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Reactivity of hexanes (2MP, MCP and CH) on W, W_2C and WC powders. Part II. Approach to the reaction mechanisms using concepts of organometallic chemistry

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Abstract

The reactivity of 2-methylpentane (2MP), methylcyclopentane (MCP) and cyclohexane (CH) on reproducible and well-characterized surfaces of W, W_2C and WC has been studied. A great deal of effort was put on the characterizations by physisorption, chemisorption and photoemission spectroscopy. The results obtained with these reference materials can be used for comparison with those appearing in the literature and sometimes debated because of the inconstancy of the active states due to non-stoichiometric compositions (excess of carbon, decarburization, oxidation by oxygen impurities). In agreement with the work of Boudart et al. [F.H. Ribeiro, R.A. Dalla Betta, M. Boudart, J. Baumgartner, E. Iglesia, J. Catal. 130 (1991) 86; F.H. Ribeiro, M. Boudart, R.A. Dalla Betta, E. Iglesia, J. Catal. 130 (1991) 498; E. Iglesia, J.E. Baumgartner, F.H. Ribeiro, M. Boudart, J. Catal. 131 (1991) 523; E. Iglesia, F.H. Ribeiro, M. Boudart, J.E. Baumgartner, Catal. Today 15 (1992) 307.] we confirmed that reforming reactions do not take place in the temperature range 80–400°C and for our experimental conditions. The dehydrogenation of cyclohexane appeared only when a strong poisoning by carbonaceous residues occurred. For 2-methylpentane and methylcyclopentane the extensive hydrogenolysis character of WC is higher than for W_2C and WC surfaces. The various hydrogenolysis mechanisms of 2MP, MCP and CH on W, W_2C and WC surfaces are interpreted by different possible reaction intermediates deduced from concepts of organometallic chemistry.
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Keywords: Tungsten carbides; Hydrogenolysis of hexanes; Reaction mechanisms; Reaction intermediates

1. Introduction

During these last years many papers have dealt with the catalytic properties of transition metal carbides and nitrides considered as possible substitutes for noble metals [1–10]. As early as 1970, Gault and Muller indicated some analogies between the catalytic properties of evaporated tungsten films assumed to be carburized, with that of platinum in the reforming reactions of hydrocarbons [1].

Tungsten carbide powders with WC and β-W_2C structures catalyze alkane hydrogenolysis

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reactions. Alkanes adsorb strongly on fresh carbide surfaces, leading to rapid deactivation by carbon fragments and to high selectivity to hydrogenolysis products. Isomerization or dehydrocyclization products from hexanes were not observed on fresh carbides. Tungsten carbide surfaces contain sites with a broad range of binding energies; these sites can be selectively titrated by chemisorbed CO, H and O adatoms. Chemisorbed oxygen introduces WO_x sites and replaces the strongest binding WC_x sites with BrÖnsted acid sites that catalyze skeletal isomerization and cracking of alkenes or cycloalkenes. Such acid sites isomerize alkanes when sufficient WC_x sites are also present to form the required alkene intermediates [11,12]. However, it was also clearly shown that the surface states of these materials as characterized by XPS, AES, XAS and catalytic tests are very inconsistent, depending on the nature of the gas mixtures, traces of oxygen, temperature of the samples, composition of the catalyst, influence of the activation process and the preparation technique followed or not by various types of passivation by carbon or oxygen etc. [8,10,12–15].

We describe the reaction chemistry of 2-methylpentane (2MP), methylcyclopentane (MCP), cyclohexane (CH) on W, W_2C and WC powders very well characterized by specific surface area, porosity, chemisorption, XRD and XPS measurements. Special attention has been paid to the in-situ preparation in the microreactor of reliably reproducible surface states in parallel with the catalytic tests to avoid uncontrolled modifications of the surface and to allow comparisons with data in the literature. The various hydrogenolysis mechanisms, dehydrocyclization and dehydrogenation reactions of 2MP, MCP and CH on W, W_2C and WC surfaces are described and related to the different possible reaction intermediates suggested in the literature. The hydrocarbon surface bonding in the postulated intermediates is related to the nature of the active sites and analyzed using concepts of organometallic chemistry.

2. Experimental

2.1. Catalyst preparation

The preparation and characterization of catalysts have already been described in Refs. [12,16–18]. All the samples were prepared in-situ in the microreactor in order to avoid any air contact and uncontrolled modifications of the surface. The starting materials were:

— WO_3 powder purchased from Johnson Matthey (impurities: Ca < 0.3 ppm, Cu 0.3 ppm, Mg 0.1 ppm, Si 0.5 ppm).

— $(NH_4)_{10}W_{12}O_{41}$, $5H_2O$ from Johnson Matthey (impurities: Ca 1 ppm, Fe < 1 ppm, Mg < 1 ppm, Si 5 ppm) or provided by Prolabo.

The W metal characterized by XRD was obtained by reduction of WO_3 or $(NH_4)_{10}W_{12}O_{41}$, $5H_2O$ for 12 h only at 650°C in a hydrogen flow to avoid excessive sintering.

The WC carbide powders were prepared by reducing WO_3 or $(NH_4)_{10}W_{12}O_{41}$, $5H_2O$ using H_2 at 650°C for 13 h followed by carburization in a flow of a CH_4 (20%)/He (80%) gas mixture by gradual temperature increase of 2.5°C/min up to 850°C for 1 to 3 h [7,13–16]. The excess surface carbon was eliminated at 700°C under a hydrogen flow for a period depending on the carburization conditions (1 to 3 h). XRD spectra showed only the characteristic lines of WC.

The preparation of the W_2C hemicarbide is more critical. It is a thermodynamically unstable transient compound, its rate of formation being faster than for WC. In our case, it was necessary to prepare W_2C samples free from any trace of WC which would be located at the upper layers of the surface of the solid where carbon issued from the gas phase will accumulate. On the basis of the XRD data, the carburization of the starting materials described above (WO_3 or $(NH_4)_{10}W_{12}O_{41}$, $5H_2O$) was done at 650°C a relatively low temperature and for a short period of 15 min under a flow of a CH_4 (20%)/He (80%) gas mixture. To obtain the W_2C hemicarbide using such a mild carburization, it was

necessary to proceed first via a reduction step to the tungsten metal phase. The XRD data for such W_2C samples revealed mainly the characteristic lines of W_2C with traces of W metal. It is well-known that the carburization occurs by diffusion of the carbon atoms at the surface. We assumed that the residual W metal detected by XRD was located inside the bulk of the powder without any contribution to the reactivity of the surface. This mild experimental procedure was preferred to a more severe carburization undetectable by XRD if present [16].

2.2. Catalyst characterization

Special attention has been given to the characterization of the various samples because of the variability of the active surfaces composition caused by non-stoichiometric compositions (excess of carbon, decarburization, oxygen fixation).

The surface characterizations of W, WC and W_2C powders have already been described in detail in Part I [16] and in Refs. [17–19]. They are summarized as follows.

2.2.1. Characterization by physisorption

The characterizations by physisorption (specific surface areas and porosity measurements) have been carried out on a separate device outside the microreactor in which the samples were prepared. Consequently the various samples of W, W_2C or WC were passivated by deposition of some equivalent monolayers of oxygen at room temperature for 10 min in a 1% O_2/He mixture following the procedure already detailed in Refs. [7,10,16,18]. Despite intensive outgassing of the samples (in the range 10^{-3}–10^{-6} Torr during 5 h at room temperature), only a portion of the passivation layers have been eliminated in our physisorption devices; therefore the characterized surfaces might be slightly modified compared with that of the samples prepared in-situ in the microreactor.

