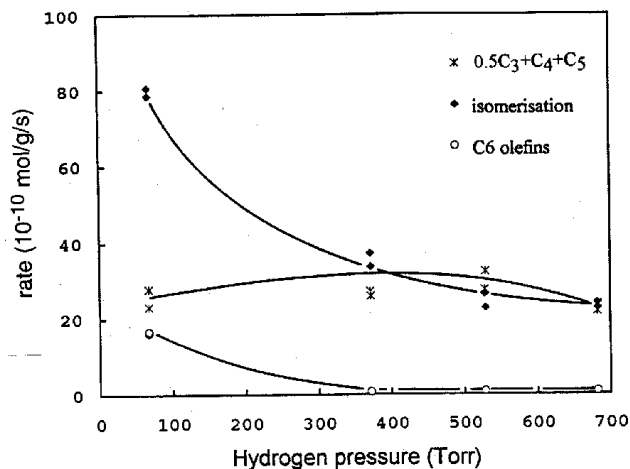
FIG. 1. Hydrogen effect on 2,2DMB reactions at 12.2 Torr hydrocarbon.

FIG. 3. Hydrogen effect on 2,3DMB reactions at 6.8 Torr hydrocarbon.

50% at 680 Torr hydrogen. The C_6 olefins are present in a significant amount only at 60 Torr hydrogen, the selectivity being about 14%. Both the isomerisation and the dehydrogenation rates decrease as hydrogen pressure increases. The total hydrogenolysis rate does not change significantly, but, as presented in Fig. 2, for each hydrogenolysis product the rate is strongly affected by hydrogen pressure. A maximum is observed with increasing H_2 pressure for isobutane (iC_4), isopentane (iC_5), and neopentane ($neoC_5$), which are primary hydrogenolysis products formed by a single C–C bond rupture of 2,2DMB, whereas the rate decreases with increasing hydrogen pressure for propane (C_3), n-butane (nC_4), and n-pentane (nC_5), which should be secondary reaction products.

Figures 1 and 2 also show that the isomerisation is preferred together with the favoured direction of hydrogenolysis, giving iC_4 plus C_2 and also iC_5 plus C_1 fragments. Such
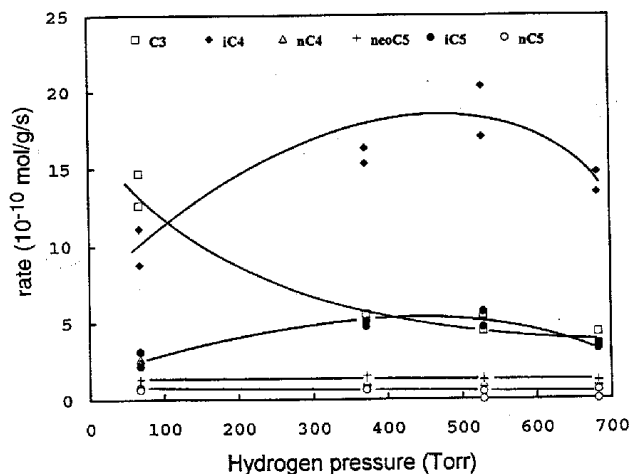
results are quite similar to those observed on supported Pt and Pd catalysts, indicating that $\alpha\gamma$ and $\alpha\gamma'$ interaction (interaction of the first and the last C atoms in a C_3 chain fragment with the catalyst) are dominant (20).

3.1.2. Reactions of 2,3DMB. The detected isomerisation product is 2,2DMB; its selectivity is a function of hydrogen pressure, the value estimated according to Fig. 3 being about 27% at 60 Torr hydrogen and around 55% at 680 Torr hydrogen. The C_6 olefins represent a significant part of the products at any hydrogen pressure; their rate of formation decreases as hydrogen pressure increases. The total hydrogenolysis rate does not change significantly with hydrogen, while a maximum rate is observed for the isomerisation reaction; i.e., the formation rate of 2,2DMB first increases, and then decreases with increasing hydrogen pressure. Figure 4 shows the effect of hydrogen pressure on the rate of each hydrogenolysis product. A maximum

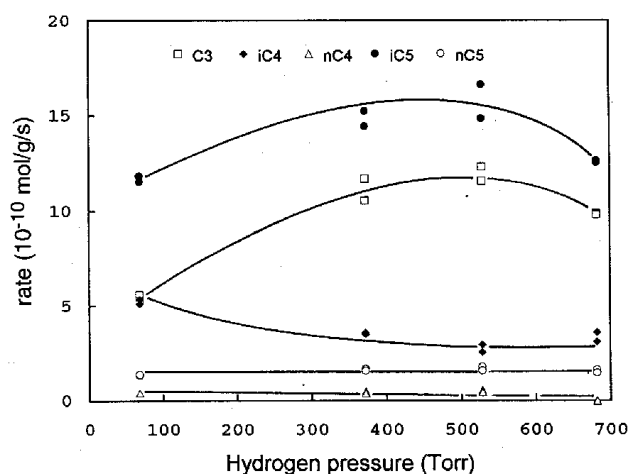**FIG. 2.** Hydrogen effect on 2,2DMB hydrogenolysis at 12.2 Torr hydrocarbon.

