Catalysis Letters 47 (1997) 63–69

Mechanism of but-1-ene hydrogenation and isomerization on oxygen-modified bulk tungsten carbides using deuterium tracer studies. Effect of oxygen treatment on hydrogen dissociation

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Received 28 January 1997; accepted 28 May 1997

The catalytic behaviours of bulk tungsten carbides differently modified by air treatments have been studied in hydrogenation (or deuteration) and double-bond isomerization of but-1-ene, in hydrogen/deuterium exchange of methylcyclopentane, as well as in hydrogen dissociation via H_2/D_2 exchange. Two kinds of catalyst samples have been studied. The first sample has been treated by air at moderate temperature (350°C) and the second at high temperature (700°C). It was found that, for but-1-ene reaction at temperatures varying between 30 and 100°C, but-2-enes are the main products formed, and only a small amount of hydrogenated products was detected for both catalysts. Two possible double-bond migration mechanisms by an intramolecular hydrogen migration, either with π-olefinic, π-allylic and metallacyclobutane or with π-olefinic and π-allylic species interconversions are deduced; these mechanisms occur without the participation of dissociated hydrogen or deuterium atoms. However, it has been demonstrated that the hydrogen dissociation temperature is a function of the air treatment of the bulk tungsten carbide, even if this property has no effect on the hydrogenation of but-1-ene to *n*-butane. Thus, in order to see the influence of oxygen modification, a more detailed study has been carried out. Starting from a bulk tungsten carbide without oxygen, several controlled oxygen additions have been made, leading to four different samples. The HD formation has been analyzed for each sample as a function of temperature.

Keywords: but-1-ene hydrogenation and isomerization, deuterium tracer studies, hydrogen dissociation, oxygen-modified bulk tungsten carbides

1. Introduction

Recent studies have shown that the oxygen modification of bulk tungsten carbides at moderate temperature leads to a bifunctional catalytic behaviour for hydrocarbon conversion [1–4], with association of metallic and acidic functions involved in dehydrogenation/hydrogenation and isomerization steps, respectively. The acidic reaction pathways have been widely studied on these catalysts in alkane [1] and olefin [2] reactions performed at 350°C and it has been demonstrated that carbenium ion intermediates are responsible for both cracking and isomerization reactions [2]. On the other hand, bulk tungsten carbides treated by a controlled air leak in H_2 at higher temperature [1] exhibit a metallic behaviour for alkane reactions at 350°C, with metallacyclobutanes and σ-alkyl species as intermediates for cracking and isomerization, respectively. However, less attention has been given to the hydrogenating properties, at lower temperatures than 350°C, of oxygen-modified bulk tungsten carbides. This implies also the study of the influence of oxygen treatment on the hydrogen dissociation temperature.

In the present work we focus our attention on the comparison of the olefin hydrogenation behaviour, between 30 and 100°C, for different kinds of oxygen-modified bulk tungsten carbide samples.

The hydrogenation and the double-bond migration mechanisms of but-1-ene were analyzed by deuterium tracer studies. As only few amounts of hydrogenated product (*n*-butane) have been detected and to investigate further the hydrogen dissociation, H_2/D_2 exchange reactions were studied.

2. Experimental

2.1. Catalyst preparation and characterization

Catalyst preparation. The catalysts were prepared at the Laboratoire de Catalyse Hétérogène et Homogène of Lille (G. and L. Leclercq) and the characterizations were performed at the Laboratoire de Catalyse Hétérogène of Brussels (A. Frennet) in collaboration under a European Community Contract (C.E.E.ST2J 04607-CCTT). The samples were prepared from WO_3 by reduction followed by carburization with a mixture of CH_4/H_2 (20/80) at 800°C and passivated by the method already described [5,6].

Catalyst characterization. The material was then

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characterized by X-ray diffraction, physical adsorption (BET using N_2 and Kr), chemical adsorption of H_2 and CO, and TPR under H_2, O_2 and inert gas [5]. The H_2 adsorption, comparable with the values obtained in the litterature, as well as the TPR (temperature-programmed reaction) under H_2 and O_2 did not allow us to have further information about the activity of the different oxygen-modified samples in the but-1-ene reaction or in the hydrogen dissociation. XPS studies of oxygen-modified bulk tungsten carbides only at temperatures below 350°C were carried out in our laboratory. These results gave us some information about the global surface composition of bulk tungsten carbides treated by oxygen, that means the presence of chemisorbed oxygen, of WO_3 and of W_2O_5 species [7]. More recent studies by XPS [8] have shown that the in situ reduction of these oxide species above 350°C (450 and 550°C) leads to the formation of WO_2 species.