The specific surface areas were determined by BET measurements by classical physisorption of N_2 at −196°C. The textural properties of the samples (distribution of pore size) were determined by analyzing the desorption isotherms of N_2 adsorbed at −196°C. They have already been presented in detail [12,16–18].

2.2.2. Characterization by chemisorption

In-situ chemisorption measurements avoiding any contact with air have been directly carried out in the microreactor and are directly representative of the surfaces on which the catalytic tests have been performed. The gases (H_2, 10% H_2/Ar, 10% O_2/Ar, 10% CO/Ar), used in the chemisorption measurements were of high purity (> 99.99%) and purchased from Air Liquide. When necessary, the trace amounts of water vapour and oxygen were removed by leading the gas flow over activated manganese oxide (MnO) and a molecular sieve. The amounts of H_2, CO and O_2 pulse chemisorbed to saturation are given in Table 1. By convention and following the proposal in Refs. [3–5] for WC and W_2C, we considered that one monolayer can be taken to be equal to 10^{15} adsorbed species per cm^2. Such a conventional approximation allows the comparison of our chemisorption measurements and estimation of TOF with those of the literature to be drawn. For a polycrystalline foil of W the authors of Ref. [19] considered that the saturation coverage of 10^{15} atoms cm^{-2} was equivalent to a monolayer.

Chemisorption at room temperature concerns only the sites having a very low activation

Table 1
Chemisorption of CO, H_2 and O_2 on WC, W_2C and W.

	θCO (RT) [a]	θH_2 (RT) [a]	θO_2 (RT) [a]	θH_2 (HT) [b]	θO_2 (100°C)	θO_2 (250°C)
W		0.15	1.30	0.50	1.70	2.80
WC	0.60 0.40 [c]	0.65 0.40 [c]	1.25	1.10	1.40	1.80
W_2C	0.20 0.20 [c]	0.10 0.20 [c]	1.00	0.20	1.40	2.00

[a] At room temperature.
[b] At 400°C.
[c] Values determined at room temperature as indicated in Ref. [7].

energy for adsorption. Our catalytic tests were made under hydrogen and alkane mixtures in the range 80–400°C. Other sites with higher activation energy can be involved in the reaction. Some chemisorption measurements of H_2 have been made by adsorption at 400°C for 15 min and cooling progressively to room temperature in H_2 (100°C per min). Then a thermodesorption up to 450°C gives the amount of hydrogen adsorbed which is considered as the maximum quantity of H_2 chemisorbed (or the maximum coverage θ_{H2}). No control of any CH_4 release during the TPD was done as observed elsewhere [10]. But H_2 chemisorption on tungsten carbides is partly an activated process and a coverage as high as 1.1 can be obtained when H_2 adsorption takes place on samples being cooled from 627°C to room temperature [18].

2.2.3. Characterization by XPS

The XPS spectra were obtained using an ESCA III, VG instrument with Al Kα radiation (200 watts, 10 kV, 20 mA) using a pass energy of the analyzer of 20 eV. All the spectral line binding energies were referred to the C1s at 284.6 eV. The photoemission spectra of W4f and of the valence band of W, W_2C and WC have been measured and the results obtained are in good agreement with information obtained by chemisorption and the literature. Argon ion bombardment (3 kV, 30 μA) was used as sputtering and reducing agent. The XP spectra of tungsten carbides (WC, W_2C) of the W4f, the valence band and the C1s energy regions before and after passivation by CH_4 at 650°C for 10 minutes as well as the use of argon ion bombardment were discussed in detail in Refs. [10,13–16].

2.3. Experimental device and catalytic tests

The preparation of the W, WC and W_2C samples and the catalytic tests were carried out in the same apparatus under H_2 plus hydrocarbon flow at atmospheric pressure. About 200 mg of catalyst were introduced onto a fritted support in a U-shaped quartz reactor (4 mm I.D.). All the connections of the device were controlled as being absolutely air-tight (10^{-7} to 10^{-6} in a static vacuum). Special attention has been paid to the purification of the reaction gases and hydrocarbons. The H_2 flow (54 ml/min) was directed over a Pt/Al_2O_3 catalyst at 200°C to convert the residual oxygen to water. The water formed was trapped by a molecular sieve. In order to make sure that all oxygen had been removed, the reaction gases were directed over a green MnO bed which blackens (MnO_2) if some oxygen is still present. The hydrocarbon was introduced via a septum into a U-tube immersed in a cooling bath whose temperature was adjusted and maintained constant, giving the following partial pressures: $p(2MP)/p(H_2) = 6.8/753.2$; $p(MCP)/p(H_2) = 3.8/756.2$; $p(CH)/p(H_2) = 3.3/756.7$. A catharometer inserted in the flow line enabled the recording of the pressure versus time curve which closely approximated a square wave pulse. Conversions were adjusted by changing catalyst weight and flow rate. During the pulse of hydrocarbon, samples were taken with an air tight syringe and the product distributions were recorded by simple GLC analysis (FID). In this way, the activity and selectivity of the catalyst could also be calculated. Details concerning apparatus and experimental conditions are described in Ref. [20].

2.3.1. Expression of the results

The conversion (α%) is given as the ratio of the number of moles of converted reactant over the number of moles of introduced reactant times 100. The selectivity (Si) in compound i is the ratio of the number of moles of reactant converted into product i over the number of moles of converted reactant times 100. The rate of disappearance of the hydrocarbon, r_A, on W and WC_x surfaces is calculated by assuming a first order reaction following the Refs. [21,22] and is given by $r_A = F/S \ln(1/(1-\alpha))$ with F, flow rate = mol · s^{-1}; S, surface area = m^2; α, conversion; r_A = mol · m^{-2} · s^{-1}. The turn

over ν in s^{-1} is given by $\nu = r_A N_a / \theta N_s$ with N_a, Avogadro number; θ, surface coverage (as measured by H_2 chemisorption); N_s, number of sites per m^2, $N_s = 10^{19}$ sites $\cdot$ m^{-2} by convention following the Refs. [3,19]. In order to estimate the depth of multiple hydrogenolysis the mean number of carbon atoms in the hydrogenolysis products $\bar{n}$ and $\bar{x}$ mean number of broken carbon–carbon bonds per converted molecule of hydrocarbon are calculated according to Ribeiro et al. [3–5].

$$\bar{n} = \frac{\sum_{i=1}^{5} i Si}{\sum_{i=1}^{5} Si} \quad \bar{x} = \frac{6 - \bar{n}}{\bar{n}}$$

where n is the number of carbon atoms in the starting product, i.e. 6 for 2MP.

3. Results

3.1. Sample characterizations

3.1.1. Physisorption data

The specific surface areas as determined by BET measurements were ca. 15 $m^{-2} \cdot g^{-1}$ for the various samples [16]. As already emphasized above the samples were passivated through the characterized surfaces might be slightly modified compared to that of the samples prepared in-situ in the microreactor.

For passivated W samples the physisorption of N_2 at -196°C indicated that the samples are almost non-porous, as described in detail in Part I [16].

The distribution of pore size of passivated WC was centered around 20 nm and therefore all the surface could be accessible to the reagents. No microporosity was seen, however this could be due to passivation treatments [10,12,16].

The samples of W_2C used in this work revealed a less open porosity compared to the WC samples. As concluded in Part I, Fig. 4 [16], the accessibility of the surface of the W_2C passivated solids to the reagents is certainly heterogeneous.

