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Study of the preparation of bulk tungsten carbide catalysts with C_2H_6/H_2 and C_2H_4/H_2 carburizing mixtures

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The influence of the preparation procedure of tungsten carbide on the mechanism of carburization is discussed. This work is focused on the reduction and the carburization of tungsten trioxide by a mixture of hydrocarbon and H_2 to form WC. Temperature-programmed reaction spectra obtained with CH_4, C_2H_6 and C_2H_4 have been measured. In presence of the CH_4–H_2 mixture, H_2 is the reducing agent and the hydrocarbon is consumed for the carburization whereas C_2H_6 or C_2H_4 participates in the reduction of the tungsten oxide. The temperatures of reduction and carburization are lower by about 150 K using C_2H_6 or C_2H_4 instead of CH_4. Such a decrease of the temperature of reduction of tungsten oxide is needed to avoid the formation of poorly reducible compounds that can occur during the preparation of supported tungsten carbide. Furthermore, the surface area of the resulting carbide is 25 m^2/g with C_2H_6 and C_2H_4 and 10 m^2/g with CH_4. During the carburization, the deposit of excess carbon on the WC surface is larger with the C_2 hydrocarbons than with CH_4, but it protects the carbide and can be removed by hydrogen treatment.

Keywords: tungsten carbide, preparation, carburization, ethane, ethylene

1. Introduction

In the past 20 years, transition metal carbides have attracted increasing interest of investigators working in the field of catalysis. Since Levy and Boudart [1] have observed qualitative similarities between the behaviour of Pt and WC with respect to their catalytic properties, the potential fields of application of tungsten carbides as heterogeneous catalysts in substitution to precious metals have grown considerably [2–8].

Several authors have shown the strong influence of the method of preparation on the catalytic activity of tungsten carbide [4,5,9–11]. Nevertheless, only few works dedicated to the explanation of the mechanisms of the carburization of such catalysts have been made [12]. Two different experimental approaches are found in the literature:

– The preparation of high purity bulk powder WC to obtain well defined structures with accurate surface compositions and reasonable surface areas (few square meters per gram). It has, however, been shown that pure tungsten carbide does not exhibit interesting catalytic properties for hydrocarbon reformulation reactions as it leads essentially to cracking, whereas some authors have shown that small amounts of oxygen induce isomerizative properties [13–16].

– The preparation of high surface area WC. In this case, WC with lower purity is often obtained, that is containing oxygen and/or large amounts of free carbon, or a W_2C phase which does not have properties similar to those of the WC phase [14].

Several methods for the preparation of tungsten carbide are proposed in the literature [6,7,12,17–19]. Some of them involve the direct reaction of solid carbon and tungsten metal or oxide and yield low specific surface areas due to the high temperatures needed to reach sufficient diffusion rates within the solid.

More successful results are obtained when reacting a solid precursor with a gas phase containing the reducing and/or the carburizing agents. The most used precursors are the metal or its oxide, but also nitrides and salts [8]. The gaseous carburizing reagent can be either a hydrocarbon [20] or CO [21], but the gas phase usually contains also hydrogen or CO_2 in order to avoid important carbon deposits at the surface of the sample.

Methane is the most widely used of the hydrocarbons. This choice is made in order to limit the amount of excess carbon deposited on the surface of the carbide during the carburization, methane being the less reactive of the hydrocarbons [22]. Such deposits are nevertheless interesting as they efficiently protect the catalyst, by avoiding its oxidation during its storage in air [11], but have to be removed prior to any use. Nevertheless, let us notice that using methane high temperatures are needed for the carburization of the WO_3 precursor and that the carburization proceeds after the complete reduction of the precursor into tungsten metal, as we will show hereafter. The result is that tungsten carbides obtained this way often exhibit small surface areas. An alternative is to prepare supported tungsten carbide or to change the carburizing mixture. The problem for supported tungsten carbide is that the high temperatures needed to reduce the tungsten trioxide induce reactions with the support, leading to the formation of poorly reducible compounds [23].

