Catalytic Activity of Bulk WO_3 for the Reforming of Hexanes and Hexenes

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The effects of the reduction process, under a hydrogen flow, of a bulk WO_3 tungsten oxide powder on the reactivity at 350°C of 2-methylpentane (2MP) and 4-methyl-1-pentene (4M1Pene) were investigated. The best experimental conditions to obtain a stable state exhibiting interesting skeletal isomerization properties were determined. Catalyst characterization by XPS, XRD, TPR, and surface area measurements allowed us to propose some intermediates phases and the corresponding nature of active sites formed during the reduction process of the WO_3 tungsten oxide. Correlations between these catalyst characterizations and the catalytic properties show that the WO_3 phase is initially inactive for both alkanes and alkenes reactions. When the $W_{20}O_{58}$ phase is formed, which corresponds to the first reduction step of WO_3, the surface becomes acidic in character, leading to the skeletal isomerization of alkenes by a monofunctional acidic mechanism. The reduction of the $W_{20}O_{58}$ tungsten oxide occurs in two parallel ways, to WO_2 and W_3O. When this reduction is performed at moderate temperature (350°C), a stable surface composed of these two phases (WO_2 and W_3O) is obtained. This surface is active and very selective for the skeletal isomerization reactions of alkanes and alkenes. This catalytic behavior has been interpreted with the aid of two mechanisms: a bifunctional one on the WO_2 phase and a monofunctional metallacycle one on the W_3O phase.   © 2000 Academic Press

Key Words: tungsten oxides; isomerization of hexanes and hexenes; reduction temperature; reaction mechanism.

1. INTRODUCTION

It is well-known from the literature that tungsten or molybdenum (bulk or supported) oxides exhibit interesting properties for skeletal rearrangements of hydrocarbons (1–7). However, it was reported that the catalytic properties of these oxides are modified under operating conditions by hydrogen due to their high reducibility. Some authors (1, 3, 6, 7) have tried to establish correlations between the oxidation state of the surface tungsten atoms and the catalytic properties, but the identification of the active phases is very difficult and different reduction mechanisms of the tungsten trioxide phase are possible, depending on the reduction conditions such as the reduction temperature, the hydro-

gen pressure, the flow rate, the heating rate, or the height of catalyst in the fixed bed flow reactor (8, 9). Ogata *et al.* (1) investigated the hydrocracking of *n*-heptane at 440°C on various tungsten oxides formed by reducing WO_3 samples under hydrogen at different temperatures (between 440 and 710°C) and characterized by XRD and thermodesorption measurements. They concluded that *n*-heptane reacted by two kinds of reaction mechanisms as a function of the oxidation state of the surface. Isomerization and central cracking took place in the presence of $WO_{2-\alpha}$ (where α represents a very small value) or $WO_{2.84}$, while demethylation, to form methane, occurred in the presence of $WO_{2+\beta}$ (where β is zero or a very small value) or W metal. Cornet and Travert (6), who studied the skeletal isomerization reactions of hexenes and hexanes, suggested that the $W_{20}O_{58}$ suboxide, formed by reducing WO_3 under a hydrogen flow at temperature less than 420°C, was an active and very selective phase for the hexenes skeletal isomerization through an acidic mechanism involving carbocation intermediates. According to these authors, higher reduction temperatures lead to the formation of a mixture of W metal and WO_2 which catalyze skeletal isomerization of alkanes through a bifunctional mechanism where W metal is the metallic hydrogenating–dehydrogenating site and WO_2 the isomerization function with the same acidic properties as $W_{20}O_{58}$. More recently, experiments carried out in our laboratory (2–5, 7) showed that WO_3 is initially inactive at 350°C toward hexanes isomerization reactions and that this oxide has no dehydrogenative properties. After an induction time under hydrogen, we observed the conversion of alkanes mainly to skeletal isomerized products, which was attributed to the presence of the WO_2 phase. A bifunctional mechanism involving W^{4+} species (in the WO_2 phase) as metallic sites and O–H groups as acidic sites was proposed. However, a continuous evolution in the reaction products distribution, which was mainly characterized by a decrease in the concentration of the isomerized products, was observed under the operating conditions using a hydrogen flow, due to the progressive reduction of the surface to W metal. In this paper, we focused our investigations on the reactivity of 2-methylpentane (2MP) and 4-methyl-1-pentene (4M1Pene) under a hydrogen flow at 350°C on a starting stoichiometric bulk WO_3 powder.

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Of course, it is well-known that bulk WO$_3$ tungsten oxide undergoes structural changes under these operating conditions which lead to modifications of the catalytic properties. However, the aim of this work was to determine if it was possible to obtain, starting from a bulk WO$_3$ sample, a stable tungsten oxide phase exhibiting interesting properties for the skeletal isomerization reactions of the reactants. For this purpose we studied the effects of the hydrogen reduction time and temperature. Catalyst characterizations by surface area measurements, X-ray diffraction (XRD), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS) were performed to determine the nature of the intermediate phases formed during the reduction process of the WO$_3$ tungsten oxide and to establish a correlation between these structural modifications of the surface and the evolutions of the catalytic properties under the same reducing conditions.

2. EXPERIMENTAL

The tungsten trioxide WO$_3$ powder used in this work was obtained from Johnson & Matthey and presented a low specific surface area (5 m^2/g).

Catalytic reactions were carried out in an all glass micropilot at atmospheric pressure. The device was equipped with a flowmeter, a U-shaped quartz fixed bed reactor, and a double thermal conductivity detector system (TCD) recording the partial pressure of the reactant (provided by a saturator) before and after the reaction. Reactions were performed at 350°C under a hydrogen flow of 54 cc/min. Before the first catalytic test, the temperature was increased at 10°C/min to 350°C. The catalyst was introduced on to a quartz frit support in the reactor. All the connections of the device were checked to be absolutely airtight. Particular attention was given to the purification of the reaction gases and of the tested hydrocarbons. The hydrogen flow was led over a Pt/Al$_2$O$_3$ catalyst at 200°C to convert residual oxygen to water, which was trapped by a molecular sieve. To make sure that all oxygen was removed, the reaction gases were led over a green MnO bed which became black (MnO$_2$) if oxygen was still present. The hydrocarbon was introduced via a septum and then drawn into the saturator which was immersed in a cooling bath whose temperature was adjusted and maintained constant, to have the following pressure ratios: $p(2MP)/p(H_2) = 6.64/753.36$; $p(4M1Pene)/p(H_2) = 4.65/755.35$. The reaction products were hydrogenated before being sampled by an airtight syringe and analyzed by gas chromatography with a FID.