3.1.2. Chemisorption data

The chemisorption data relative to CO, H_2 and O_2 on W, WC and W_2C samples at room temperature and at 400°C are presented in Table 1. As discussed in detail in Part I [16], the interest of chemisorption measurements was for us the control of the reproducibility of the surfaces submitted to the catalytic tests. The technique used here (saturation by pulses) gave only the amount of irreversibly chemisorbed species at a given temperature. The results given in Table 1 show some striking differences between the three solids W, WC and W_2C versus CO, H_2 and O_2 chemisorptions. It is especially clear for fresh W samples that the very small amounts of H_2 chemisorbed at room temperature were due to contamination by oxygen. It is well known that the reduction step of WO_3 to the W metal is easy but the elimination of the oxygen located at the surface is extremely difficult. Our experimental reduction conditions were inadequate to obtain well decontaminated surfaces. From the work of King et al. [19], we deduced that two equivalent monolayers of O_2 remained on the surface of our W samples. The low chemisorption of H_2 observed at room temperature ($\theta_{H2} = 0.15$) was correlated to some oxygen localised in the bulk as already discussed [12–16]. But it is important to emphasize that our W, WC and W_2C samples were easily reproduced samples as deduced from physisorption, chemisorption, XRD, XPS measurements and catalytic tests and could be compared to the data of the literature [3–6,10,11].

3.2. Catalytic tests

Three alkane molecules have been chosen for comparison with metals and alloys:

— 2-Methylpentane (2MP) to estimate hydrogenolysis (single or extensive) or isomerization in large excess in H_2 ($pH_2/pHC = 150$).

— Methylcyclopentane (MCP) for hydrogenolysis (single ring opening or extensive) or ring enlargement.

— Cyclohexane (CH) for hydrogenolysis (single or extensive) or dehydrogenation.

3.2.1. Reactivity of 2MP, MCP and CH on W metal surfaces

As previously emphasized, special attention has been paid to the reproducibility of the results (preparation, characterization and catalytic tests) obtained on W surfaces well known for their versatility of the composition of the surface described in detail elsewhere [12,16].

Concerning the catalytic results, in view of the rapid deactivation of W surface (Table 2), we considered the initial measurements as representative of the fresh surface even if not perfectly clean.

3.2.1.1. Reactivity at 330°C on fresh reproducible W surfaces. On our powdered W sample prepared and tested in-situ at our reference temperature of 330°C, the data obtained with 2MP, MCP and CH for the same contact time show that:

— For 2MP, there is general agreement with the data obtained on a polycrystalline W ribbon [8,23] decontaminated in UHV conditions and characterized by XPS-AES: total conversion, extensive hydrogenolysis, mostly CH_4 (no isomerization) in agreement with the kinetic model already proposed by us [11].

— For MCP and CH, we note here too a very high activity with extensive hydrogenolysis. No traces of BZ were detected for CH reaction in these experimental conditions.

— The values of $\bar{x}$ were 3.43 for 2MP, 3.20 for MCP and 4.50 for CH at 330°C respectively and confirmed the data in the literature concerning the affinity of W for carbon–carbon bond formation.

3.2.1.2. Changes in reactivity. A complete study in the temperature range 100 to 350°C and as a function of contact time of the surface with the reactant mixtures have shown changes in both activity and selectivity. To simplify the reading of this paper, the intrinsic turn over v in s^{-1} and the activation energies determined for 2MP, MCP and CH on fresh and carbon contaminated W surfaces will be given subsequently in order to establish comparisons with the results ob-

Table 2
Influence of the temperature and contact time with reactants for reactions on clean W surfaces.

(a) 2MP reaction

T (°C)	t (s)	α (%)	C1	C2	C3	iC4	C4	iC5	C5	$\bar{n}$	$\bar{X}$
188	0	21.5	43.6	3.3	6.2	3.2	2.0	10.2	31.5	2.98	1.01
	300	6.4	38.7	3.1	4.1	2.8	—	11.9	39.4	3.24	0.84
330	0	99.4	78.4	13.1	5.0	0.8	1.1	0.7	0.9	1.35	3.43
	300	63.6	34.7	16.4	17.9	6.3	4.7	9.4	10.6	2.65	1.26

(b) MCP reaction (RS% = selectivity in single ring opening)

T (°C)	t (s)	α (%)	RS (%)	C1	C2	C3	iC4	C4	iC5	C5	CP	2MP	3MP	nH	$\bar{n}$	$\bar{X}$
150	0	11.4	71.2	14.1	1.2	0.9	0.5	1.8	5.5	4.8	5.5	25.8	26.9	13.0	2.60	1.31
	480	6.2	43.8	13.5	0.9	0.5	0.4	0.9	5.1	4.9	6.0	28.0	28.3	11.5	2.69	1.23
330	0	91.5	0	77.9	10.6	5.0	0.6	2.7	1.4	1.8	—	—	—	—	1.43	3.20
	900	26	14.8	49.6	11.3	7.4	1.5	4.6	5.2	5.4	1.5	7.0	4.7	1.6	2.02	1.97

(c) CH reaction

T (°C)	t (s)	α (%)	C1	C2	C3	C4	C5	nH	BZ
274	0	61	53.5	8.9	5.3	4.5	4.7	1.2	21
	30	55	42.1	6.8	4.0	3.4	4.4	1.6	37.7

tained with W_2C and WC surfaces and data of the literature (see general discussion).

The results reported in Table 2 for 2MP, MCP and CH on W surfaces summarize the influence of two important parameters: the reaction temperature and the modifications of the surface properties with time under the reactant mixtures.

Sets of results for 2MP at 188 and 330°C are shown in Table 2a. In both cases the conversion α% decreases with time under the reactant mixture i.e. from 21.5 to 6.4 at 188°C and 99.4 to 63.6 at 330°C after 300 s respectively. But at 188°C intermediate data between 0 and 300 s reveals neither change in the product distribution nor in $\overline{X}$ the number of carbon–carbon bonds broken by converted hydrocarbon molecule (the error bars for $\overline{X}$ are ± 0.15). The reactions at temperatures higher than 200–210°C (eg 330°C) as indicated in Table 2 show a general decrease of both the conversion and the selectivity in extensive hydrogenolysis. The same trends occur for MCP and CH: the decrease of the conversion for MCP corresponds to an increase in single ring opening (RS%) and in the case of CH to an increase of dehydrogenation to BZ. We ascribe the decrease of conversion at low temperature to disordered carbonaceous deposits without formation of superficial tungsten carbidic entities corresponding only to a poisoning by surface coverage whereas at higher temperature interactions between the carbonaceous deposits and the metallic W atoms can form certain tungsten carbidic species. These results are in agreement with the observations of two kinds of carbon entity (i.e. polymeric and carbidic carbon) on metallic W surfaces as shown by XPS and AES on W ribbons [8,23,24]. The disordered polymeric carbonaceous deposits are partially reversibly adsorbed. Treatments under H_2 at 350°C for 1 h allow the reactivation of the tungsten surface.