Catalyst treatments. Before each catalytic experiment, the catalyst was activated under H_2 (D_2) flow at atmospheric pressure, at 700°C for 5 h. On these samples, oxygen was introduced by a controlled air leak of $\sim$ 1–2% O_2 in H_2 at different temperatures and for different times:

- at 350°C during a few minutes; this sample will be denoted $WC_{(O\text{-}350)fm}$,
- at 350°C during 3 h; the catalyst will be denoted $WC_{(O\text{-}350)3h}$,
- at 700°C during 4 h; it will be denoted as $WC_{(O\text{-}700)4h}$.

2.2. Catalytic reactions

H_2 or D_2 was purified by passing through a Pt/Al_2O_3 catalyst heated at 150°C, followed by a trap at −198°C. The catalytic reaction was carried out in a glass flow system including a reactor operating at atmospheric pressure. After catalytic activation and cooling to the reaction temperature, a known quantity of but-1-ene (Air Liquide), at constant hydrocarbon pressure of 8 Torr ($760\ \text{Torr} = 1.013 \times 10^5$ Pa), was passed over the catalyst in H_2 or D_2 flow. Two catharometers were inserted upstream and downstream with respect to the reactor, their signals representing the hydrocarbon pressure as a function of time. By this way, the hydrocarbon flow rate could also be calculated. During the catalytic experiment, small amounts of the reaction products were taken off after the reactor at different times. Then, they were analyzed by gas liquid chromatography (GLC) using a 2.5 m, 3.175×10^{-3} m o.d. dimethyl sulfolane column operating at 0°C with a FID. When deuterium was used instead of hydrogen, each product of the reaction was separated by GLC and further analyzed by mass spectrometry (MS) (type CH7 Varian spectrometer).

The but-1-ene reaction at low temperature under hydrogen flow can lead to different products, issued from hydrogenation, double-bond isomerization or skeletal isomerization giving *n*-butane, trans-but-2-ene and cis-but-2-ene or isobutene, respectively. Isobutene was never detected under our experimental conditions.

In this reaction, the isomers selectivity was defined by the following ratio:

$$S_i = \frac{m(\text{trans-but-2-ene}) + m(\text{cis-but-2-ene})}{m(n\text{-butane}) + m(\text{trans-but-2-ene}) + m(\text{cis-but-2-ene})} \times 100 \qquad (1)$$

and the hydrogenation selectivity as:

$$S_H = \frac{m(n\text{-butane})}{m(n\text{-butane}) + m(\text{trans-but-2-ene}) + m(\text{cis-but-2-ene})} \times 100 . \qquad (2)$$

and the conversion as:

$$C = \frac{m(n\text{-butane}) + m(\text{trans-but-2-ene}) + m(\text{cis-but-2-ene})}{m(n\text{-butane}) + m(\text{trans-but-2-ene}) + m(\text{cis-but-2-ene}) + m(\text{but-1-ene})} \times 100 . \qquad (3)$$

The rates of hydrogenation and isomerization are given respectively by:

$$R_H = S_H \frac{CF}{w}; \quad R_i = S_i \frac{CF}{w}, \qquad (4)$$

where F is the but-1-ene flow rate, w the catalyst weight and m(i) the number of moles for the i species.

3. Results

3.1. But-1-ene reaction

Figure 1 shows an example of the evolution of both conversion and isomers selectivity as a function of time during a catalytic test where the contact time of the hydrocarbon is constant. The selectivity is constant

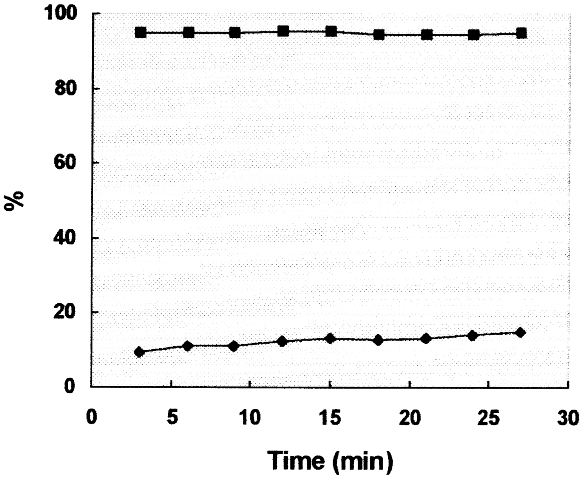


Figure 1. But-1-ene conversion and double-bond migration (isomerization) on $WC_{(O\text{-}700)4h}$ at 50°C. (◆) Conversion (%), (■) S_i (%).