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This is why, in this work, more reactive hydrocarbons have been chosen instead of methane: ethane and ethylene. By using these hydrocarbons, we hope to enlighten the understanding of the mechanisms of carburization, to decrease the temperature of carburization of the WO_3 precursor and to start the carburization process before the complete reduction of WO_3 into W metal. Such modifications of the carburization process may induce formation of tungsten carbides with larger values of surface area. Moreover, the decrease of the temperature of carburization can limit the formation of irreducible compounds during the preparation of supported tungsten carbide and could be a new route for the preparation of highly dispersed catalysts.

2. Experimental

In this work, WO_3 powder (Fluka, high purity grade: 99.9%; BET surface area about 3 m^2/g) was used as precursor.

The carburizing gas mixtures are composed of Ar 99.999% from UCAR, H_2/Ar 9.93% from UCAR (Certified Standard), CH_4/Ar 10.0% and C_2H_6/Ar 10.0% from UCAR (Certified Standard), C_2H_4 99.95% from AIR LIQUIDE, O_2/Ar 10.0% from BOC (Alpha Standard).

The reactions were conducted under temperature-programmed (TPR) conditions in a classical flow microreactor working at total atmospheric pressure with partial pressures of reactive gases ranging from 15 to 76 Torr and argon as carrier gas. The analysis of the gas composition at the outlet of the reactor is performed by a quadrupole mass spectrometer (QMG-420-5 from Balzers).

Samples of 50 to 100 mg of WO_3 were placed in a quartz reactor (volume = 1–3 ml) connected to the apparatus through Cajon adapters.

The bulk structure of the materials was determined by X-ray diffraction using the Debye–Sherrer technique (Cu Kα radiation, $\lambda = 1.54178$ Å, Ni filter). The diffractions are made ex situ after the carburization of the catalysts protected by an excess of free carbon.

The total surface area was determined by physisorption of N_2 at liquid nitrogen temperature in a conventional volumetric apparatus which is described elsewhere [24].

3. Results

3.1. Preparation of a reference catalyst, using a CH_4–H_2 mixture

As mentioned previously, some authors have prepared WC catalysts by carburization of WO_3 without previous reduction. It has been shown by several authors that carburization of WO_3 with a 20% CH_4/H_2 mixture occurs in different steps [11,12]. In order to render our results obtained using C_2 hydrocarbons comparable to those obtained using CH_4, we first have conducted reactions using that hydrocarbon under the most similar experimental procedure and in the same apparatus.

For this experiment, 80 mg of WO_3 powder were placed in a flow reactor made of quartz and the system was purged with pure argon (flow of 2.4 $\ell\,h^{-1}$ during 20 min) at room temperature until the signals typical of air composition (N_2 and O_2) returned to the baseline of the mass spectrometer. During this time, a flow of CH_4/H_2 in Ar ($P_{CH_4} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) at a flow rate of 2.4 $\ell\,h^{-1}$, was established in by-pass. Then this mixture was switched to the reactor. After a few minutes, the temperature increase was started (linear increase of 360 K h^{-1} from room temperature to 1273 K, this last temperature being maintained for 20 min). Two types of information can be obtained from such TPR experiments. First, the phenomena occurring during the treatment can be studied by analyzing the type of molecules that are produced and the temperature at which they appear. Second, the elementary composition of the sample can be obtained by elementary mass balance calculations.

The results of this experiment are presented in figure 1, where CH_4, H_2O and CO pressures are plotted versus temperature.

H_2O and CO are the products of WO_3 reduction. As can be seen in the TPR spectrum, the reduction starts at about 873 K. H_2O production is characterized by two maxima. The first, between 873 and 1123 K, corresponds in terms of mass balance to the formation of WO_2. In the second step, between 1123 and 1273 K, a second peak of H_2O is observed simultaneously to a small production of CO and consumption of CH_4. It should be noted that the amount of CO produced corresponds quantitatively to the CH_4 consumption, which means that no carbon is retained by the solid. The second wave of H_2O corresponds to the formation of tungsten metal in term of mass balance.

Just after the total reduction of WO_2 to W metal, a sudden and important increase of the CH_4 consumption occurs, corresponding to the carburization step [12,22]. The integration of the peak of carbon consumption leads to a value of the C/W ratio equal to 1.1. This value, slightly in excess as compared to 1 which would correspond to the WC stoichiometry, shows that some free carbon has been deposited.