Table 3
Activity and selectivity on WC surfaces versus temperature

(a) 2MP reaction

T (°C)	α (%)	S (%)	C1	C2	C3	iC4	C4	iC5	C5	$\overline{n}$	$\overline{x}$
282	100	0	99.8	0.2	—	—	—	—	—	1	4.99
235	96.0	0	71.2	17.8	7.5	1.4	0.8	0.7	0.6	1.45	3.15
188	48.3	0	43.0	13.4	18.0	6.8	2.9	7.1	8.8	1.77	2.39
141	9.8	0	41.4	9.1	13.9	7.0	1.3	11.2	16.1	2.71	1.21
85	0.5	0	40.4	9.3	4.3	2.9	—	16.8	26.7	3.01	0.99

(b) MCP reaction

T (°C)	α (%)	HS(%)	C1	C2	C3	iC4	C4	iC5	C5	CP	M2P	M3P	nH	$\overline{n}$	*overlinex*
282	100	0	98.7	1.3	—	—	—	—	—	—	—	—	—	1.01	4.94
239	45.5	6.6	62.3	13.2	7.8	1.9	3.5	2.8	1.8	1.7	2.6	1.9	0.4	1.68	2.57
191	10.8	26.9	44.3	7.8	5.8	2.2	4.5	5.3	3.2	7.0	10.8	7.7	1.4	2.00	2.00
144	3.2	45.0	35.9	4.1	2.8	1.6	3.5	4.2	2.9	10.9	18.3	13.8	2.0	1.97	2.04

(c) CH reaction

T (°C)	α (%)	C1	C2	C3	C4	C5	nH	BZ
281	100	99.9	0.1	—	—	—	—	—
236	65.8	65.4	19.7	8.8	4.1	1.9	0.1	—
193	20.3	47.2	17.0	11.1	8.9	7.2	8.6	—
149	3.3	42.8	11.2	7.0	8.1	10.8	20.4	—

Table 4
Activity and selectivity for 2MP at 140°C, influence on time under the reactive flow

t (s)	α (%)	C1	C2	C3	iC4	C4	iC5	C5	$\bar{n}$	$\bar{x}$
0	23	40.6	8.6	12.6	7.0	1.5	13.0	16.7	2.78	1.16
60	20	40.9	8.9	12.8	6.7	1.3	12.9	16.5	2.76	1.17
180	12	31.2	8.2	13.9	8.9	1.5	16.6	19.7	3.12	0.92
300	12	35.1	8.2	13.2	7.5	1.5	15.0	19.7	2.94	1.03

3.2.2. *Reactivity of 2MP, MCP and CH on WC surfaces*

The experiments were carried out with the same care as for W surfaces to avoid any contamination by oxygen.

3.2.2.1. Reactivity at 330°C on fresh reproducible WC surfaces. The experimental conditions were strictly identical to those used for W surfaces.

The fresh WC surfaces lead to total conversions of 2MP, MCP and CH exclusively in an extensive hydrogenolysis to CH_4 at 330°C.

3.2.2.2. Changes in reactivity. It can be seen in Table 3a, b and c and Table 4 that hydrogenolysis on WC surfaces becomes more extensive when the temperature increases compared to W. As for metallic W samples, we observed under the reactant mixtures a decrease of the activity and a decrease of the extensive hydrogenolysis for 2MP, MCP and CH. We ascribed the changes in reactivity under the reactant mixtures again to disordered polymeric carbonaceous deposits as cited in the literature [3–6]. However, WC has a better resistance to poisoning compared to W as exemplified in Table 5. Here too, the carbonaceous residues are partially reversible under hydrogen at 350°C. When no oxygen is present on the surface as WO_x entities, reforming reactions do not occur with 2MP and MCP nor does dehydrogenation of CH in the temperature range we studied (85 to 400°C).

3.2.2.3. Reactivity of 2MP, MCP and CH on W_2C surfaces. The W_2C fresh reproducible surfaces revealed a high activity in extensive hydrogenolysis at higher temperatures as observed for W and WC fresh reproducible surfaces. The product distributions for the three hydrocarbons studied (2MP, MCP, CH) were placed between those of W and WC surfaces. Neither isomerization of 2MP, nor ring enlargement of MCP were observed.

4. Analysis and general discussion of the results

In accordance with previous results obtained in Strasbourg [7,8,10–12,23,24] and those of

Table 5
Turnover rates calculated from H_2 chemisorption at high temperature, versus reaction temperature on W, WC and W_2C surfaces

	W		WC		W_2C	
	T (°C)	$v \cdot 10^3 \cdot s^{-1}$ (θ_{H2}^{HT})	T (°C)	$v \cdot 10^3 \cdot s^{-1}$ (θ_{H2}^{HT})	T (°C)	$v \cdot 10^3 \cdot s^{-1}$ (θ_{H2}^{HT})
2MP	235	8.53	—	—	235	64.5
	186	0.58	188	6.12	188	9.48
	150	0.11	141	0.93	141	0.69
MCP	282	28.7	—	—	286	9.75
	237	11.1	239	3.86	236	2.38
	193	6.60	191	0.72	195	1.44
	151	1.61	144	0.20	—	—
CH	233	0.81	236	5.62	244	12.9
	212	0.45	—	—	—	—
	190	0.19	193	1.21	197	2.04
	—	—	149	0.18	153	0.12

[a] At $T = 235$°C for 2MP and 282°C for MCP on WC, the conversions α% were too high.

Boudart et al. [2–6,21], it is confirmed in the temperature range 80 to 400°C that tungsten carbide powders with WC and W_2C structures catalyze hydrocarbon hydrogenolysis reactions. Hydrocarbons adsorb strongly on fresh carbide surfaces, leading to deactivation by carbonaceous deposits changing the selectivity from extensive to single hydrogenolysis as a function of θ_C and temperature. Neither isomerization nor dehydrocyclization occur with 2MP, MCP or CH. The same features occur on metallic W powders in accordance with the previous results of Anderson et al. for hydrocarbon reactions on vacuum evaporated and deposited W films if hydrogenolysis is considered [25,26]. We will successively consider:

(i) The catalytic activity (turnover ν in s^{-1} and the mean number of broken carbon–carbon bonds $\bar{x}$) for the three W, WC and W_2C surfaces in order to compare and evaluate our results with regard to those of the literature.

(ii) The selectivities in single and multiple hydrogenolyses in order to analyze the different carbon–carbon bond ruptures for 2MP and MCP.

(iii) The possible surface intermediates and active sites in hydrocarbon reactions on W, WC, W_2C surfaces in comparison with those on metallic or alloy catalysts [27–30].

4.1. Catalytic activity and extensive hydrogenolysis of 2MP, MCP and CH

4.1.1. Catalytic activity

In order to compare the turnover rates for the three distinct surfaces, we used the chemisorption data presented in Table 1. In Table 5 the turnover rates ν in s^{-1} are reported as obtained at low conversion ($\alpha\% < 10$) and using the chemisorption data for H_2 measured at high temperature as described above (e.g. catalyst characterization).

Both for 2-methylpentane and *n*-butane, the turnover rates are similar for WC and W_2C but higher than that obtained on metallic W [17].

The turnover rates on WC and W_2C are close to those observed by Ribeiro et al. [4] in the case of *n*-hexane, but in our case the turnover rates have been calculated from the hydrogen coverage θ_{H2} measured at high temperature. The activation energies on both carbides and on metallic tungsten for 2MP hydrogenolysis are similar to those measured by Ribeiro et al. [4] for *n*H on the same types of carbide (~ 22 $kcal \cdot mol^{-1}$). It has been shown for 2MP that the conversion $\alpha\%$ drops with time on stream at constant hydrocarbon partial pressures (e.g. at 188°C) but less rapidly on WC or W_2C than on W. In Table 6 the turnover rates for 2MP with time on stream at 188°C and constant 2MP partial pressure are reported.