Table 1
Catalytic activities and selectivities for but-1-ene reaction on $WC_{(O\text{-}350)fm}$. S_H are not represented in these tables, but they can easily been deduced from $S_H = 100 - S_i$. T/C represents the trans-but-2-ene/cis-but-2-ene ratio [a]

Temp. (°C)	Flow (mol/s) $\times 10^{-8}$	R_H (mol/(s g_{cat})) $\times 10^{-8}$	R_i (mol/(s g_{cat})) $\times 10^{-8}$	S_i (%)	Conv. (%)	T/C
30	29.8	3.3	44.4	93.0	40.0	1.6
30	51.5	3.2	48.7	93.8	25.2	1.7
50	67.5	–	–	96.0	80.3	1.6
50	80.8	–	–	94.8	73.0	1.8
75	72.0	–	–	94.6	91.1	1.6

[a] Hydrogen pressure: 752 Torr, but-1-ene pressure: 8 Torr.

while the conversion slightly increases. Consequently, the results are compared at the same time for different catalysts. These results have been obtained at 50°C on the $WC_{(O\text{-}700)4h}$ sample, but the same observations have been done for the catalytic tests performed on all the catalysts.

Tables 1 and 2 show the comparison of the catalytic activities and selectivities for but-1-ene reaction at different but-1-ene flow rates and different temperatures for $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$ catalysts, respectively. When the reactions lead to conversions higher than 40%, the hydrogenation and isomerization rates have not been calculated because the approximation of eq. (4) is not valid any more.

Varying the flow rate, the rates of hydrogenation and isomerization remain quite the same; it means that no diffusion occurs. It is evident that the least modified sample, $WC_{(O\text{-}350)fm}$ is the most active, both for hydrogenation and for double-bond isomerization. Hydrogenation reaction is negligible for $WC_{(O\text{-}700)4h}$; R_H does not increase with temperature, it could be an artefact because the very low observed value for butane is in the range of the but-1-ene impurity. The $WC_{(O\text{-}350)fm}$ sample is much less active for hydrogenation than for isomerization. Among the isomers, the trans-but-2-ene is present in majority. The trans-but-2-ene/cis-but-2-ene ratio is independent of the but-1-ene flow (1.3 for $WC_{(O\text{-}350)fm}$ and 1.7 for $WC_{(O\text{-}700)4h}$), of the oxygen treatment and of the reaction temperature.

Table 2
Catalytic activities and selectivities for but-1-ene reaction on $WC_{(O\text{-}700)4h}$ [a]

Temp. (°C)	Flow (mol/s) $\times 10^{-8}$	R_H (mol/(s g_{cat})) $\times 10^{-8}$	R_i (mol/(s g_{cat})) $\times 10^{-8}$	S_i (%)	Conv. (%)	T/C
30	16.3	0.2	4.5	97.7	4.5	1.3
30	19.6	0.05	3.2	98.0	3.2	1.3
50	7.8	0.03	7.1	99.8	22.6	1.4
50	8.6	0.03	7.5	99.8	21.8	1.4
50	15.2	0.05	9.2	99.9	15.4	1.4
100	177.2	–	–	99.5	46.3	1.5

[a] Hydrogen pressure: 752 Torr, but-1-ene pressure: 8 Torr.

3.2. Deuterium tracer studies

3.2.1. Hydrogen/deuterium exchange in the but-1-ene reaction

The tracer studies using deuterium instead of hydrogen were performed on $WC_{(O\text{-}350)fm}$ and on $WC_{(O\text{-}700)4h}$ in the same experimental conditions as those used with hydrogen. The comparison of the deuterium distributions for both kinds of samples are given in table 3. Comparing the results obtained on the two catalysts, the same general features are obtained, i.e.:

– among the *n*-butane obtained, mainly d2 species are formed, coming from the addition of two deuterium atoms in the but-1-ene molecule;

– among the isomerization products, as well as for the remaining but-1-ene, a large majority for the d0 spe-