FIG. 4. Hydrogen effect on 2,3DMB hydrogenolysis at 6.8 Torr hydrocarbon.

is observed for C_3 and iC_5, which are initial hydrogenolysis products of 2,3DMB. nC_4, iC_4, and nC_5 are secondary products, their rates slightly decreasing with increasing hydrogen pressure. nC_4 and nC_5 represent only a very small part of the hydrogenolysis products, while the amount of iC_4 is significant. iC_4 may result from the further hydrogenolysis of iC_5 and/or from the hydrogenolysis of 2,2DMB, which is the dominant product in 2,3DMB reactions.

3.1.3. Reactions of 3MP. The detected isomerisation products are 2MP and nH. The product ratio of 2MP/nH is 0.25 ± 0.04 and the selectivity toward the isomerisation products is around 14%. Both of these values do not change significantly with hydrogen pressure. As shown in Fig. 5, the C_6 olefins are the main products at 60 Torr hydrogen (about 57%) while at 680 Torr hydrogen the hydrogenolysis products are dominant (around 60%). Both the dehydrogenation and the isomerisation rates decrease as hydrogen pressure increases, the former being much more significant. In contrast to the 2,2DMB and 2,3DMB reactions, here the total hydrogenolysis rate exhibits a maximum value. Figure 6 shows the effect of hydrogen pressure on the rate of each hydrogenolysis product. A maximum is observed for nC_4, nC_5, and iC_5, which are primary hydrogenolysis products of 3MP. C_3 and iC_4, which are secondary products, are detected and slightly decrease with increasing hydrogen pressure.

No reaction mechanism is available in the literature which is consistent with the observed low ratio of 2MP/nH in 3MP reactions. However, we have learned that at least six C_6 olefin isomers are detected in 3MP reactions, of which only four dehydrogenation isomers correspond to the dehydrogenation of 3MP; thus the other dehydrogenation isomers must originate from the isomerisation products of 3MP. If the dehydrogenation of 2MP is faster than nH, a low product ratio of 2MP/nH is expected.

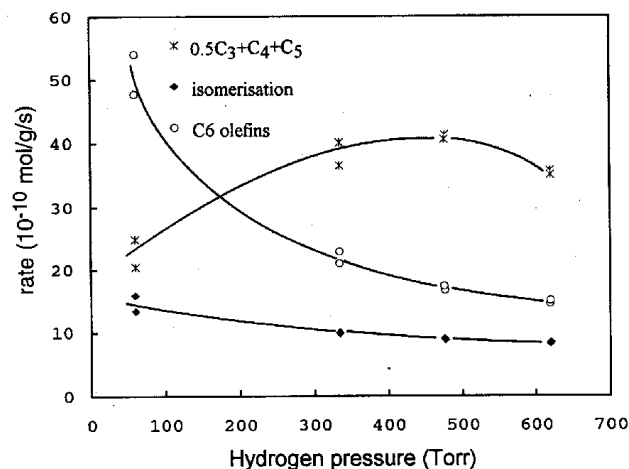*3.1.4. Reactions of nH.* The detected isomerisation products are 2MP and 3MP. The product ratio of 2MP/3MP
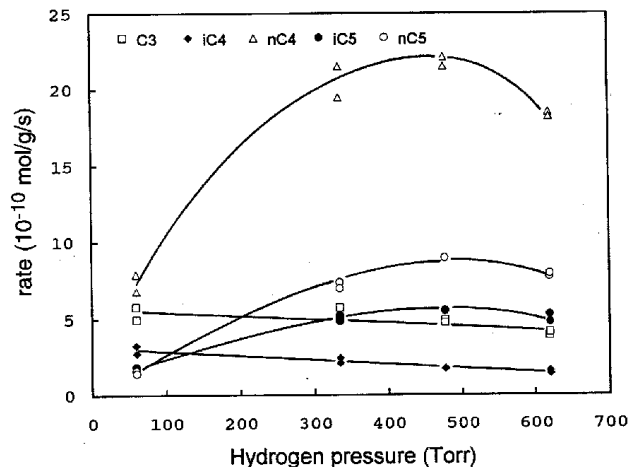