In-situ surface area measurements of the various samples were made directly in the catalytic micropilot to avoid any contact with air. Thus, they were directly representative of the surfaces on which the catalytic tests were performed. The sample was placed in the microreactor at liquid nitro-

gen temperature and then submitted to a 10%Ar/He mixture. The reactor was then warmed to room temperature. The amount of argon desorbed was measured with a thermoconductivity detector.

The crystal structure was analysed by X-ray diffraction (XRD) using a Siemens Model D500 apparatus using Cu $K\alpha$ radiation ($\lambda = 1.54$ Å) over a 2θ range of 15° and 65°. XRD patterns were recorded after various treatments of 100-mg samples under hydrogen in the catalytic micropilot at atmospheric pressure with a heating rate of 10°C/min. All diffractograms were compared with those of the JCPDS data file for identification.

TPR analyses were performed in an XSORB (IFP-Gira) apparatus. 5%H$_2$/Ar, purified on molecular sieves, was used as the reducing agent, with a 25 cc/min flow. H$_2$ consumption was measured by means of a catharometric detector. One hundred milligrams of sample was placed in a quartz reactor. After an in-situ pretreatment in air at 400°C for 2 h, the temperature was increased at 8°C/min to 900°C where it remained steady for 2 h. After the sample was cooled down to room temperature, a new calcination treatment at 400°C followed by a new TPR experiment were performed. Three successive TPRs were thus recorded.

XPS spectra were obtained using an ESCA III VG spectrometer with Al $K\alpha$ radiation. All experimental details concerning the XPS apparatus as well as the curve-fitting analysis were given elsewhere (3, 7).

3. RESULTS

3.1. WO$_3$ and H$_2$ Interaction

A previous study (6) showed that the reduction of bulk WO$_3$ above 420°C leads to the formation of a mixture of WO$_2$ and W metal exhibiting interesting properties for the isomerization of hexanes. With reference to these results, we investigated in this first section the catalytic behavior of a 200-mg bulk WO$_3$ sample for the isomerization of 2MP at 350°C as a function of time under atmospheric pressure of hydrogen and for a reduction temperature of 520°C. The conversion (α%) and reaction products distribution are presented in Table 1. An increase of the surface area (S) of the WO$_3$ bulk sample, measured *in situ* in the catalytic micropilot, and important modifications of both the activity and product distribution occur during this experiment. The reduction of WO$_3$ at 520°C occurs progressively without reaching a stable state. The conversion increases continuously while the selectivity in isomerized products reaches a maximum after 20 min of reduction and then decreases progressively. Concerning the surface area, only two values are measured, at the beginning and at the end of the experiment. These two values cannot allow us to point out if the surface area shows a continual increase, as for conversion, or shows a maximum, as for selectivity

TABLE 1

2MP Reaction on 200 mg of the WO₃ Sample at 350°C as a Function of Time of Exposure at 520°C under Hydrogen at Atmospheric Pressure

Time (min)	5	12	20	31	61	124
S (m²)	1.4	—	—	—	—	9.5
α (%)	4.1	9.0	22.9	28.4	51.1	62.6
S_{iso} (%)	77.4	81.8	89.0	83.5	73.4	61.3
Σ(C1 + C2 + C3)	11.8	10.2	8.0	12.3	19.5	26.1
Σ(C4 + C5)	4.5	3.1	3.0	3.9	7.2	12.6
22DMB	0.9	1.6	1.9	1.9	2.7	4.7
23DMB	(6.5)[a]	7.4	9.1	9	9.4	8.7
3MP	49.5	48.3	52.1	43.6	34.8	26
nH	19.2	23.3	25.3	28.2	26.3	21.7
Olefins Cr	6.3	4.9	—	0.3	—	—
Olefins C6	1.3	1.2	0.6	0.8	0.2	0.2
3MP/nH	2.6	2.1	2.0	1.5	1.3	1.2

[a] The presence of some traces of olefins have been detected in the 23DMB chromatographic peak at very low conversion.

in isomerized products, at 20 min of reduction. However, other experiments, presented in Section 3.3.1, indicate that, during the exposure of the WO₃ samples, the surface area first increases to a maximum and then remains constant at this maximum value (see Fig. 2).

Catalytic tests, using 2MP as a reactant, performed at 350°C on a WO₃ sample, reduced at 350°C for 12 h, showed the formation of a quasi stable state. In Table 2 are presented the results of catalytic tests performed on such a stabilized surface at different reaction temperatures from 210 to 330°C, with an intermediate decontamination of the surface at 350°C under a hydrogen flow for 10 min between the different tests. The surface starts to be active for a reaction temperature higher than 210°C with mainly the formation of 3MP. At higher temperatures nH as well as cracking products are produced. The 3MP/nH ratio decreases from 30 to 2.5 as the reaction temperature increases.

TABLE 2

2MP Reaction on 200 mg of a WO₃ Sample Reduced under a Hydrogen Flow at 350°C for 12 h as a Function of the Reaction Temperature

T (°C)	210	235	258	282	329
α (%)	1	3.6	9.7	19.7	31.2
S_{iso} (%)	100	90.1	91.9	89.2	75.4
Σ(C1 + C2 + C3)	—	6.3	6.6	6.5	15.5
Σ(C4 + C5)	—	3.6	1.5	4.3	8.1
22DMB	—	0.4	—	1.0	2.4
23DMB	(4.2)[a]	(4.1)[a]	4.5	6.3	8.1
3MP	95.8	82.9	83.7	73.8	47.0
nH	—	2.7	3.7	8.1	18.8
3MP/nH	∞	30.7	22.6	9.1	2.5

[a] The presence of some traces of olefins have been detected in the 23DMB chromatographic peak at very low conversion.