Table 3
Comparison of the deuterium distributions for $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$. d*i* means that i hydrogen atoms have been exchanged by *i* deuterium atoms [a]

Catalyst $WC_{(O\text{-}350)fm}$

Flow (mol/s) $\times 10^{-8}$	R_H (mol/(s g_{cat})) $\times 10^{-8}$	R_i (mol/(s g_{cat})) $\times 10^{-8}$	Conv. (%)	T/C
65.7	2.0 (5.9%)	31.9 (94.1%)	12.9	1.9

	n-butane	But-1-ene	Trans-but-2-ene	Cis-but-2-ene
d0	10.60	98.20	93.20	93.00
d1	14.80	1.30	6.40	6.50
d2	69.20	0.06	0.30	0.30
d3	4.30	0.03	0.10	0.14
d4	1.10	0.03	0.00	0.06
d5	0.00	0.03	0.00	0.00
d6	0.00	0.04	0.00	0.00
d7	0.00	0.08	0.00	0.00
d8	0.00	0.14	0.00	0.00
d9	0.00	/	/	/
d10	0.00	/	/	/

Catalyst $WC_{(O\text{-}700)4h}$

Flow (mol/s) $\times 10^{-8}$	R_H (mol/(s g_{cat})) $\times 10^{-8}$	R_i (mol/(s g_{cat})) $\times 10^{-8}$	Conv. (%)	T/C
24.6	0.05 (1.8%)	2.9 (98.2%)	3.0	1.9

	n-butane	But-1-ene	Trans-but-2-ene	Cis-but-2-ene
d0	0.00	99.45	98.11	97.22
d1	30.00	0.33	1.89	2.78
d2	70.00	0.22	0.00	0.00
d3–d10 or d3–d8	0.00	0.00	0.00	0.00

[a] Deuterium pressure: 752 Torr, but-1-ene pressure: 8 Torr, reaction temperature: 30°C.

cies, especially for the $WC_{(O-700)4h}$ sample is formed.

In order to explain the results observed for the but-1-ene reaction at 30°C and whatever the oxygen treatment, it can be concluded that:

(i) differently from observed on noble metals, there is no large scrambling of hydrogen and deuterium atoms at the surface since only little amount of *n*-butane resulting from hydrogen incorporation into the molecule is detected (d0, d1);

(ii) concerning the double-bond isomerization it can be explained by an intramolecular hydrogen migration. Two mechanisms could be proposed: the first derived from a mechanism already proposed by Rooney [9,10], implying interconversions between π-olefinic, π-allylic and metallacyclobutane species, as described in scheme 1; the second is similar to the one proposed by Goetz et al. [11], as shown in scheme 2.

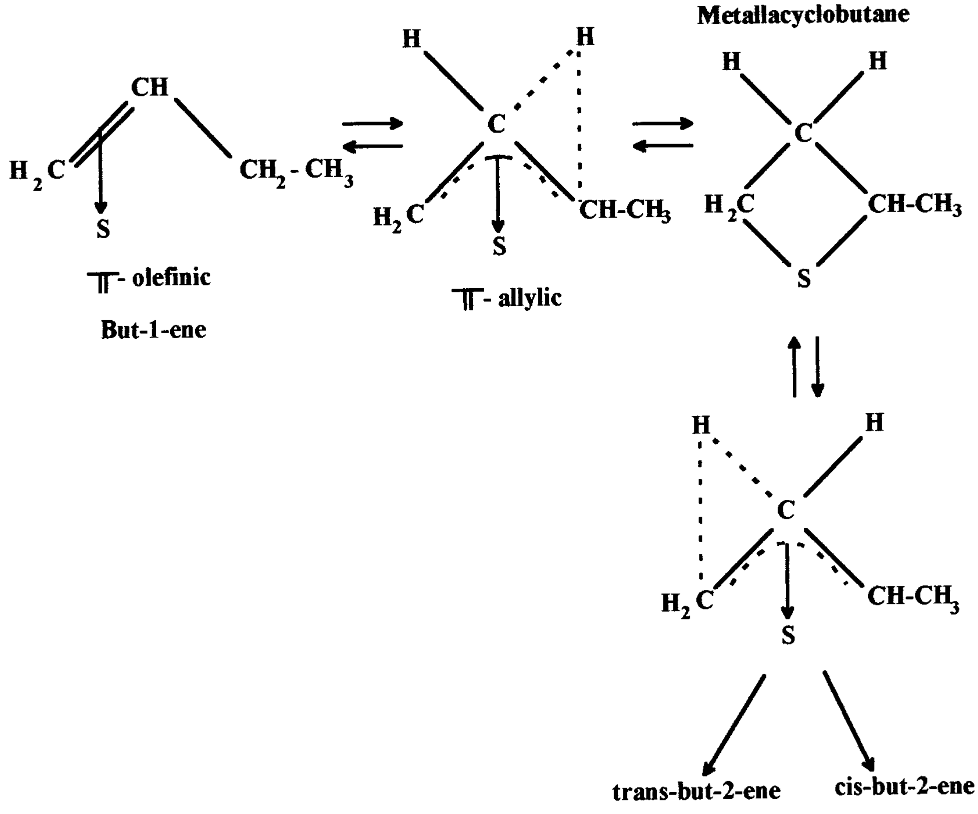
In the first case the hydrogen migration takes place from carbon 3 to carbon 2, then from carbon 2 to carbon 1 and in the second case it proceeds directly from carbon 3 to carbon 1. At this stage of the study it is not possible to distinguish between these two reaction pathways.