FIG. 6. Hydrogen effect on 3MP hydrogenolysis at 12 Torr hydrocarbon.

does not change with hydrogen pressure, the value being 1.5 ± 0.07, close to thermodynamic equilibrium (20). The selectivity towards the isomerisation products slightly decreases from 19% at 60 Torr hydrogen to 15% at 680 Torr hydrogen as estimated according to Fig. 7. The C_6 olefins are the main products at 60 Torr hydrogen (about 46%), while at 680 Torr hydrogen the hydrogenolysis products are dominant (around 70%). Both the dehydrogenation and isomerisation rates decrease as hydrogen pressure increases; however, the decrease is more significant for the dehydrogenation. A maximum value is observed for the total hydrogenolysis rate. All of these results are similar to the 3MP reactions. Figure 8 shows the effect of hydrogen pressure on the rate of each hydrogenolysis product. A maximum is observed for nC_3, nC_4, and nC_5, which are primary hydrogenolysis products of nH. iC_4 and iC_5 are secondary products and only represent a very small part of the hydrogenolysis products.
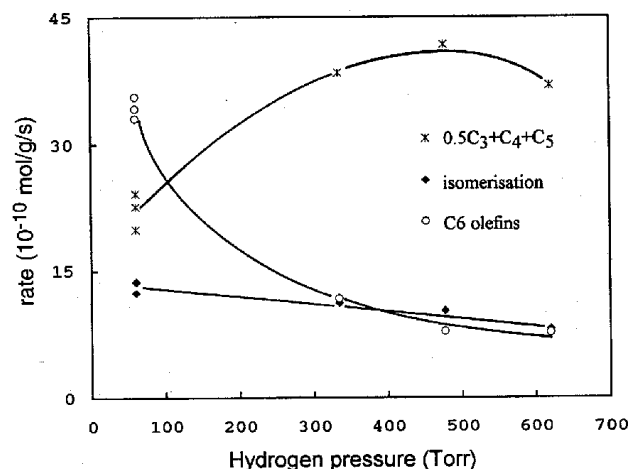

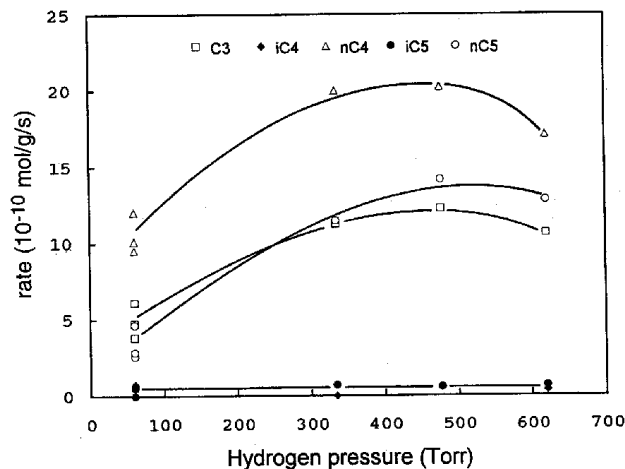**FIG. 5.** Hydrogen effect on 3MP reactions at 12 Torr hydrocarbon.

FIG. 7. Hydrogen effect on nH reactions at 9.2 Torr hydrocarbon.

FIG. 8. Hydrogen effect on nH hydrogenolysis at 9.2 Torr hydrocarbon.

FIG. 9. Hydrogen effect on MCP reactions at 8.6 Torr hydrocarbon. ○, Methylcyclopentenes; ◇, benzene; ∗, extensive hydrogenolysis; △, MCP ring opening; ◆, demethylation (cyclopentane).

3.1.5. Reactions of MCP.

The following reactions may take place for the MCP molecule: dehydrogenation to methylcyclopentenes, ring enlargement to cyclohexane and benzene, single C–C bond rupture to cyclopentane (demethylation), and 2MP, 3MP, and nH (ring opening), as well as extensive hydrogenolysis to $<C_6$ molecules. Both metal and acid catalysts can catalyse these reactions. Numerous mechanisms have been proposed for these reactions. Using MCP ring opening as an example, at least two mechanisms are proposed on platinum catalysts: these are a nonselective one producing 2MP, 3MP, and nH in a statistical ratio of 40 : 20 : 40 and a selective one only forming 2MP and 3MP (22). Acid catalysts catalyse MCP ring opening through a carbenium ion mechanism; Chow et al. (23) have shown that at low MCP pressure, the main products are branched hexane isomers.