TABLE 3

2MP Reaction at 350°C on Three WO₃ Samples of 2, 20, and 130 mg after a Treatment under Hydrogen Stream (54 cc/min) at 400°C for 4 h

	Catalyst weight (mg)		
	2	20	130
S (m²)	0.04	0.4	0.7
α (%)	26.4	49.5	29.4
r (μmol/(m² s))	2.67	0.6	0.18
S_{iso} (%)	87	79.1	84
Σ(C1 + C2 + C3)	8.2	12.7	9.5
Σ(C4 + C5)	4.8	8.2	6.5
22DMB	1.5	2.3	1.8
23DMB	9.7	11.2	11.4
3MP	53.1	40.4	45.0
nH	21.9	25.1	24.1
3MP/nH	2.4	1.6	1.9

3.2. Effect of the Height of Catalyst in the Fixed Bed Flow Reactor

The 2MP reaction was investigated at 350°C on three samples of different weights (2, 20, and 130 mg). These samples were pretreated *in situ* under a hydrogen stream (54 cc/min) at atmospheric pressure at 400°C for 4 h before the first catalytic test. The 2- and 20-mg samples were placed in a reactor of 2-mm diameter while a reactor of 5-mm diameter was used for the 130-mg sample. The *in situ* measured surface area (S), the specific rate (r), and the product distribution obtained for these experiments are reported in Table 3. We can see that the specific rate is extremely dependent on the catalyst weight. This one decreases when the weight of the samples increases. It is interesting to note that, at the end of the catalytic tests, the 2-mg catalyst sample in the fixed bed flow reactor showed a completely brown color over the whole catalyst bed, while the 20- and 130-mg samples showed a gradient along the height of the catalyst, which was brown at the upper part and purple at the bottom. This result reveals an heterogeneity in the reduction of the catalyst.

The activation energy determined for the reaction of 2MP on a 2-mg WO₃ sample treated by a hydrogen flow at 350°C for 13 h was measured between 270 and 350°C. We obtained a value of 43.1 kJ/mol which is characteristic of the participation of an acidic kind of catalysis (10) and confirms that under these operating conditions there is no diffusional limitation.

3.3. Influence of Temperature and Time of Exposure under the Hydrogen Stream

The influence of the hydrogen reduction time and temperature was investigated for the 2MP and the 4M1Pene reaction on the WO₃ catalyst. The catalytic tests were always

performed at 350°C by introduction of a 2.5-μl pulse of reactant on a 2-mg WO₃ sample. Between two pulses, the surface was maintained at the chosen reduction temperature under a hydrogen stream.

3.3.1. Reactivity of 2-methylpentane (2MP). The 2MP reaction was studied at four different reduction temperatures: 350, 400, 450, and 500°C. A fresh catalyst sample was used for each reduction treatment. The evolution of the conversion, the global selectivity in isomerized products, and the surface area are presented in Figs. 1 and 2. The surface area of the 2-mg WO₃ sample (Fig. 2) was measured *in situ* in the catalytic micropilot. Table 4 summarizes the distribution of the reaction products for a reduction temperature of 400°C.

As shown in Figs. 1 and 2, the catalytic activity, the surface area, and the global selectivity in isomerized products are modified as a function of the exposition time of the samples under the hydrogen stream. As already reported (3, 7), the fresh WO₃ surface ($t = 0$) exhibits no activity for this reaction. An induction time is required to initiate the reduction process of WO₃ and so the reaction. This induction time as well as the evolution of the catalytic properties of the WO₃ samples for the time we studied (about 10 h) depends on the reduction temperature under hydrogen (Fig. 1).

For exposure under the hydrogen stream at 350°C, the surface area progressively increases with time from 110 to 380 cm² (Fig. 2). This development of the surface area reveals that strong modifications in the structure of the catalyst occur. This leads to an increase of the activity which reaches a steady state after 10 h of reduction (Fig. 1a). The selectivity in isomerized products, which is relatively low at the beginning of the reduction, increases with a significant
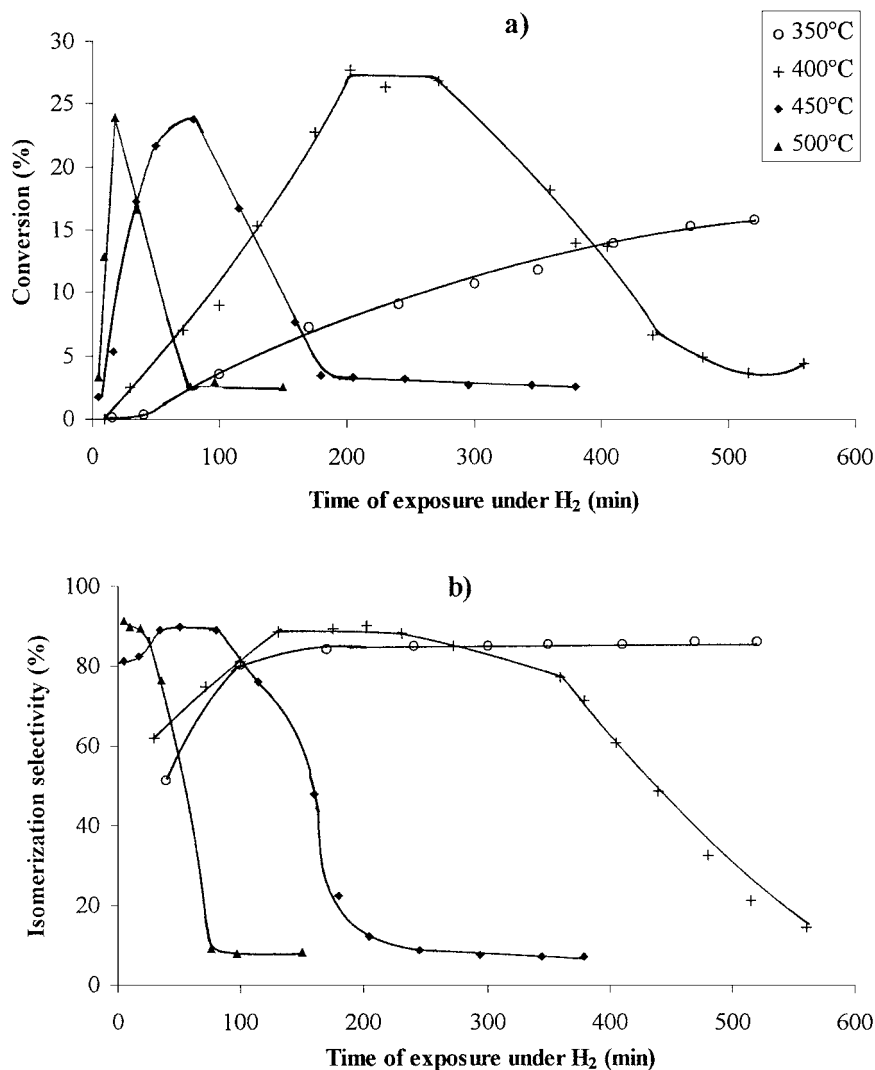