3.2.2. *Hydrogen/deuterium exchange for the methylcyclopentane reaction*

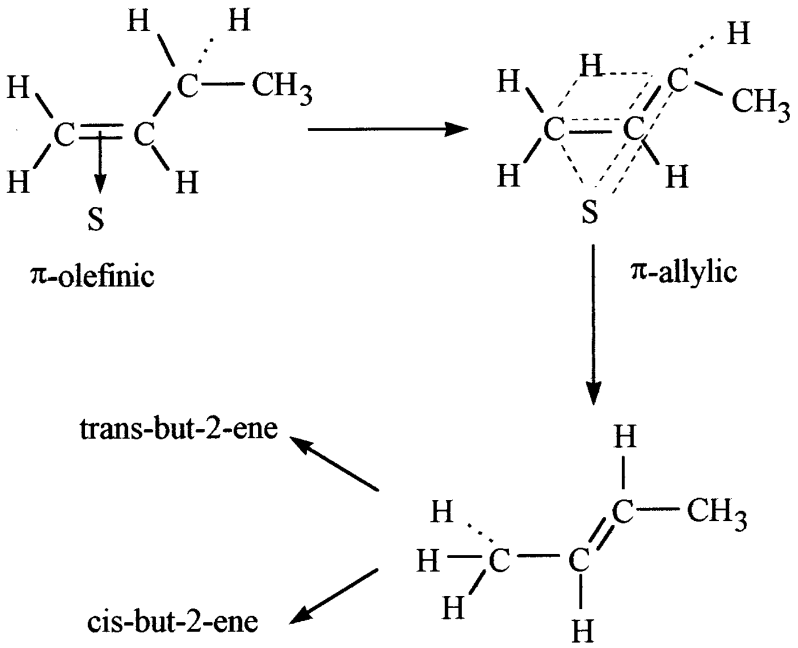
It has been shown, in the first part of this paper, that bulk tungsten carbides treated by air at 350°C ($WC_{(O-350)fm}$) or at 700°C ($WC_{(O-700)4h}$) exhibit very weak hydrogenating properties at low temperatures, between 30 and 100°C. However, the same modified bulk tungsten carbide samples lead to complete hydrogenation of C_6 olefins between 300 and 350°C [1]. As hydrogenation implies hydrogen dissociation on the catalyst, we studied the hydrogen dissociation in presence of methylcyclopentane as reactant. The catalytic tests have also been carried out at 150, 250 and 350°C, which are temperatures comparable with those currently used for C_6 alkane and cycloalkane reactions; hydrogen/deuterium exchange in methylcyclopentane has been analyzed as a function of temperature on the two catalysts previously studied. The comparative results obtained on $WC_{(O-350)fm}$ and $WC_{(O-700)4h}$ are reported in table 4.

On the two catalysts, at 150°C, almost no hydrogen atoms are exchanged. From 250°C hydrogen/deuterium exchange begins, leading mainly to d12 species; this tendency is confirmed and amplified at 350°C. The multiple exchange of 12 hydrogen atoms by 12 deuterium atoms can be explained by the well known "roll-over" mechanism, already proposed for saturated hydrocarbons [12,13]; olefins in the gas phase have never been observed.