In the present work, the main products of MCP reactions are methylcyclopentenes and benzene. As presented in Fig. 9, the formation rates of methylcyclopentenes and benzene dramatically decrease with increasing hydrogen pressure, while the rates of single C–C bond rupture and extensive hydrogenolysis increase. Cyclohexane is not detected due to the fact that its concentration is lower than the detection limitation of the GC (0.003 Torr). nH can be detected, but its amount is equivalent to that contained in the MCP reactant. The product ratio of 2MP/3MP is 0.76 ± 0.06 and does not change significantly with hydrogen pressure. The ratio 2MP/cyclopentane is about 0.65, except at 60 Torr hydrogen where the value is 0.22.

3.2. Effect of Exposure Time of the Catalyst to Oxygen

The presence of oxygen on bulk tungsten carbides dramatically affects the product distribution of hydrocarbon reactions (5–8, 19). Increasing exposure time of the catalyst to oxygen leads to an increase in selectivity towards isomerisation products. In order to investigate the effect of
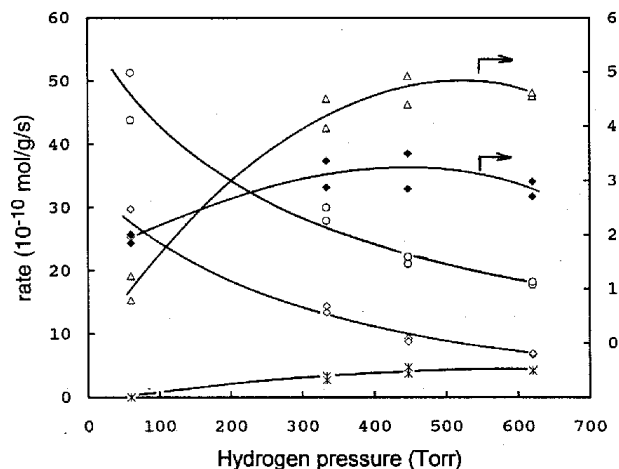
surface oxygen on nH reactions, the catalyst used above was exposed to oxygen and the reaction rates were measured according to the procedure as described under Experimental. The results are presented in Fig. 10, which shows that the total activity of the catalyst quickly decreases with an increase of the exposure time and reaches a stable state after 15 min exposure. The initial product distribution is 65% for hydrogenolysis and 22% for isomerisation, while with a 5-min exposure it is 5% for hydrogenolysis and 64% for isomerisation. After 15 min exposure, both the activity and product distribution do not change significantly, indicating that the composition and structure of the catalyst surface no longer change. The hydrogenolysis rate quickly decreases from initial 60.10^{-10} mol/g/s to about 3.10^{-10} mol/g/s with a 5-min exposure, showing that the oxygen chemisorption on the catalyst surface is fast and that the adsorbed oxygen
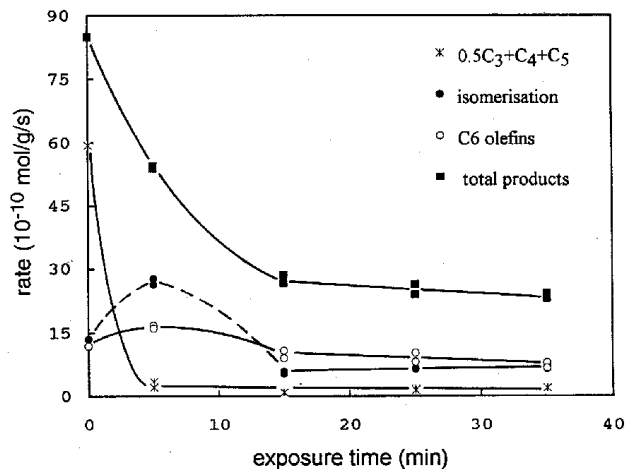

FIG. 10. Effect of exposure time of the catalyst to oxygen on nH reactions at 9.2 Torr hydrocarbon.

inhibits the formation of the precursor of hydrogenolysis products. The initial increase of the isomerisation rate from 0 min to 5 min exposure may result from an increase of active sites corresponding to isomerisation reactions. A decrease of the isomerisation rate after a further exposure to oxygen can be attributed to a decrease of active surface for nH chemisorption. As the product ratio 2MP/3MP is equal to 1.31 ± 0.02 and does not change with the exposure time, the isomerisation mechanism does not seem to change during such an exposure process. The dehydrogenation rate has a minor change with the exposure time, indicating that this is a fast reaction and that a quasi-equilibrium may exist in the hydrocarbon dehydrogenation–hydrogenation process (7).