It has been checked by X-ray diffraction that the resulting material is WC. No other phase could be observed.

3.2. Preparation of WC with C_2 carburizing mixtures

3.2.1. C_2H_6/H_2 mixture

A blank experiment has been made by analysing a flow of a C_2H_6/H_2 mixture in an empty reactor under TPR

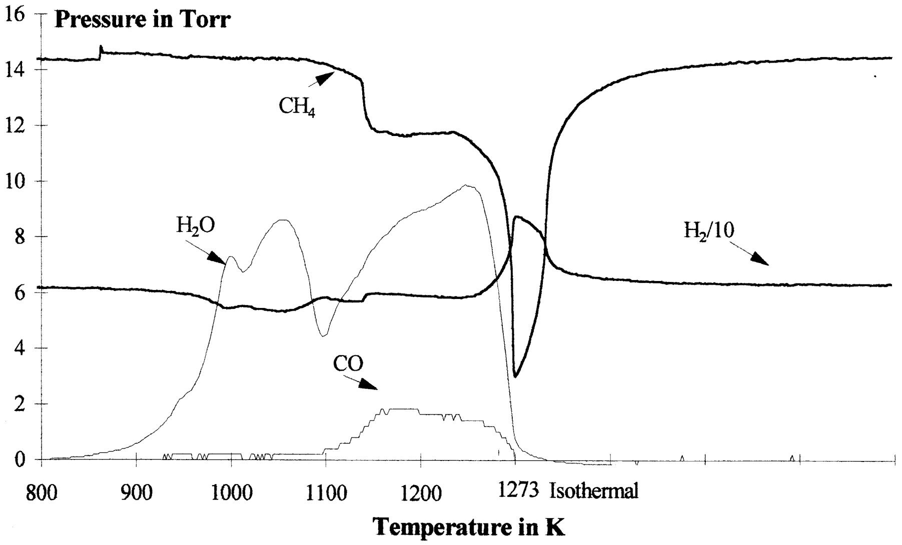

Figure 1. Temperature-programmed reduction/carburization of 80 mg WO_3 powder with a 2.4 $\ell\,h^{-1}$ mixture of CH_4/H_2 in Ar ($P_{CH_4} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) at 360 K h^{-1}.

conditions. A flow of C_2H_6/H_2 in Ar ($P_{C_2H_6} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) at a volumetric flow rate of 2.4 $\ell\,h^{-1}$ was prepared in by-pass. After switching to the reactor a linear temperature increase of 720 K h^{-1} from room temperature to 1123 K was applied. The results of this experiment are presented in figure 3.

One observes from about 950 K a progressive dehydrogenation into C_2H_4, followed, at higher temperatures (1100 K), by a production of CH_4 and C_2H_2 as well as an important carbon deposit on the wall of the reactor.

Carburization of WO_3 by a $C_2H_6/H_2 = 1/9$ mixture. A typical experiment is presented in figure 4 where C_2H_6, C_2H_4, H_2, H_2O and CO pressures are plotted versus the increase of the temperature. For this experiment, 100 mg of WO_3 have been carburized in a C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 7.5$ Torr, $P_{H_2} = 65$ Torr, $P_{Ar} = 697$ Torr) and a 2.7 $\ell\,h^{-1}$ flow rate. A linear increase of temperature (360 K h^{-1}) was applied from room temperature to 1173 K. This experiment shows three main steps in the carburization process. Reduction starts only around 850 K with H_2O production which is still characterized by two maxima. The first, between 850 and 1023 K, corresponds to WO_2 formation (calculated in terms of mass balance). The second step of reduction (between 1023 and 1123 K) corresponds to a smaller production of H_2O, as compared to the first peak, and is accompanied by an increase of the production of CO due to the reduction of WO_2 by the hydrocarbon. It should be noted that during this period, no carbon consumption is observed. After the total reduction of WO_2 into tungsten metal at