Thus, hydrogenolysis is a structure-sensitive reaction as shown also by Ribeiro et al. [3,4]. These authors invoked the surface decarburization under the stream in excess of H_2 which could be responsible for the deactivation observed in experiments with *n*H. By complementary experiments they demonstrated that the observed deactivation was characteristic of stoichiometric surfaces [4]. However our results confirm a stronger poisoning by carbonaceous deposits on W than on W_2C and WC, even when an initially significant depletion of carbon occurs for WC and W_2C surfaces. The Fig. 1 illustrates the depletion in carbon for a standard WC surface under a stream of H_2 at 330°C. The significant effect acts first for 1 to 4 min and decreases to a much lesser extent with time. At lower temperatures (100 to 200°C) the amount of CH_4 formed is undetected. The decreases of $\alpha\%$, υ in s^{-1} and $\bar{x}$ led us to assume that the

Table 6
Turnover rates for 2MP with time on stream at 188°C and constant 2MP partial pressure

t (min)	W $\upsilon \cdot 10^3$ (s^{-1})	WC $\upsilon \cdot 10^3$ (s^{-1})
0	2.92	9.14
1	1.97	4.39
3	1.41	2.31
5	0.08	2.26

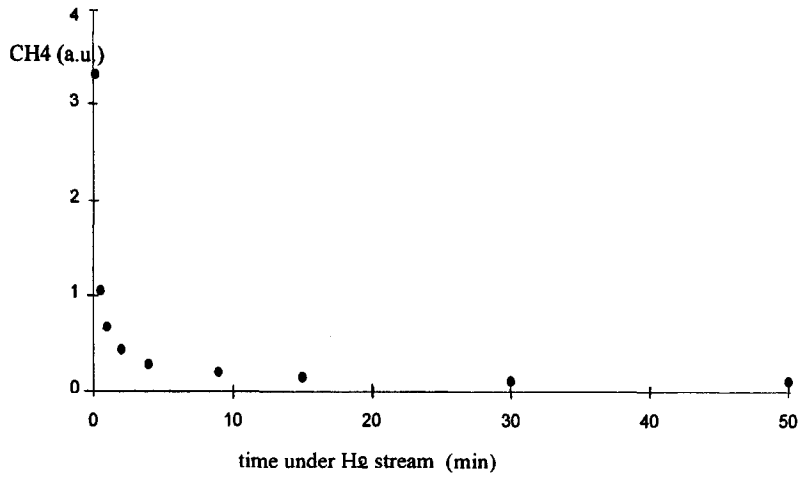


Fig. 1. Depletion in carbon for a WC surface under H_2 at 330°C.

poisoning of the active sites could modify the adsorbed sticking time of the molecule or prevent the readsorption. This raises the question of the nature of the active sites on W, W_2C and WC surfaces.

In the case of MCP we noticed a great difference with 2MP concerning the turnover rates calculated from H_2 chemisorption data at high temperature as seen in Table 5. The turnover rates are much higher on W surfaces compared to W_2C and WC surfaces at lower temperatures which seems to be an effect inherent to the structure of the molecule. At higher temperatures the turnover rates are comparable for all three surfaces, the activation energies also being similar 23 kcal · mol$^{\pm 1}$. The remarks concerning the poisoning and their consequences on α%, v in s^{-1} and $\bar{x}$ remain the same for MCP. The results agree with those of Anderson et al. [31] showing exceptional turnover rates for MCP on W films in the range 164 to 186°C but rapidly poisoned by deposit of carbonaceous residues.

The results obtained with CH showed production of benzene (BZ) mainly on W and W_2C. The formation of BZ is higher when the surfaces are poisoned by θ_C. For the three surfaces, at low temperature (~ 150°C), we note a single ring hydrogenolysis leading to n-hexane and an extensive hydrogenolysis that increases rapidly with the temperature.

Referring to the work of Leclercq et al. [7,32] on tungsten or molybdenum carbides, it has been emphasized that the dehydrogenation activity of CH depends strongly on the carbide surface stoichiometry. A stoichiometric deficit in carbon in the case of WC favors CH dehydrogenation. In our case, we indeed find that the formation of BZ is the most important on metallic W when there is a surface poisoning by carbonaceous residues. Fresh WC and W_2C surfaces do not lead to the CH dehydrogenation in BZ, that we consider as an intrinsic property of these carbides.

The principal reactions of the CH on the three surfaces are the single and extensive ring hydrogenolyses with activities following the order: $W_2C \geq WC > W$ between 190 and 233°C with single hydrogenolysis and $W_2C \sim WC \sim W$ at higher temperatures with an extensive hydrogenolysis. The apparent activation energies are the same on W, WC and W_2C surfaces 16 kcal · mol$^{\pm 1}$.

4.1.2. Extensive hydrogenolysis of 2MP, MCP and CH

In Section 3 we noticed a shift towards extensive hydrogenolysis with the increase of the

Table 7
Mean number of broken carbon–carbon bonds per converted molecule $\bar{x}$ versus temperature

	2MP		MCP	
	T (°C)	$\bar{x}$	T (°C)	$\bar{x}$
W	150	0.89	151	1.03
	330	2.71	330	3.20
WC	141	1.21	144	2.04
	330	5	330	5
W_2C	195	1.04	195	2.15
	330	3.09	330	2.92

temperature for the three surfaces W, W_2C and WC. In Table 7 are compared the values for $\bar{x}$ at different temperatures which show for both 2MP and MCP at lower temperatures (~ 150°C) the following ordering: WC > W_2C > W then changing at 330°C to the ordering: WC ≥ W_2C > W. These results agree also with those obtained by Ribeiro et al. [4] for hydrogenolysis of *n*H at 157°C on WC and W_2C surfaces. If one considers the characteristic differences of $\bar{x}$ at isotemperature on the surfaces studied for each hydrocarbon studied (2MP, MCP, CH) and the maximum in the yield curves with temperature in Refs. [7,12], the WC carbide seems to be more agressive towards the C–C bonds which could be related to the properties of fresh surfaces of WC, W_2C and W.

4.2. Analysis of the various carbon–carbon bond breakages for W, W_2C and WC surfaces

The analysis of the data reported in Table 8, on the single bond breaking C_{III}–C_I, C_{II}–C_I, C_{II}–C_{II} and C_{III}–C_{II} (C_{III} tertiary, C_{II} secondary, C_I primary carbon atom) as well as the ratios corresponding to *iso*C5/*n*C5 and Σisomode/ΣC2 mode as defined by Anderson [33] leads to the following order for the Σisomode/ΣC2 mode for 2MP: W > W_2C > WC. Fig. 2 represents the plot of the ratio Σisomode/ΣC2 mode versus the ratio *iso*C5/*n*C5 for 2MP single hydrogenolysis reactions on various metals or alloys obtained by Garin et al. [30], where the data at low temperature (140 to 180°C) and low conversion (α% < 10) obtained on W, W_2C and WC are inserted.

Therefore it appears that at low temperature W has an isomode/C2 mode character similar to Ni, this character being moderated in the presence of carbon shifting progressively for W_2C and WC to that of Pt or Pd. It never looks like for Rh, Ir or Ru although Ru is often taken

Table 8
Comparison of the single carbon–carbon bond cleavage modes of 2MP on W, WC and W_2C surfaces

Catalyst	T°C	C_{III} - C_I	C_{II} - C_I	C_{II} - C_{II}	C_{III} - C_{II}	isoC5 / nC5	Σ isomode / Σ C2 mode
W	216	0.70	0.18	0.07	0.05	0.26	3.00
	197	0.65	0.21	0.08	0.06	0.32	2.40
	188	0.63	0.23	0.09	0.05	0.36	2.10
	174	0.61	0.24	0.10	0.05	0.39	1.90
WC	200*	0.26	0.25	0.20	0.23	0.96	1.09
	188	0.28	0.22	0.22	0.28	0.78	1.27
	141	0.39	0.27	0.17	0.17	0.69	1.27
W_2C	188	0.29	0.16	0.23	0.32	0.55	1.56
	141	0.31	0.19	0.18	0.32	0.61	1.70
Statistical values		0.40	0.20	0.20	0.20	0.50	1.50

[a] From Ref. [7].