3.3. Effect of Reaction Time on Activity

To check whether a reproducible activity of the sample can be obtained and to see the effect of reaction time on activity, a new 2.5-g sample was used and the reactions of MCP and 2,3DMB were performed on the sample pretreated by the standard activation procedure. The choice of these two molecules is based on the fact that MCP deactivates metal catalysts more seriously than other alkanes while 2,3DMB presents the highest activity in this work. As shown in Fig. 11, a good reproducibility in activity is obtained as compared to Figs. 2 and 9 and no significant deactivation is observed up to 20 min of reaction. The effect of the catalyst deactivation on the reactions can then be neglected under our conditions. A good resistance of tungsten carbides to poisoning by hydrocarbon was also observed by Keller *et al.* (17) in MCP reactions.

4. DISCUSSION

4.1. Activity and Selectivity

The results obtained in this work quite differ significantly from those reported earlier by Frennet *et al.* (8), where the same sample of tungsten carbide was used but was activated in hydrogen at 873 K instead of 1073 K in this work. No significant amount of C_6 olefins were observed in their work and the specific rate for hydrocarbon conversion was about 10 times higher than in this work. However, as C_6 olefins represent an important part of the products in this work, and the dehydrogenation is fast and may be at quasi-equilibrium, the specific rate presented here for hydrocarbon conversion is believed to be somewhat underestimated.

The low activity is consistent with high selectivity towards dehydrogenation products Iglesia *et al.* (7) found that the selectivity towards dehydrogenation products in *n*-heptane reactions increases from 3.5 to 27.8% with increasing temperature from 623 to 723 K, while the total activity concomitantly decreases from 0.17 to 0.069 s^{-1} as expressed in terms of turnover frequency (TOF). Katrib *et al.* (19) reported that at 623 K, the total olefins represent only about 0.4% of the products for nH reactions on an oxygen-modified
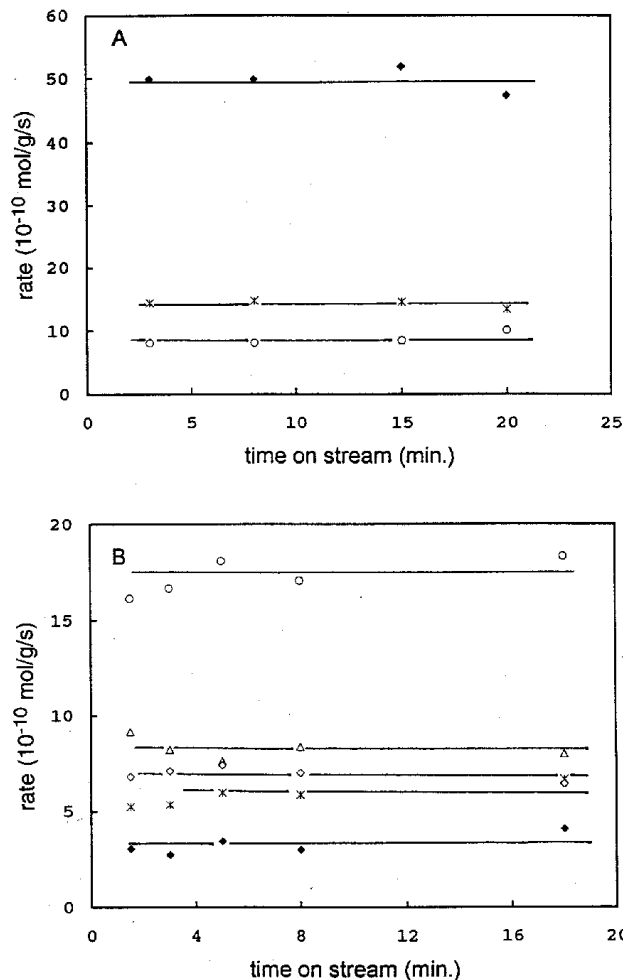

FIG. 11. Effect of reaction time on activity. (A) 6.8 Torr 2,3DMB, symbols as in Fig. 3; (B) 7.6 Torr MCP, symbols as in Fig. 9. The reactions are performed at 633 K and about 620 Torr H_2.

bulk tungsten carbide with a N_2 adsorption area of 13 m^2/g, while the specific activity is 2×10^{-7} mol/g/s, about 30 times higher than this work.