FIG. 1. Isomerization of 2MP on 2 mg of WO₃ at 350°C as a function of reduction temperature: (a) conversion (%) and (b) isomerization selectivity (%).
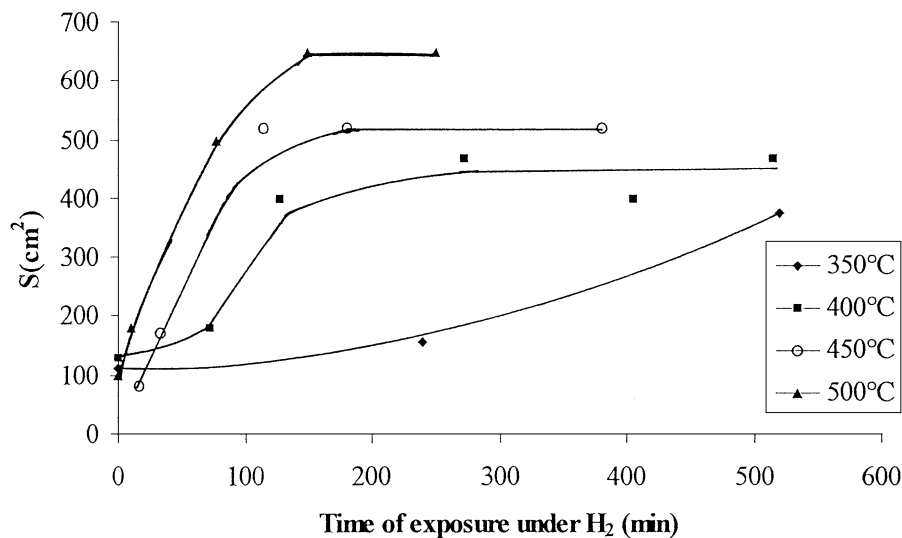
FIG. 2. Evolution of the surface area of the WO_3 samples with time of exposure to a hydrogen stream as a function of the reduction temperature (350, 400, 450, or 500°C).

rise during the first hour to reach a maximum at about 85% (Fig. 1b). The main product formed is then 3MP (~60%). Lower amounts of 23DMB and nH are produced, about 10% and 15%, respectively. This distribution of isomerized products leads to a 3MP/nH ratio close to 4. It is important to note that the production of unsaturated products is not negligible during the first 2 h of reduction (>6%) and then decreases to less than 2% when the steady sate is reached. Traces of 22DMB are formed, but no cyclic products are detected.

As observed in Fig. 3 this steady state remains for several hours at this temperature of 350°C. The difference that we can observe in the data conversion presented in Fig. 1 ($\alpha \sim 15\%$) and in Fig. 3 ($\alpha \sim 30\%$) after respectively 10 and 13 h of reduction under a hydrogen stream at 350°C is attributed to a difference in the experimental conditions between these two experiments. Indeed, in the experiment

presented in Fig. 3 the sample was pretreated *in situ* under a hydrogen stream at atmospheric pressure at 350°C for 13 h before the first catalytic test which indicates a conversion of 30% and a global selectivity in isomerized products of 88%, whereas in the experiment presented in Fig. 1 catalytic tests were regularly performed as a function of the reduction time of the sample between a few minutes and 10 h. Then, it is reasonable to think that, in this later case, a contamination of the sample surface by the hydrocarbons occurs. This poisoning of the surface is then characterized by a deactivation, 15% regarding 30% when the first catalytic test is performed on a fresh surface pretreated under a hydrogen stream at 350°C for 13 h (Fig. 3). This point concerning the poisoning of the tungsten oxide surfaces by the hydrocarbons will be the purpose of a next publication.

When the reduction temperature is increased to 400°C, the reduction process of the upper layers of the WO_3

TABLE 4

2MP Reaction on 2 mg of the WO_3 Sample at 350°C as a Function of Time of Exposure at 400°C under Hydrogen at Atmospheric Pressure

| Time (min)	30	72	128	202	272	405	440	515	560
S (cm^2)	130	180	400	—	470	400	—	470	—
α (%)	2.5	7.1	15.4	27.8	26.9	13.8	6.6	3.7	4.5
r (μmol/(m^2 s))		0.8	1.9	—	2.9	1.7	—	0.4	—
S_{iso} (%)	67.7	86.2	91.2	90.3	82.1	60.9	48.8	21.1	14.4
Σ(C1 + C2 + C3)	28.5	10.1	5.6	5.8	12.3	28.4	37.4	58.1	63.6
Σ(C4 + C5)	3.8	3.7	3.3	3.9	5.6	9.8	12.5	19.7	21.0
22DMB	0.2	0.6	1.2	1.5	0.8	0.2	0.1	0	0
23DMB	15.8	7.4	9.6	10.1	5.1	3.6	4.1	5.0	4.7
3MP	41.0	67.7	59.6	56.2	63.7	52.4	41.8	14.6	8.3
nH	3.6	6.9	19.6	21.9	11.7	4.4	2.4	1.1	0.8
Olefins C6	7.3	3.6	1.2	0.6	0.8	0.3	0.4	0.4	0.6
3MP/nH	11.3	9.7	3.0	2.6	5.5	12.1	17.7	12.8	9.9
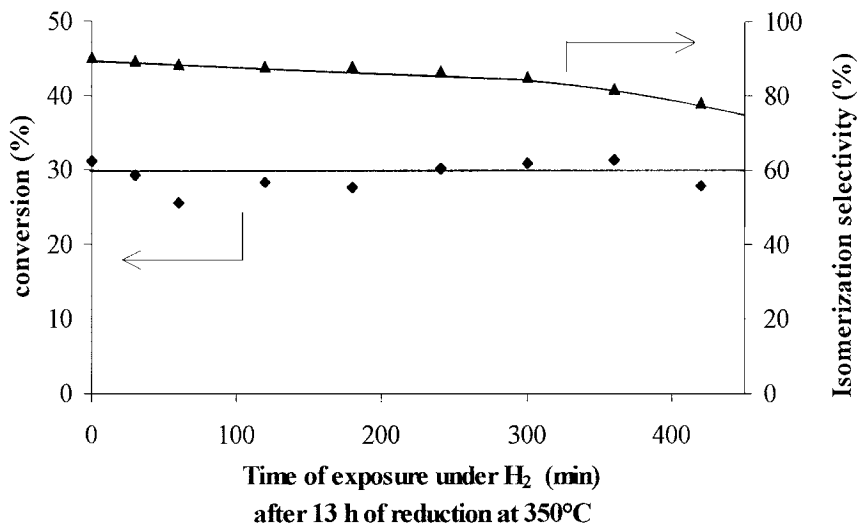
FIG. 3. 2MP conversion (%) and selectivity to isomerized products (%) on 2 mg of WO_3 at $350°C$ after *in situ* prereduction under a hydrogen flow at $350°C$ for 13 h.