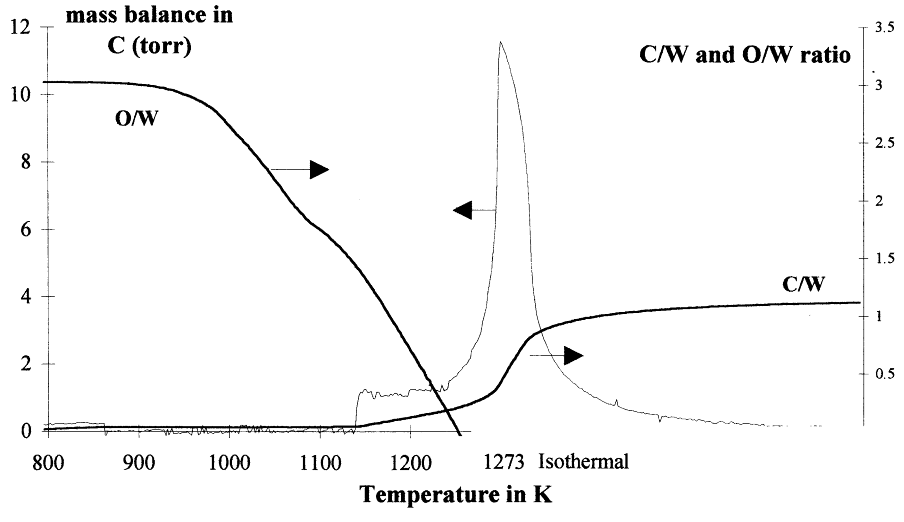

Figure 2. C and O mass balance during the carburization.

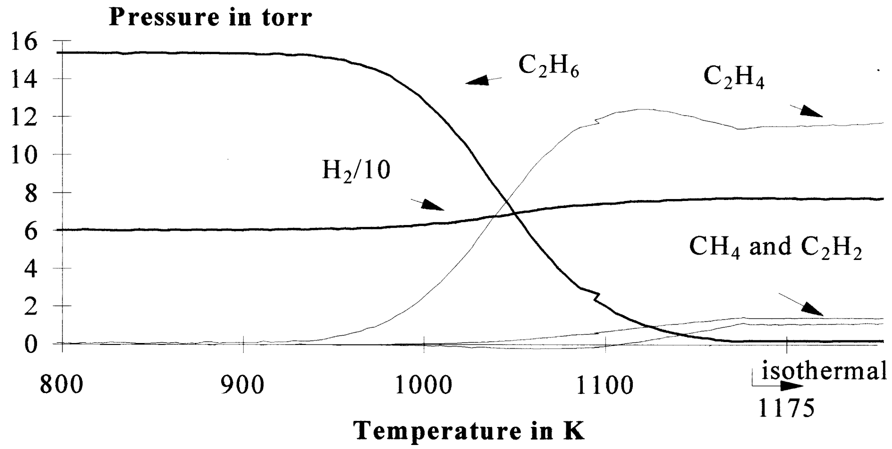

Figure 3. Blank experiment with a 2.4 ℓh^{-1} mixture of C_2H_6/H_2 in Ar ($P_{C_2H_6} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) at 720 K h^{-1}.

1123 K a third step corresponding to an important carbon consumption during about 10 min is observed. This one corresponds to the W carburization. Afterwards, an increase of the C_2H_4 signal is observed up to a value corresponding to that observed in the blank experiment. Integration of the peak of carbon consumption leads to a value of C/W ratio equal to 1.1 and the X-ray diffraction pattern of the resulting material is characteristic of WC.

Carburization of WO_3 by a $C_2H_6/H_2 = 1/4$ mixture. In this experiment, 60 mg of WO_3 have been carburized in a flow of 2.4 ℓh^{-1} of a C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) with a heating rate of 360 K h^{-1} from room temperature to 1123 K. This last temperature was maintained during 15 min. The results are presented in figure 6, where C_2H_6, C_2H_4, H_2, H_2O and CO pressures are plotted versus the temperature.

It can be seen that the reduction of tungsten trioxide occurs in a different way as compared to the $C_2H_6/H_2 = 1/9$ mixture. The production of H_2O shown in previous experiments is replaced by a large production of CO in two steps. The first one appears between 973 and 1023 K with a small production of H_2O, and the second occurs between 1023 and 1123 K with a decrease of the production of H_2O. The carbon consumption is mainly detected when the second peak of CO production decreases.