The low activity may relate to the following facts: (i) lack of necessary carbon on the catalyst surface after the standard activation, (ii) low accessible catalytic surface to hydrocarbon molecules. After the standard activation, the adsorption amount of H_2 and CO increases from about 0.1–0.5 to 100 μmol/g and the bulk atom ratio of C/W is around 1, indicating that most free carbon and oxygen on the sample surface are removed (8). However, as shown by the Strasbourg group (9, 17–19), to obtain a high activity in hydrocarbon reactions, the sample should be passivated by a mixture of 20% CH_4/H_2 and furthermore by a gas flow of CH_4 at about 1113 K after the activation in hydrogen; on this catalyst, methane is the only product at a reaction temperature higher than 573 K. The resulting material after the standard activation is a microporous one; about two-thirds of the Kr adsorption surface is not accessible to the

CF$_4$ molecule (5.4 Å) (16). As the kinetic diameter of C$_6$ alkane is larger than this value, it is expected that only a small fraction of the surface is used in these reactions.

It was shown that bulk tungsten carbides catalyse only hydrogenolysis reactions; a carbon deposit during the reactions leads to a quick deactivation, but the product distribution does not change (6). If the tungsten carbide is contaminated by oxygen, acid sites or maybe a new catalytic phase (oxycarbide) is introduced on the catalyst surface leading to a decrease of activity, but to a significant increase of the selectivity towards isomerisation (5–8). As significant amounts of isomerisation products were observed in the present work, one may conclude that a small amount of oxygen was still present on the catalyst surface after the activation in hydrogen. The oxygen may result from bulk tungsten oxide, which was used as the starting material for the preparation of the tungsten carbide. XPS investigations show that a small amount of oxidic oxygen is always present on the catalyst surface after the activation and cannot be removed even by an extensive Ar$^+$ bombardment (19).

4.2. Hydrogenolysis Reactions

It is generally accepted that the tungsten carbide phase provides active sites for hydrogenolysis and dehydrogenation of hydrocarbons. Acid sites can also catalyse hydrogenolysis reactions. Once the latter mechanism is applied, the hydrogenolysis rates of 3MP and 2,3DMB should be larger than that of nH and 2,2DMB because the carbenium ion is much more easily formed at the tertiary C atom than the other C atoms (24). However, this is not the case in this work. A quick decrease of the hydrogenolysis rates in nH reactions after a 5-min exposure of the catalyst to oxygen at 633 K (Fig. 10) provides a further proof that the hydrogenolysis reactions take place on the tungsten carbide phase.

A maximum rate with hydrogen pressure was observed for products resulting from a single C–C bond rupture in the studied hydrocarbon molecules. Such a result should not be affected by extensive hydrogenolysis because the product amount from extensive hydrogenolysis only represents a small part of hydrogenolysis products. The observed effect of hydrogen on the rate of single hydrogenolysis may be explained as on metal catalysts (14). Increasing hydrogen pressure leads to an increase of hydrogen coverage but to a decrease of hydrocarbon coverage due to the fact that hydrocarbon adsorption is a dehydrogenation process and/or there is a competitive adsorption between hydrogen and hydrocarbon on the same sites. If hydrogenolysis reactions are controlled by surface steps such as the C–C bond rupture and product hydrogenation desorption, in which the hydrogen in the gas phase or the other surface species like vacant sites and hydrogen atoms are involved, a maximum rate is expected with a variation of hydrogen pressure. As a low activation energy of about 10 kcal/mol is observed

for C$_6$ alkane hydrogenolysis on a bulk tungsten carbide, Keller *et al.* (9) suggested that hydrogenolysis reactions are controlled by the desorption of hydrocarbon residues from the surface.

The position of prevailing chain rupture in hydrogenolysis varies from metal to metal (25). The positions of favoured bond rupture of dimethylbutane, and to some extent that of 3MP over the tungsten carbide, are close to the values observed on Pt rather than to Ir. The splitting of nH is closer to that observed with Ir although Ir produced more C$_3$ and C$_4$ (20). The position of preferred splitting of nH gave a much stronger hydrogen dependence on Pt than on the tungsten carbide, shifting from predominant C$_5$ plus C$_1$ fragments to 2C$_3$ as the hydrogen pressure increased; however, an important difference is that C$_4$ was never preferred on Pt (26).

Single hydrogenolysis includes demethylation, deethylation, and depropylation. Demethylation can take place in all the studied molecules, deethylation can be involved in nH, 3MP and 2,2DMB reactions, and depropylation occurs only in nH and 2,3DMB reactions. Their relative rates depend on hydrogen pressure. Deethylation gives the highest maximum rate (around 21×10^{-10} mol/g/s), whereas for depropylation the maximum rate is 6×10^{-10} mol/g/s and for demethylation it is about 2×10^{-10} mol/g/s, except in nH reactions and for the C$_I$–C$_{III}$ bond rupture in 3MP reactions, where the value is about 7×10^{-10} mol/g/s.