necessary to initiate the reaction requires a little more than an hour of exposure. Then, the activity, the surface area, and the global selectivity in isomerized products rapidly increase to a maximum (Figs. 1 and 2). The evolution of the selectivities of the different isomerized products (Table 4) during this first period of reduction leads to a decrease of the 3MP/nH ratio from 11 to 2.6. Both the activity and global selectivity in isomerized products stabilize at this relative stable state for about 2.5 h and then decrease progressively, while the surface area remains constant at its maximum value of 450 cm². The decrease in selectivity in isomerized products from 90% to 10% is accompanied by a relative increase in the hydrogenolysis reaction products (Table 4). Among the cracked products, methane is mainly formed (its selectivity reaches 40% after 9 h of reduction). Ethane and propane are present at about 10%. This product distribution is characteristic of the formation of metallic-like tungsten at the surface (11).

For reduction temperatures of 450 and 500°C, the catalytic properties of the samples follow the same trend as obtained at the reduction temperature of 400°C. However, their evolution as a function of time of exposure under the hydrogen stream is faster at higher temperatures. No stable level in terms of activity and selectivities is observed when the reduction temperature is higher than 400°C, which is in accordance with previous results performed on a 200-mg WO₃ sample presented in the first section of this paper.

3.3.2. Reactivity of 4-methyl-1-pentene (4M1Pene). The catalytic properties of a 2-mg WO₃ sample for the 4M1Pene reaction were studied as a function of hydrogen reduction of the surface at 400°C (Table 5). The sample was heated from room temperature to the reaction temperature (350°C) in a helium stream. The helium stream was then replaced by a hydrogen stream and the first catalytic test ($t = 0.1$ min)

TABLE 5

4M1Pene Reaction on 2 mg of the WO₃ Sample at 350°C as a Function of Time of Exposure at 400°C under Hydrogen at Atmospheric Pressure

Time (min)	0.1	48	86	146	217	260	320	365	440
S (cm²)	100	—	180	—	400	—	—	600	—
α (%)	27.0	13.3	15.5	19.7	23.0	20.3	13.6	8.0	6.4
r (αmol/(m² s))	10.0	—	3.2	—	2.2	—	—	0.5	—
S_{iso} (%)	99.6	93.8	83.6	78.8	75.2	57.2	43.4	24.0	12.0
$\Sigma(C1 + C2 + C3)$	0.2	4.1	8.9	12.4	14.4	28	39.2	55.3	66.1
$\Sigma(C4 + C5)$	0.2	2.1	6.5	8.8	10.4	14.8	17.4	20.7	21.9
22DMB	0.2	0.1	0.2	0.6	0.8	0.5	0.2	0	0
23DMB	3.8	1.8	2.9	4.3	5.5	3.6	1.7	0.8	0.6
3MP	91.3	88.5	77.1	67.9	59.9	47.4	38.5	21.6	10.3
nH	4.3	3.4	3.4	6.0	9.0	5.7	3.0	1.6	1.1
3MP/nH	21.2	26.0	22.7	11.3	6.7	8.3	12.8	13.5	9.4

performed by introduction of the reactant by a pulse of 2.5 μl. The reaction products were hydrogenated before being analyzed.

The first catalytic test (Table 5) reveals that the sample is active and very selective in 3MP ($\sim$91%), while under the same conditions of treatment, an induction period of 30 min is necessary to initiate the reaction of 2MP (see section 3.3.1). As we can observe in Table 5, the 3MP/nH ratio exceeds 20 during the first 2 h of reduction which is representative of an acidic character. The selectivity in 3MP decreases progressively from 91% to 10% with time of exposure under hydrogen in favor of the cracked products, mainly C1, C2, and C3.

It is important to note that a catalytic test using 4M1Pene as the reactant performed at 350°C on a fresh WO_3 sample under a pure helium stream instead of hydrogen stream (as presented in Table 5) revealed no activity.

3.4. Catalyst Characterizations

The XPS characterizations of the surface of the bulk WO_3 sample as a function of *in situ* hydrogen reduction time and temperature were presented in Refs. (3) and (7). These experiments revealed that a treatment of the WO_3 surface under a hydrogen atmosphere at 350°C or 450°C leads rapidly to the formation of structural defects at the WO_3 surface containing oxygen vacancies which progress toward a complete transformation of the WO_3 oxide to the $W_{20}O_{58}$ phase. This $W_{20}O_{58}$ oxide is composed of both W^{6+} and W^{5+} ions in a ratio W^{5+}/W^{6+} of 0.25 (7, 17, 18). We have shown that this $W_{20}O_{58}$ surface remains stable for more than 13 h of exposure at 350°C under an atmosphere of hydrogen and that its appearance is accompanied by a change of color of the sample to blue purple. The XP spectra showed a progressive reduction of the W^{6+} and W^{5+} oxidation states as a function of time of exposure at 450°C to W^{4+} and W^0 species. These results were attributed to the formation at first of WO_2 oxide then of metallic tungsten.