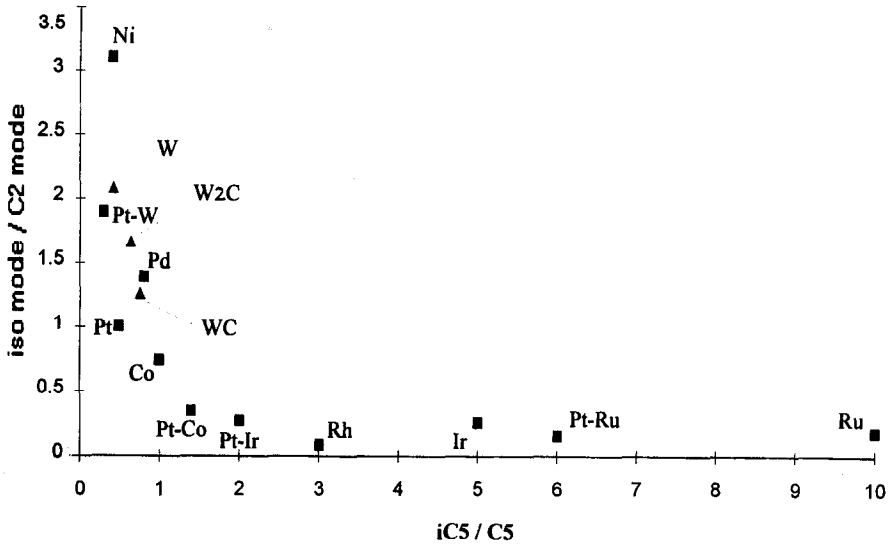


Fig. 2. 2MP single hydrogenolysis on W, WC, W_2C and on metals and alloys from [30].

for comparison with WC or W_2C. Furthermore the poisoning of W, W_2C and WC versus time under the flow of reactant proceeds by a selective deposit of carbonaceous entities on the sites responsible for the isomode mechanism [12].

We assume the presence of two different active sites responsible for the isomode and the C2 modes respectively. The 'isomode sites' are more important on metallic W surfaces while the 'C2 mode sites' would be favored on W_2C and WC surfaces. As seen in Table 8, the temperature in the range 140 to 200°C has little influence on the ratios Σisomode/ΣC2 mode and *iso*C5/*n*C5. At higher temperatures (> 200°C) these ratios are disrupted by the contribution of extensive hydrogenolysis. The analysis of the data for the single C–C bond ruptures of MCP are reported on Table 9. The ratios Σisomode/ΣC2 mode and 3MP/*n*H are, respectively, lower and higher than expected by statistics and almost constant in the temperature range 120 to 240°C. Comparison of the results

Table 9
MCP single carbon-carbon bond ruptures on W, WC and W_2C surfaces

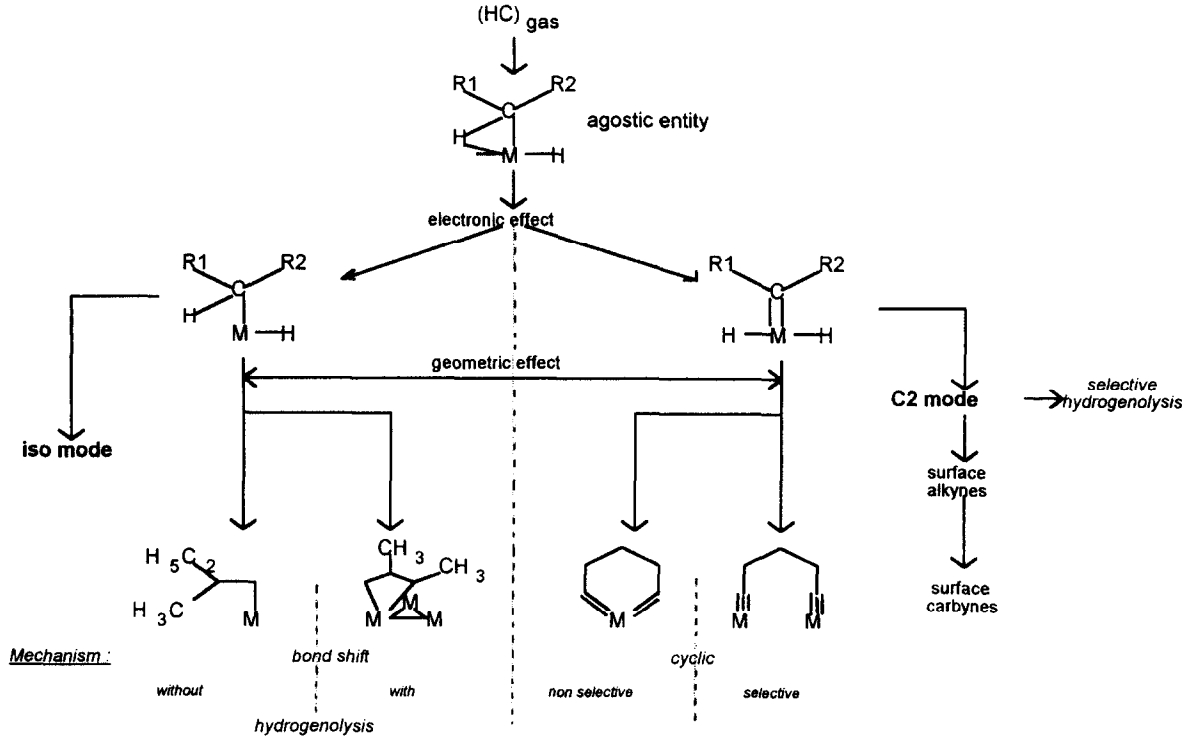
Catalyst	C_I - C_{III}	C_{II}-C_{III}	C_{II}-C_{II}	C_{II}-C_{II}	$\frac{\sum \text{isomode}}{\sum \text{C2mode}}$	
W	0.10	0.17	0.37	0.36	0.37	2.11
WC	0.25	0.05	0.40	0.30	0.43	7.00
W_2C	0.16	0.08	0.38	0.38	0.31	4.75
statistical values	0.17	0.33	0.33	0.17	1	0.50
WC *	0.17	0.10	0.43	0.30	0.37	3.00

[a] From Ref. [7].

obtained with Rh catalysts shows important differences in the various C–C bond breakages. Here again, W, WC and W_2C surfaces behave more like Pt, Pd catalysts [34]. The 3MP/nH ratio is characteristic of the hydrogenolysis of MCP on Pt single crystals or Pt large particles [28–30]. The single hydrogenolysis of MCP is favoured via the C2 mode. No ring enlargement is detected whatever the experimental conditions we used on the three surfaces studied.