Although the conversion of hydrocarbon reactant was kept below 7%, secondary reaction products were still detected, in particular with the production of <C$_6$ molecules. Secondary products of <C$_6$ can result from the following three reactions: extensive hydrogenolysis, isomerisation of hydrogenolysis products, and hydrogenolysis of isomerisation products of the hydrocarbon reactant. For example, in 2,2DMB reactions iC$_4$, iC$_5$, and neoC$_5$ are primary products, while C$_3$, nC$_4$, and nC$_5$ are secondary ones. nC$_5$ can be accounted for only by the isomerisation of iC$_5$ and neoC$_5$; nC$_4$ may result from a further hydrogenolysis of iC$_5$ or may be an isomerisation product of iC$_4$; for C$_3$, it can be a hydrogenolysis product of iC$_4$ and iC$_5$, but is most likely to be a hydrogenolysis product of 2,3DMB, which is a dominant product in this reaction, because the formation rates of 2,3DMB (Fig. 1) and of C$_3$ (Fig. 2) present a similar hydrogen dependence. Figure 12 shows a possible reaction scheme for the production of <C$_6$ hydrocarbons.

4.3. Isomerisation Reactions

Hydrocarbon molecular structure affects the isomerisation selectivity. In nH and 3MP reactions, the selectivity is about 15%, while in 2,2DMB and 2,3DMB reactions it is higher than 30%. MCP mainly produces methylcyclopentenes and benzene.

The following experimental results show that the isomerisation reactions proceeds through a bond-shift
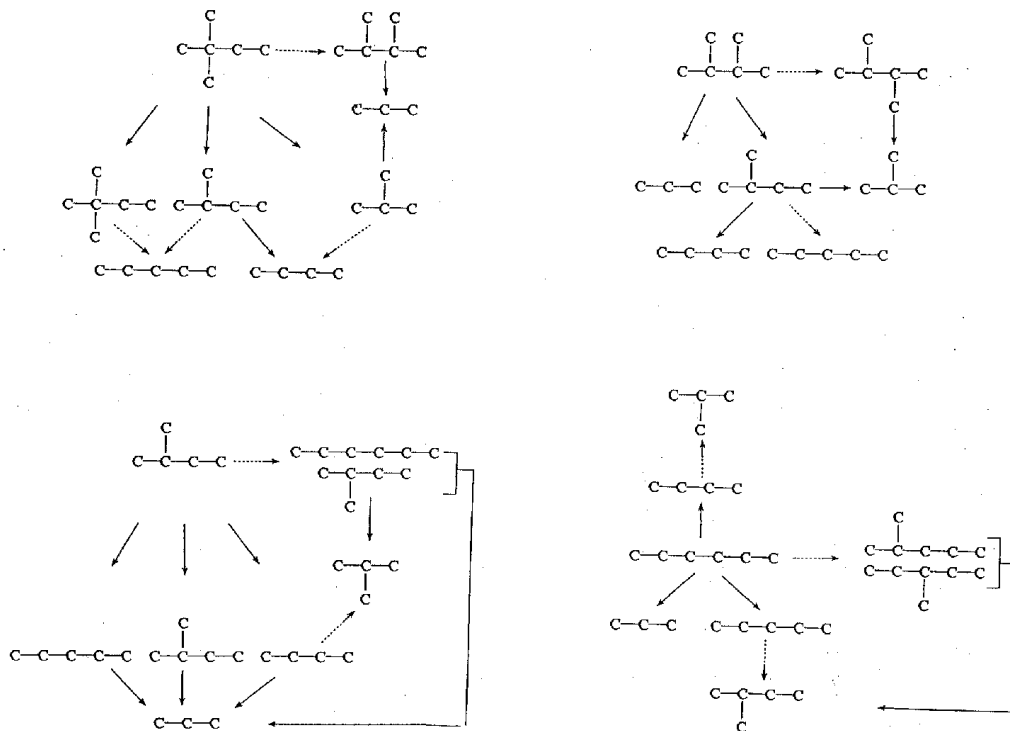
FIG. 12. Possible reaction scheme for the production of $<C_6$ molecules ($\rightarrow$, hydrogenolysis; --->, isomerisation).