XRD patterns of 100-mg bulk WO_3 samples before and after treatments under a hydrogen stream at atmospheric pressure at 450 or 350°C for respectively 2 and 64 h in the catalytic micropilot are presented in Fig. 4. For the fresh sample (Fig. 4a) diffraction lines corresponding to WO_3 are observed (JCPDS data file no. 43-1035). After a reduction treatment at 450°C for 2 h the diffraction pattern always shows the presence of WO_3 and another phase which was identified as $W_{20}O_{58}$ (JCPDS data file no. 36-0102) (Fig. 4b). The reduction of WO_3 to $W_{20}O_{58}$ is complete after an hydrogen exposure at 350°C during 64 h (Fig. 4c). As shown in Fig. 5a, a partial reduction of the $W_{20}O_{58}$ phase occurs after a hydrogen treatment at 450°C for 9 h. The diffraction pattern is then composed of the diffraction lines corresponding to the $W_{20}O_{58}$, WO_2 (JCPDS data file no. 32-1393) and W_3O (JCPDS data file no. 341-1230) oxides. Further reduction for 14 h leads to the disappearance of both the $W_{20}O_{58}$ and

WO_2 diffraction lines (Fig. 5b) and results in the coexistence of the W_3O phase and tungsten metal.

The TPR experiments are reported in Ref. (12). Three successive TPR profiles were registered as explained in the experimental part. The first TPR exhibited five peaks between 572 and 900°C, showing that the reduction of WO_3 proceeds in several steps. In the following two TPR profiles three only peaks were detected respectively at 707, 792, and 900°C. The total consumption of hydrogen per mole of tungsten oxide gave a H_2/WO_3 ratio in the first TPR equal to 2.7 which corresponds to an almost complete reduction of WO_3 into tungsten metal. This value decreases in the following two TPRs to 2.0 and 1.5, respectively, which is probably due to an incomplete re-oxidation of tungsten.

4. DISCUSSION

In accordance with previous results (1–7), we have shown that starting from WO_3 it is possible to obtain, under specific experimental conditions under hydrogen, a material which exhibits interesting properties for skeletal rearrangement of both hexanes and hexenes. It is confirmed too that the catalytic properties of tungsten oxides depend on the oxidation state of the surface and that the reduction of WO_3 is a multistep process.

The reduction process of WO_3 was largely studied by XPS (3, 4, 7, 13–19), TPR (20–24), or TGA (1, 8, 9, 25–27). However, the identification of the different reduction steps, and therefore the nature of the intermediate phases, and moreover the correlations between the catalytic properties and the oxidation state of the surface are still under discussion. As pointed out by Sahle and Berglund (9), these discrepancies about the possible reduction steps are probably due to the kinetics of the evolution of water vapor formed during the reduction process, which depends on the hydrogen flow and pressure, the height of the catalytic bed in the flow reactor, the reduction temperature, and the heating rate, as confirmed by Schubert (8). These considerations explain the heterogeneity of reduction of the catalytic bed, which has an influence on the evolution of the surface area and therefore on the specific reaction rate, observed in Section 3.2 as a function of the weight of catalyst introduced in the reactor. The reduction of the complete amount of catalyst introduced in the reactor allows us to get rid of this heterogeneity phenomenon.

In this work we followed the modifications of the catalytic properties of a starting bulk WO_3 powder for both the 2MP and 4M1Pene reactions as a function of the reduction of the surface under a hydrogen flow at atmospheric pressure. As we described in Section 3.3, an induction period under hydrogen, which depends on the reduction temperature, is necessary to induce an activity for the alkane reactions, while under the same conditions the surface is active and very selective for the 4M1Pene skeletal isomerization.
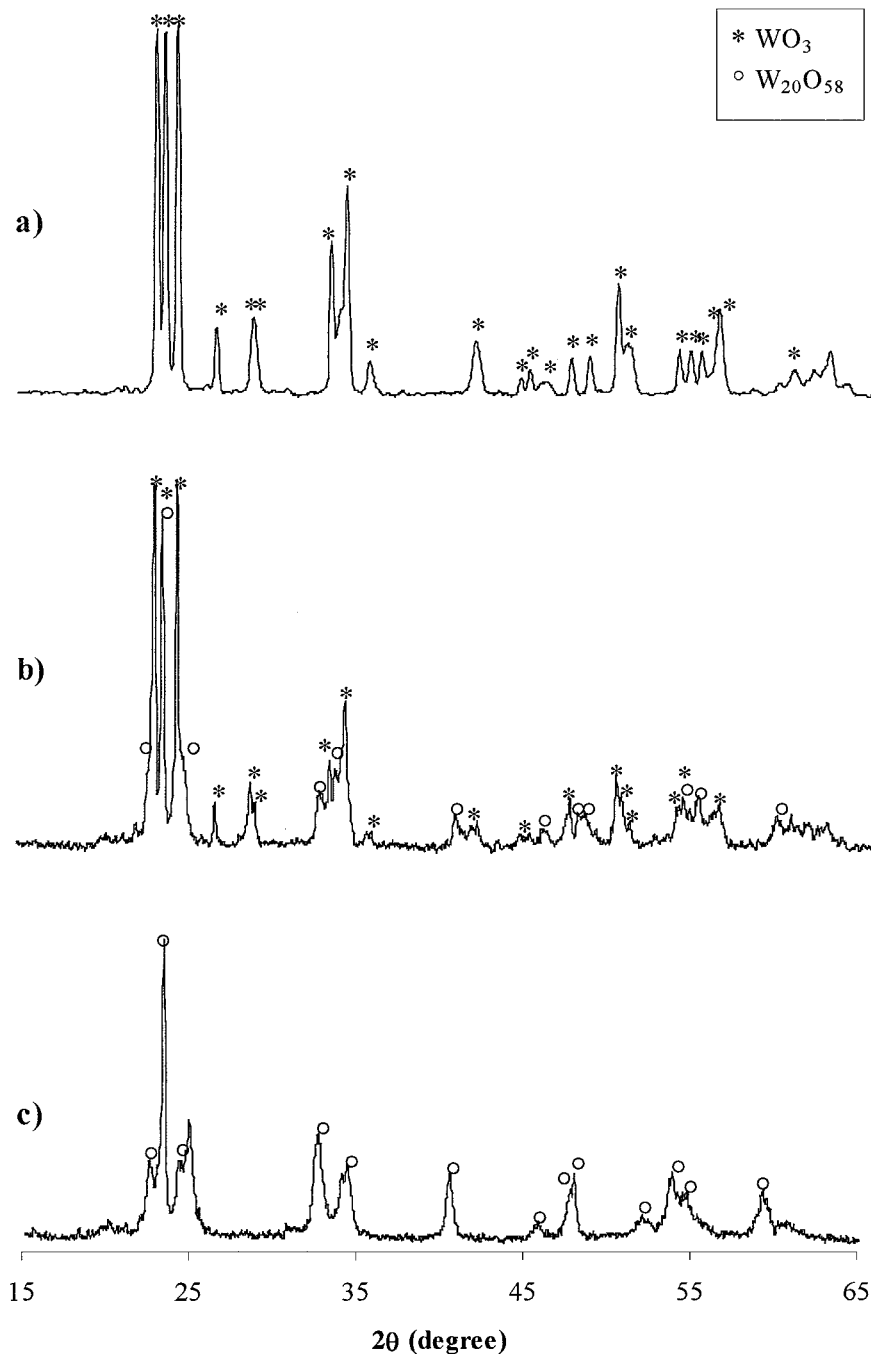
FIG. 4. XRD patterns of 100 mg of WO$_3$ before (a) and after reduction under a hydrogen stream at atmospheric pressure at 450°C for 2 h (b) and 350°C for 64 h (c).