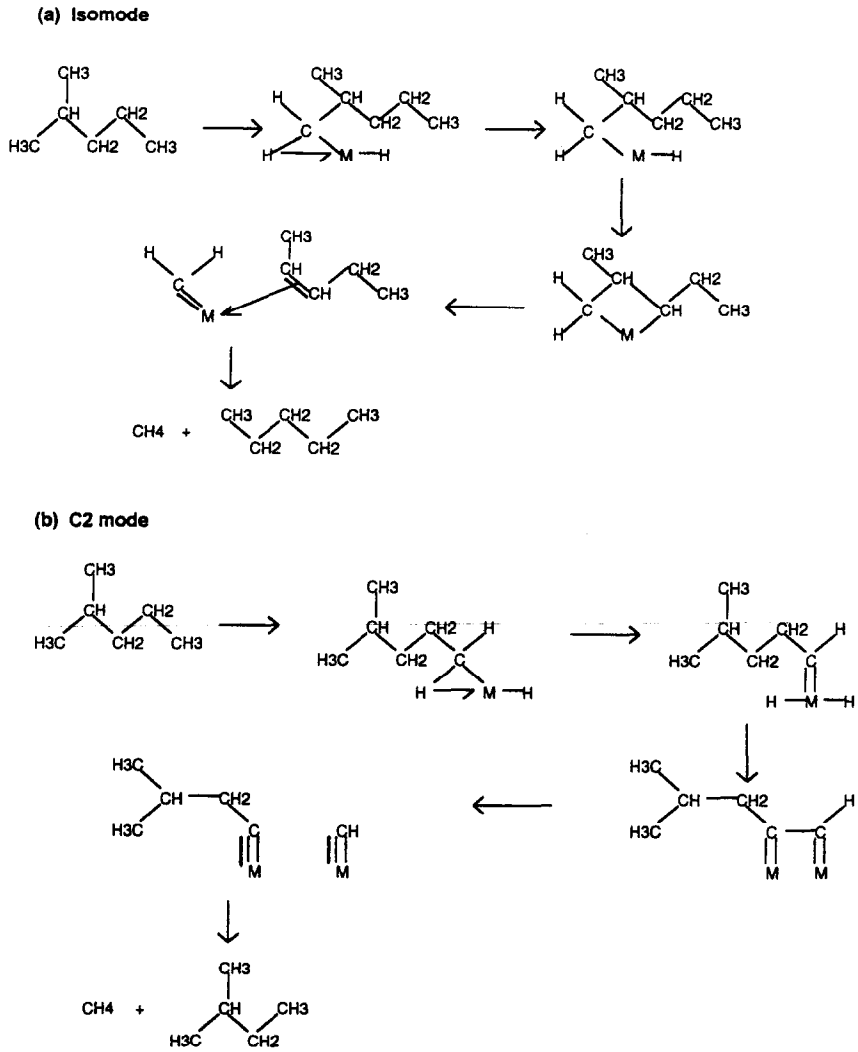
4.3. Approach to the mechanisms and the possible intermediate species

The analysis of the results developed above for the reactions of 2MP, MCP, CH on W, W_2C, WC surfaces confirm the metallic character of the carbided W surfaces placing them between Ni and Co for both single and extensive hydrogenolysis of 2MP and MCP which leads to the following order: Ni > W > W_2C > WC > Co > Rh ≈ Ir ≈ Ru. Some analogies with Pt or Pd are stressed for W_2C and WC but neither isomerization, dehydrocyclization nor ring enlargement were observed under our experimental conditions, in agreement with the literature [3–6]. On monometallic catalysts like Pt or Pd, the relative rates for isomerization are much higher than those for hydrogenolysis and the bond-shift and cyclic mechanisms were interpreted according to geometric and electronic factors [27,28]. However, on other monometallic catalysts like Ir and Ru, or on bimetallic catalysts, the relative rates for isomerization are much lower compared to those for hydrogenolysis. Furthermore, the changes in the selectivity of hydrogenolysis (isomode versus C2 mode) are important from one catalyst to another. For Ir or Ru monometallic catalysts, as for bimetallic catalysts compared to Pt or Pd monometallic catalysts, we consider that other species may be activated complexes of the adsorbed species as previously proposed [29,30]. In this manner on W, W_2C and WC surfaces, the question to be



Scheme 1. General mechanism for isomerization and hydrogenolysis of C5 hydrocarbons (taken from Ref. [30]: (1) R1 = H, R2 = sec. butyl for metallacyclobutane species and σ-alkyl species; (2) R1 = H, R2 = n-butyl for cyclic mechanisms.

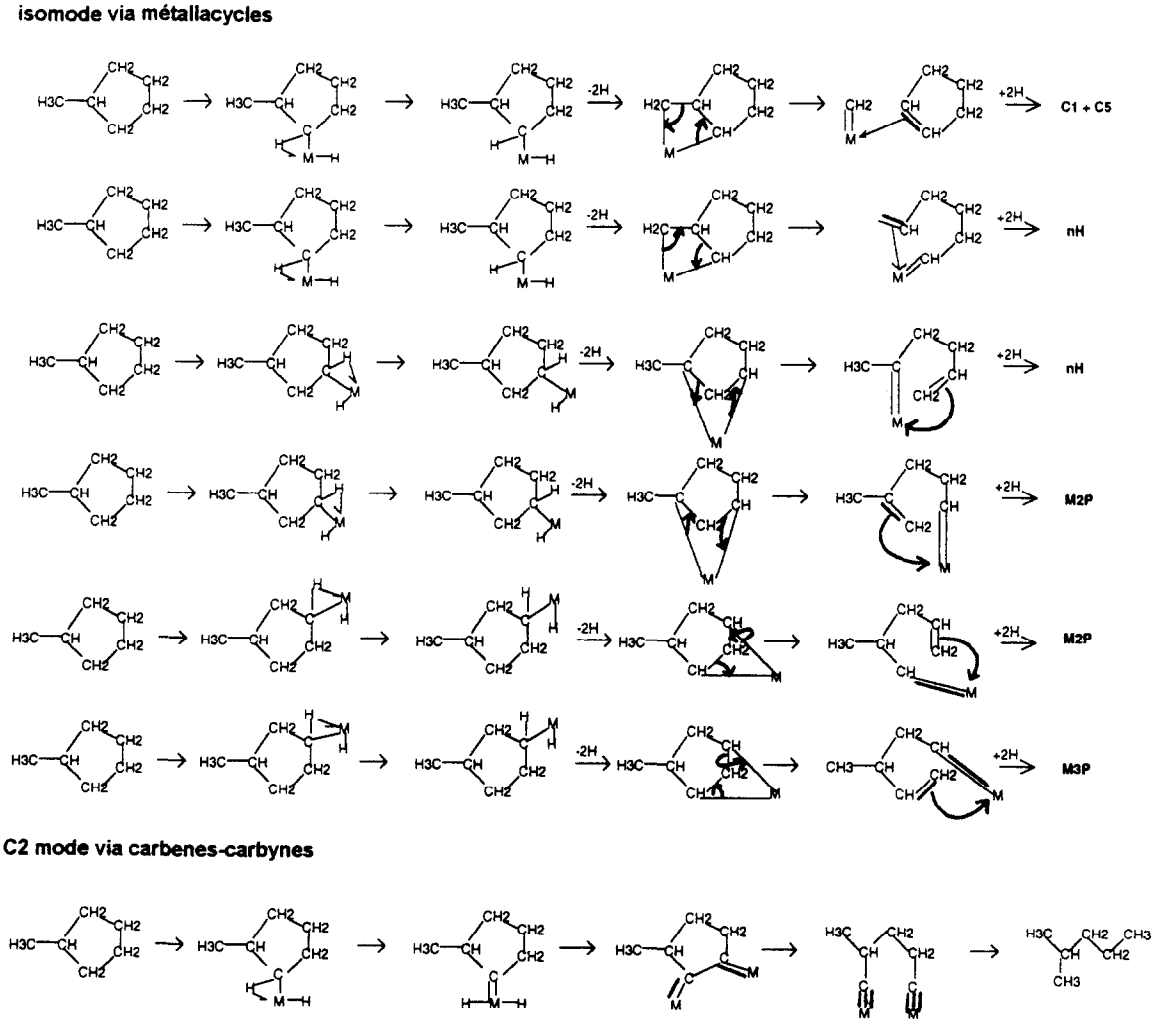
addressed is, how is the C2-unit mode or iso-unit mode formed and how are interconverted species involved in these two modes? For the reactions of hydrocarbons on metals and alloys we already postulated intermediates related to the nature of the active sites and analyzed using concepts based on organometallic chemistry [29] and more generally we developed a proposal for an agostic precursor species simplifying the interpretation of the various reaction mechanisms for isomerization and hydrogenolysis via a limited number of precursor species [29,30]. It also allows us to account for the first steps of adsorption on Pt, Pd and Ir catalysts as on bimetallic or alloy catalysts and agrees very well with the kinetic model proposed by Frennet [35,36], where a reactive adsorption step occurs, followed by reactive surface dehydrogenation steps without any release of the sites occupied by adsorbed hydrogen. In Scheme 1, the agostic species is shown to be the first species adsorbed on the surface. This species leads to the precursors σ-alkyl for the isomode or the carbene for the C2 mode. The relative contribution of these two precursors must be governed by the nature of the active sites on the surface and in terms of