mechanism and not via a methylcyclopentane-like inter-mediate as observed on platinum catalysts: (i) the isomeri-sation rate of 2,2DMB and 2,3DMB is higher than that of 3MP and nH while the former molecules cannot form a methylcyclopentane-like intermediate (compare Figs. 1 and 3 with Figs. 5 and 6); (ii) the isomerisation rate of 3MP and nH is always larger than the single hydrogenolysis rate of MCP (compare Figs. 5 and 6 with Fig. 9); (iii) in 3MP and nH reactions no methylcyclopentane product is observed. Two bond-shift mechanisms have been proposed for the isomerisation reactions on tungsten carbide: one involves a metallacyclobutane-like intermediate formed on an oxy-carbide phase (9–11) and the other through a carbenium ion formed on a tungsten oxide phase (5–7). In the latter mechanism, tungsten carbide may provide active sites for hydrocarbon dehydrogenation to form alkene intermedi-ates; such a reaction is then called bifunctional catalysis. According to Zhan *et al.* (27), the carbenium ion mecha-nism would give much dimethylbutane from nH. However, this is not the situation here. The low isomerisation rate observed in this work may favour the mechanism involving a methylcyclobutane-like intermediate as applied on Mo$_2$C (10). One may note that the density and acid strength of the Brønsted sites introduced by chemisorbed oxygen depend on the amount of surface oxygen and the crystal structure of the tungsten oxide. It was shown that the acid strength on small WO$_x$ crystallites with tetrahedral co-ordination of tungsten atoms is much greater than on large WO$_3$ crystal-

lite containing W atoms only in octahedral sites (28). The present work cannot rule out the possibility that the exist-ing tungsten oxide on the catalyst surface is in the latter form, leading to a low activity.

Increasing hydrogen pressure leads to a decrease in the isomerisation rate in 2,2DMB, 3MP and nH reactions, while a maximum of the rate is given in 2,3DMB reactions (Fig. 3), which was often observed on metal catalysts (13, 14).

The isomerisation rate catalysed only by acid catalysts does not depend on hydrogen pressure (24). The bond-shift mechanism involving a metallacyclobutane-like intermedi-ate formed on an oxycarbide phase contains three reaction steps: the adsorption–dehydrogenation of hydrocarbon re-actant, isomerisation, and hydrogenation–desorption of products. Such a reaction process is quite similar to that on metal catalysts (13); therefore, it can account for the ob-served maximum rate in 2,3DMB reactions if the surface reactions such as the C–C bond rupture/formation or prod-uct hydrogenation is rate controlling and the other surface species like vacant sites, adsorbed hydrogen atoms, or gas hydrogen are involved in these steps. Concerning bifunc-tional catalysis, dehydrogenation on carbide sites and iso-merisation through a carbenium ion on oxide sites has been used by Ribeiro and co-workers (5–7) to explain the prod-uct distribution observed over tungsten carbides modified by oxygen; the reactions are suggested to be controlled by the isomerisation step on acid sites. If it is also valid in this work, the rates would decrease with increasing hydrogen

pressure (29), which is true in 2,2DMB, 3MP, and nH reactions but not in 2,3DMB reactions.

The present results seem to favour the bond-shift mechanism involving a metallacyclobutane-like intermediate. However, one should note that if the isomerisation is controlled by product hydrogenation, or even if the reaction is controlled by the isomerisation step but the number of acid sites increases with increasing hydrogen pressure, a maximum rate can also be predicted according to bifunctional catalysis. Thus it has been reported that the chemisorbed oxygen on tungsten carbides can react with hydrogen to form tungsten bronze and water (30). If such a reaction corresponds to the formation of acid sites, it may be expected that the number of acid sites would increase with increasing hydrogen pressure.

5. CONCLUSION

The effect of hydrogen pressure on the reactions of nH, 3MP, 2,2DMB, 2,3DMB, and MCP have been studied over a bulk tungsten carbide prepared by direct carburisation of WO_3 in a 20% CH_4/H_2 flow. The catalyst activated in H_2 at 1073 K for 5 h has a low activity and a good resistance to poisoning by hydrocarbon. Olefins are a substantial part of the products in all the reactions. The isomerisation reactions are significant, indicating the presence of some oxygen on the catalysts after such activation.

Increasing hydrogen pressure leads to a decrease of iomerisation rates in nH, 3MP, and 2,2DMB reactions, while a maximum value was observed in 2,3DMB reactions. Whatever the hydrogen pressure used, the isomerisation rate is always higher than the MCP ring opening rate, indicating that isomerisation takes place through a bond-shift mechanism and not via a methylcyclopentane-like intermediate. However, a discrimination between the mechanisms involving a metallocyclobutane-like intermediate on tungsten oxycarbide and a carbenium ion on tungsten oxide seems difficult according to the kinetic data reported here. The exposure of the catalyst to oxygen leads to a fast decrease of the hydrogenolysis rate and a high selectivity to the isomerisation products in nH reactions, indicating that hydrogenolysis takes place on a tungsten carbide phase. A maximum rate with hydrogen pressure is observed for all the single hydrogenolysis products, indicating that a competitive adsorption may exist between hydrogen and hydrocarbon on the same active sites.

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