Indeed, as shown in Table 5, the selectivity in cracked products is then negligible, the major isomerized product formed is 3MP (>91%), and the ratio 3MP/nH is equal to 21. Such a product distribution is representative of the participation of a monofunctional acidic mechanism. However, in the same catalytic test, 4M1Pene revealed no activity at 350°C on a fresh WO$_3$ sample under a helium stream instead of hydrogen stream. So the presence of hydrogen in the reaction stream is necessary to activate the surface. This result leads us to the conclusion, as suggested earlier by Cornet (6), that the WO$_3$ phase is inactive for both alkane and alkene reactions but in contact with hydrogen the WO$_3$ surface is immediately modified; active acidic sites for alkene skeletal isomerization are formed.

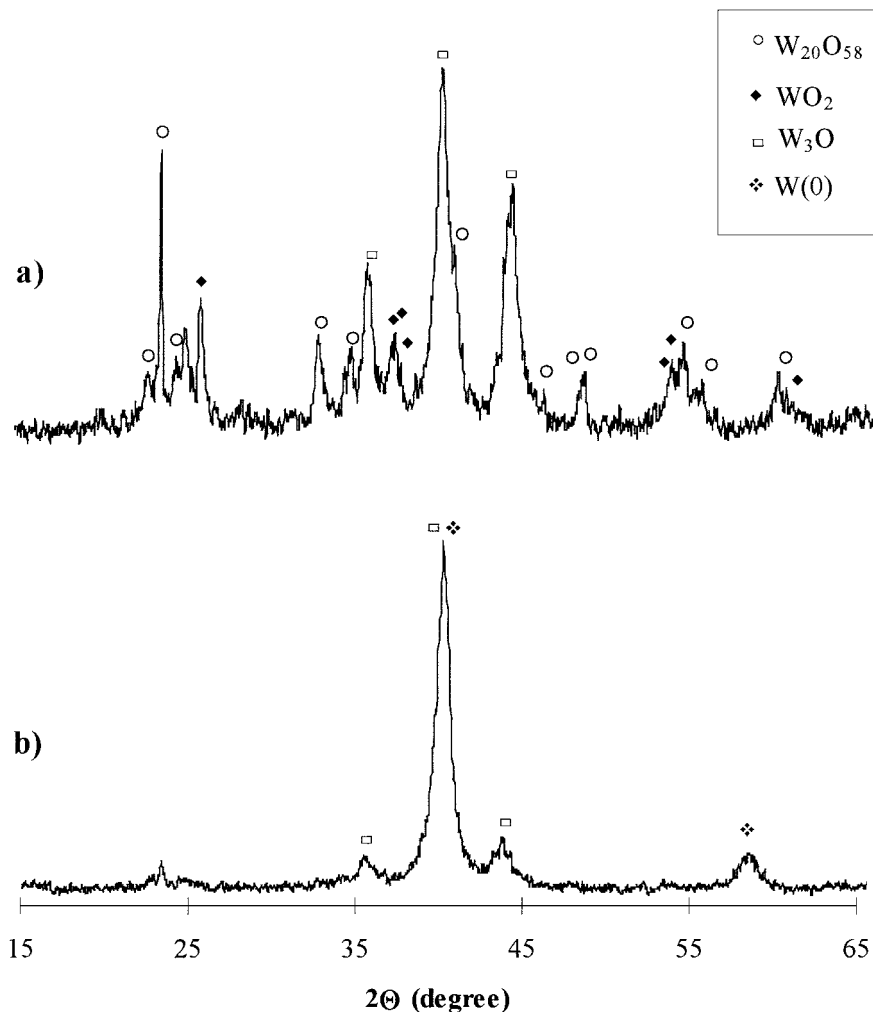Although our XPS and XRD measurments were not performed under exactly the same experimental conditions,

FIG. 5. XRD patterns of 100-mg WO_3 samples after reduction under a hydrogen stream at atmospheric pressure at 450°C for 9 h (a) and 14 h (b).