Scheme 2. Single hydrogenolysis of 2MP: leading via (a) isomode to nC5 and (b) C2 mode to iC5.

electronic or geometric factors. We consider that Scheme 1 is also valid for our results obtained with 2MP and MCP on W, W_2C and WC surfaces. Therefore the single hydrogenolysis via the isomode assumes firstly an agostic precursor species [37] which will initiate the formation of σ-alkyl species then leading to tungstenacyclobutane and carbene–olefin complexes as proposed by Garin et al. [38] to explain the bond shift mechanism in isomerization accompanied by hydrogenolysis on Pt catalysts. The single hydrogenolysis via the C2 mode supposes that the agostic species leads to the precursor carbene species and then to dicarbyne species also responsible for single hydrogenolysis. Schemes 2 and 3 represent examples of single hydrogenolysis for 2MP and MCP via the iso and C2 modes.

The activation energies obtained for hydrogenolysis of 2MP and MCP are nearly the same on the three surfaces, 22 ± 4 kcal · mol$^{\pm 1}$; they are relatively low in comparison with metals like Pt or Ru [38]. However they correspond to the cracking of the hydrocarbon by single or extensive hydrogenolysis. Keller et al. [7] have already found that on WC, the activation energies are comparable to the desorption energies of adsorbed hydrocarbons on metals [39].



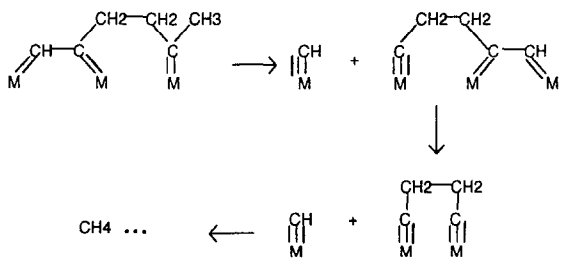
Scheme 3. Single hydrogenolysis of MCP: (a) isomode and (b) mode.

The W, WC and W_2C surfaces reflect the same properties (single and extensive hydrogenolysis) as on metals (Ni, Co, Rh, Ir, Ru); it is reasonable to consider that the binding energies are nearly the same as on metals and that the limiting step on the W, WC and W_2C surfaces is the desorption. There must be competition between the kinetic production of a molecule and its subsequent hydrogenolysis. This can be explained by the presence of multiadsorbed species on the surface, as mentioned earlier by Gault [27] to account for the extensive hydrogenolysis on Ni, Co or even Pt metals leading to a large excess in CH_4 according to the Scheme 4.

The extensive hydrogenolysis will then be more consistent with the C2 unit mode. Further the poisoning of W, W_2C and WC versus time under the flow of reactant is more selective for the isomode itself greater on W than on W_2C or WC surfaces.

At this stage of the discussion we should be able to correlate the changes in the mechanisms responsible for the single hydrogenolysis (via isomode and C2 mode) and extensive hydrogenolysis (via multiadsorbed species) with various contributions of the surfaces sites that we called 'isomode sites' and 'C2 mode sites'.

The main question to be addressed is: Are the active sites responsible for the single or extensive hydrogenolysis the same on W, W_2C and WC surfaces? We have seen that there is a selective poisoning of the 'isomode sites' on W (excluding the decarburization of W_2C and WC). Furthermore an increase in the carbonaceous residues coverages decreases the contribution of the extensive hydrogenolysis apparently in favour of the single hydrogenolysis. The reversible and irreversible carbonaceous residues strongly dehydrogenated CH_x ($x \leq 2$) can induce important effects on the geometric and electronic structures of the W atoms constituting the W, W_2C and WC structures. As shown by Maire et al. [40,41] large work function changes were observed on Ni single crystal surfaces (111), (100), (110) as a function of θ_C resulting from strong adsorption of CH_4, C_2H_6 or neo-C_5H_{12}. On the W, W_2C, WC surfaces substantial surface dipoles or changes in Fermi level can be induced by carbon as already observed by XPS spectra of the valence band when passing from W to WC bulk samples [13–15,42].



Scheme 4. Extensive hydrogenolysis according to Gault [27].

If Ru, Co, Ir and Mo behave differently from Ni, Pd, Pt (even W_2C, WC) it may be, as pointed out by Saillard et al. [43] from the plot of relative electron distribution as a function of electron count, that, to the right side of the transition series, surfaces should be negative with respect to the bulk, and at the left side of the transition series, surfaces should be positive.

Our knowledge about the active sites for (single or extensive) hydrogenolysis is still insufficient and unclear at this time: they remain the subject of continuing study on model surfaces by surface science techniques [44].

5. Conclusion

From this study we have confirmed the difficulty of preparing and maintaining clean, stoichiometric surfaces of W, W_2C and WC [12,16]. Special attention has been paid to the characterization of the various samples because of the versatility of the active surfaces due to non-stoichiometric compositions (excess of carbon, decarburization, oxidation by oxygen [17]). The use of 2MP, MCP and CH as test molecules allowed us to determine the intrinsic properties of W, W_2C and WC surfaces in favour exclusively of simple or multiple hydrogenolysis. In

agreement with the work of Boudart et al. [3–6], we confirmed that reforming reactions do not take place in our experimental conditions and in the temperature range of 80 to 400°C. In previous work, traces of isomerization products due to skeletal rearrangement of 2MP, were observed at low temperature, on bulk tungsten carbides, but they represented only a few percent of the total reaction process [7]. It has been proven that these WC and W_2C surfaces were not representative of total oxygen free fresh reproducible WC and W_2C samples. The reactions of dehydrogenation of CH to BZ were almost absent under our experimental conditions, they appeared only when a strong poisoning by carbonaceous residues was observed.

The turnover rates obtained with 2MP on the three different surfaces show the activity ordering: WC > W_2C > W. With MCP the ordering was changed: W > WC > W_2C. The extensive hydrogenolysis character of WC is higher than for W_2C and W surfaces.

It is a surface property of fresh and reproducible WC, W_2C and W samples. The various mechanisms of hydrogenolysis reactions of 2MP, MCP and CH on W, W_2C and WC surfaces are described and related to different possible reaction intermediates deduced from concepts of organometallic chemistry.

The analysis of the data for the reactions of 2MP, MCP and CH on W, W_2C, WC surfaces confirm their metallic character placing them between Ni and Co for both single and multiple hydrogenolysis.

Two reaction mechanisms (the isomode and C2mode according to Anderson [33]) have been proposed to explain the single hydrogenolysis on WC, W_2C and W surfaces. The hydrogenolysis by isomode is attributed to tungstenacyclobutane intermediates and the C2mode of hydrogenolysis to the interconversion of dicarbene into dicarbyne species. The mechanism leading to multiple hydrogenolysis could be explained by the existence of multiadsorbed species as already proposed by Gault on Ni and Co surfaces [27]. The isomode mechanism is selectively poisoned by carbonaceous residues. The question concerning the nature of the sites responsible for the isomode and the C2 mode hydrogenolysis remains the subject of continuing study on model surfaces by surface science techniques [44].

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