According to this mechanism, the hydrogen atoms on the same side of the cycle are first exchanged, then after rotation of the molecule the hydrogen atoms on the other side of the cycle can be exchanged. So, it is possible



Scheme 1.



Scheme 2.

to exchange 12 hydrogen atoms by 12 deuterium atoms in one sejourn of the molecule to the surface.

3.2.3. Hydrogen/deuterium exchange

In this part, hydrogen/deuterium exchange will be studied without the presence of any hydrocarbon. Starting from H_2/D_2 mixture, analyzed by mass spectrometry upstream and downstream of the catalyst, it was possible to determine the HD formation ($m = 3$). The MS has been focused on mass 4, denoted $m(4)$; thus the $m(3)/m(4)$ ratio is not equal to the molar ratio of HD/D_2, but is proportional because no calibration was made. By this way, the hydrogen dissociation temperature of four samples could be determined. Starting from a pure bulk tungsten carbide without oxygen, the preparation of which has already been described [1,2], this catalyst was modified by adding chemisorbed oxygen at −65°C until oxygen saturation of the surface was reached. This procedure has been described in more detail in a previous paper [1]. The $m(3)/m(4)$ ratios are reported in table 5 for different temperatures (−65, −35, 25, 100 and 150°C).

It can be observed that the maximum value obtained

Table 4
Comparison of the hydrogen/deuterium exchange in methylcyclopentane as a function of temperature [a]

Catalyst $WC_{(O-350)fm}$

	150°C	250°C	350°C
d0	99.55	81.11	33.74
d1	0.00	0.00	0.04
d2	0.00	0.00	0.36
d3	0.00	0.08	0.02
d4	0.00	0.03	0.05
d5	0.00	0.06	0.09
d6	0.00	0.11	1.04
d7	0.03	0.15	0.11
d8	0.05	0.31	0.37
d9	0.12	0.61	1.04
d10	0.20	2.26	4.93
d11	0.05	2.38	11.87
d12	0.00	12.88	47.05

Catalyst $WC_{(O-700)4h}$

	150°C	250°C	350°C
d0	99.47	72.43	20.23
d1	0.00	0.00	0.22
d2	0.00	0.00	0.51
d3	0.00	0.02	0.05
d4	0.00	0.08	0.13
d5	0.00	0.17	0.16
d6	0.00	0.32	0.45
d7	0.00	0.34	0.24
d8	0.00	0.53	0.61
d9	0.00	0.81	0.95
d10	0.07	2.28	3.79
d11	0.10	3.95	13.47
d12	0.37	19.07	59.18

[a] Deuterium pressure: 755 Torr, methylcyclopentane pressure: 5 Torr.

Table 5
$m(3)/m(4)$ ratios at different temperatures as a function of oxygen addition

Catalyst	−65°C	−35°C	25°C	100°C	150°C
"pure WC"	0.64	0.65	0.66	–	–
after 1st oxygen addition	0.03	0.09	0.11	–	–
after 2nd oxygen addition	0.0	0.0	0.03	0.22	0.66
after 3rd oxygen addition	0.0	0.0	0.0	0.18	0.49

for the $m(3)/m(4)$ ratios is around 0.65 which corresponds probably to the equilibrium value reached from the initial mixture, H_2–D_2. It is well known that hydrogen dissociation occurs at very low temperatures on metallic surfaces but at higher temperatures on acidic oxides [14]. It can be deduced from these results that on pure bulk tungsten carbide, the hydrogen dissociation occurs at very low temperature (−65°C) confirming the metallic behaviour of this sample as already deduced for hydrocarbon reforming reactions at 350°C [2,15]. After the first oxygen addition, only little exchange is observed at −65°C and it is necessary to increase the temperature to dissociate hydrogen (or deuterium), because at 25°C, the $m(3)/m(4)$ ratio is only 0.11 compared to 0.65 at −65°C on pure bulk tungsten carbide. The evolution is the same after the second oxygen addition. It means that after the first and second oxygen additions the metallic behaviour of the initial pure bulk tungsten carbide decreases. This is in good agreement with the results obtained for hydrocarbon reforming at 350°C on oxygen-modified bulk tungsten carbide, where it has been demonstrated that modification of a pure tungsten carbide (characterized by metallic properties) by adsorbed oxygen reduces the metallic properties, induces acidic sites [15] and results in a partial oxidation of the surface. The "in situ" reduction of these species under hydrogen flow at temperatures lower than 350°C results in the formation of some reduced species WO_{3-x}. These reduced tungsten oxides species are known to exhibit acidic properties for hydrocarbon conversion at 350°C. That is why we assume the presence of some non-stoichiometric tungsten oxide species [8] after the different oxygen additions and reductions under the hydrogen (or deuterium) reactant flow.