especially concerning the heating rate and the regime of reduction (static or dynamic), they revealed that whatever the reduction temperature (350 or 450°C) the first reduction step of WO_3 corresponds to the formation of the $W_{20}O_{58}$ phase. This result is in agreement with the WO_3 reduction study with kinetic and morphological considerations presented by Schubert (8) who proposed that the reduction of WO_3 to $W_{20}O_{58}$ always occurs, whatever the operating conditions. In the same way, Cornet (6) observed the formation of the $W_{20}O_{58}$ oxide by reducing WO_3 under a hydrogen flow at a temperature less than 420°C. This author attributed this to $W_{20}O_{58}$ tungsten oxide skeletal isomerization properties for the hexenes reaction with the participation of an acidic mechanism involving carbocations intermediates. However, he could not determine the nature of the active acidic sites. More recently, Ponec *et al.* (28, 29) considered that the reduction of some W^{6+} ions to W^{5+} enhances the adsorption of *n*-butene on WO_3/γ-Al_2O_3 catalysts. According to these authors, selective catalysts for the *n*-butene skeletal isomerization have Lewis acidic W^{5+}

ions as well as Brönsted acidic OH groups. On this basis and considering both our catalytic and characterization results, we propose first that the W^{5+} ions present along the shear planes in the $W_{20}O_{58}$ structure, formed during the first step of reduction of the WO_3 phase, are Lewis acidic sites responsible for the adsorption of 4M1Pene on the surface, and second that Brönsted acidic sites, as O–H groups, generated by the adsorption of hydrogen, account for the skeletal isomerization itself through a monofunctional acidic mechanism involving carbenium ions as intermediates, leading to surface alkoxy species, as earlier proposed on bulk tungsten carbide surfaces modified by chemisorbed oxygen (31, 32) or tungsten oxide supported on porous α-alumina (32).

The appearance, after an activation period under the hydrogen stream, of an activity for the 2MP reaction is representative of the formation on the surface of hydrogenating–dehydrogenating sites able to dissociate C–H bonds. The product distribution, using the 2MP as the reactant, is then characterized by a global selectivity in isomerized products

near 70% with a ratio of 3MP/nH equal to 11 (Table 4). A comparison between the reactivity of 2MP (Table 4) and 4M1Pene (Table 5) revealed that, at this duration of reduction, the reaction rate of 2MP is 4 times lower than that of 4M1Pene. These catalytic properties are representative of the participation of a bifunctional mechanism in which the slow step is the C–H bond rupture from alkane to form the olefin which is next isomerized on acidic sites via the formation of carbenium ions. Further exposition of the surface under the hydrogen stream leads, for the 2MP reaction, to a progressive increase in both the activity and the global selectivity in isomerized products to a maximum. The evolution of the product distribution is then charaterized by a progressive decrease in the 3MP/nH ratio and the disappearance of the production of unsaturated products (Table 4) which is representative of the development of a metallic character at the surface. A correlation between these evolutions in the catalytic behavior and the structural and morphological modifications, observed by the characterization experiments (Section 3.4), allows us to assign the progressive evolutions of catalytic properties, until the production of the steady state, on the one hand to the reduction of the $W_{20}O_{58}$ oxide, in two parallel steps to both WO_2 and W_3O, and on the other hand to an evolution of the strength of the acidic sites. Indeed, it is reasonable to say that the W^{x+}–OH bond is all the more strengthened since the oxidation state of the tungsten ion is high. Thus, during the reduction of the tungsten ions ($W^{6+} \rightarrow W^{5+} \rightarrow W^{4+} \rightarrow W^{\varepsilon+}$, where ε is a very small value) the W^{x+}–OH ionic bond is weakened and therefore the strength of the O–H bond is increased; the hydrogen atoms become then less labile which involves a decrease in the acidity of the surface as observed by the decrease of the 3MP/nH ratio.

For a reduction at 350°C, we showed that it is possible to maintain the surface state represented by a maximum in the global isomerized products stable during a long period (Fig. 3). This surface state is characterized by a high global selectivity in isomerization ($\sim$90%) with a ratio of 3MP/nH close to 4. The reaction rates of both 2MP and 4M1Pene are then equal. An exclusive bifunctional mechanism cannot explain such a catalytic behavior. The contribution of two mechanisms seems to occur: a bifunctional one and a monofunctional metallacycle one, as proposed by Ribeiro *et al.* (33), involving the formation of tungstenacyclobutane intermediates.

All these considerations lead us to explain the participation of a bifunctional mechanism by the presence of metallic hydrogenating–dehydrogenating sites, attributed to the free *d* electrons of W^{4+} ions located along the *c* axis of the deformed rutile structure of the WO_2 phase, and the presence of isomerizing acidic sites, attributed to the O–H surface groups. The metallic character of this WO_2 oxide was underlined in our laboratory by UPS and XPS studies on bulk WO_3 and WO_2 catalysts (2–4). The participation

of a monofunctional metallacycle mechanism is therefore attributed to the presence of the W_3O surface entities.

The decrease in the global isomerization selectivity observed after a certain time for exposure temperatures higher than 350°C (Fig. 1), and consequently the increase in the concentration of the hydrogenolysis products (and mainly in the methane selectivity), can be explained by the formation of metallic tungsten species. Indeed, previous studies (5, 11) showed that tungsten metal surfaces catalyze hydrocarbon hydrogenolysis reactions.

5. CONCLUSION

In this study, we confirmed that the catalytic properties of tungsten oxides are extremely dependent on the oxidation state of the surface. We showed that starting from a bulk WO_3 sample, it is possible to obtain, after an activation period under hydrogen flow, a material which exhibits interesting properties for skeletal rearrangement for hexanes and hexenes reactions. The investigations on the effect of the height of the fixed bed flow reactor and the hydrogen reduction time and temperature allowed us to determine the best conditions to obtain a stable state exhibiting skeletal isomerization properties for a 2MP and 4M1Pene reaction without the production of aromatic products.

Correlations between the catalyst characterizations and its catalytic behavior led us to conclude that the WO_3 phase is inactive for both alkanes and alkenes reactions, as verified under a pure helium flow. When the formation of the $W_{20}O_{58}$ phase occurs, which corresponds to the first reduction step of WO_3, an acidic character of the surface appears, leading to the skeletal isomerization of alkenes toward a monofunctional acidic mechanism involving carbeniums ions as intermediates. The reduction of the $W_{20}O_{58}$ tungsten oxide occurs in two parallel ways to WO_2 and W_3O. When this reduction is performed at moderate temperature (350°C), we showed that a stable surface composed of these two phases (WO_2 and W_3O) is obtained. This surface is active and very selective for the alkanes and alkenes skeletal isomerization reactions. This catalytic behavior was interpreted using the participation of two mechanisms: a bifunctional one on the WO_2 phase and a monofunctional metallacycle one on the W_3O phase.

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