4. Conclusion

But-1-ene hydrogenation studied between 30 and 100°C on both modified bulk tungsten carbides, $WC_{(O\text{-}350)fm}$ and $WC_{(O\text{-}700)4h}$, treated by an air leak of ~ 1–2% O_2 in H_2 at 350 and 700°C, allows us to put forward the following points:

(i) Between 30 and 100°C, there is almost no hydrogenation (deuteration) on the two kinds of samples studied, but only double-bond isomerization occurs, explained by an intramolecular hydrogen migration. This mechanism could proceed via two different reaction pathways, one implying an interconversion between π-olefinic, π-allylic and metallacyclobutane species and the other an interconversion between π-olefinic and π-allylic species.

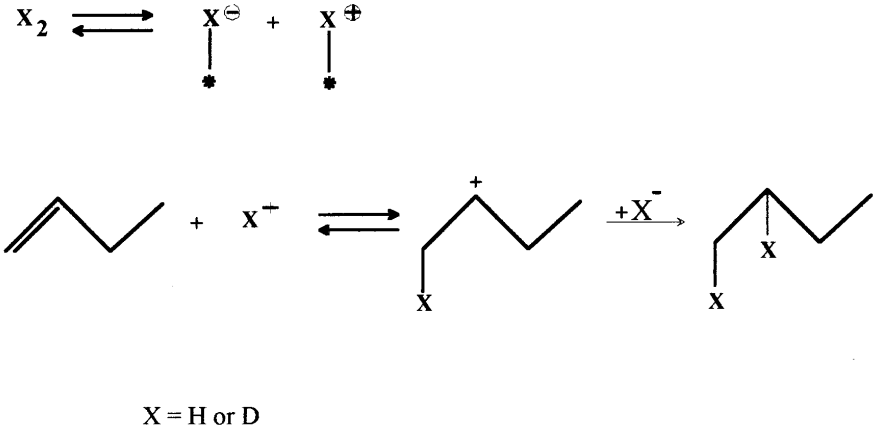
(ii) Concerning the sample $WC_{(O\text{-}700)4h}$ presenting a metallic behaviour for hydrocarbon reforming at 350°C, it has already been demonstrated, that, at this temperature [2], alkane skeletal isomerization and cracking proceed by σ-alkyl and metallacyclobutane species, respectively. The same kind of intermediates could also be considered for but-1-ene isomerization at 30°C. Although the hydrogen dissociation could be possible on this "metallic" surface, hydrogenation does not occur. Two reasons could be proposed:

– either the hydrogen dissociation and the olefin adsorption take place on the same surface sites and thus the hydrocarbon layer prevents the hydrogen dissociation,

– or the hydrogen dissociation and the olefin adsorption sites are not the same and thus the hydrocarbon layer does not prevent the hydrogen dissociation but it is responsible for geometrical blocking by hindering the H migration up to the olefin [16].

(iii) It is possible that on the more acidic sample, the limiting factor for n-butane formation is the hydrogen dissociation, because we have shown that for the acidic surfaces hydrogen dissociation is a function of the oxygen treatment. It could also be possible that at 30°C hydrogen dissociation only begins slightly giving only a little amount of n-butane as described in scheme 3.

(iv) Previous XPS studies [7] have shown that the



X = H or D

Scheme 3.

treatment of bulk tungsten carbides by oxygen leads to the formation of chemisorbed oxygen, of W_2O_5 and WO_3 species. The relative ratios of these species are a function of the temperature treatment by oxygen; at moderate temperature ($\leqslant 350°C$), chemisorbed oxygen, as well as W_2O_5 have been detected in majority and at higher temperature there is a predominance of WO_3. More recent XPS studies [8] have revealed that the "in situ" reduction of WO_3 above 350°C (450 and 550°C) leads to the formation of WO_2, characterized for its metallic properties. That explains why bulk tungsten carbides modified by air at moderate temperature exhibit acidic properties for but-1-ene reaction and hydrogen dissociation, and that the samples treated at high temperature show metallic properties.

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