After carburization, an increase of C_2H_4 production is observed until it reaches the equilibrium value with C_2H_6 at this temperature. This value is in agreement with that measured in the blank experiment (figure 2). At this time, the carburization is completed and the remaining carbon consumption corresponds to the deposition of carbon at the surface of the sample.

A ratio of C/W equal to 1.2 is obtained for this experiment and the X-ray diffraction pattern of the final product is characteristic of WC. Anyway, the X-ray diffraction pattern let appear very fade lines that might correspond to small amounts of W_2C.

After carburization, this catalyst has been treated for 2 h at 1073 K under a flow of 100% H_2 in order to remove the excess of free carbon. It is well known that

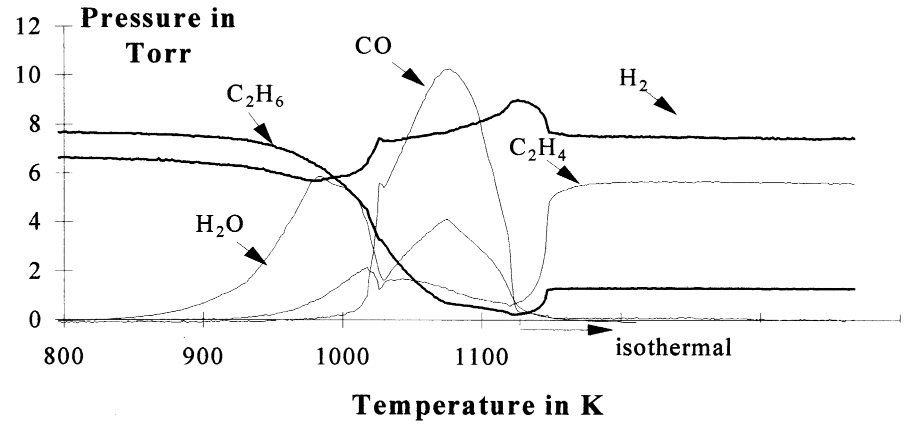

Figure 4. Temperature-programmed reduction/carburization of 100 mg WO_3 powder with a 2.7 ℓh^{-1} C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 7.5$ Torr, $P_{H_2} = 65$ Torr, $P_{Ar} = 697$ Torr) at 360 K h^{-1}.

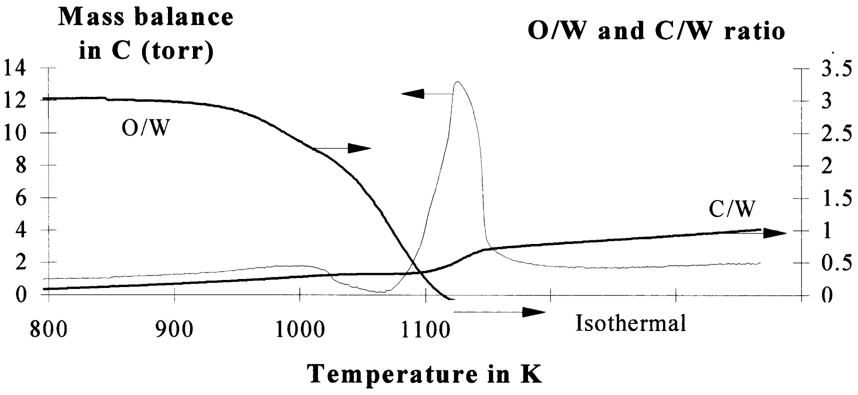

Figure 5. C and O mass balance during the carburization.

this free carbon can obstruct the porous system of the catalyst and might contain itself another porous system. The BET surface area, as measured from N_2 adsorption at liquid nitrogen temperature, is 25 m^2/g [22].

Carburization of WO_3 by a $C_2H_6/H_2 = 1/1$ mixture. Figure 8 represents the carburization of 100 mg of WO_3 in a flow of 2.7 ℓh^{-1} of a C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 35$ Torr, $P_{H_2} = 35$ Torr, $P_{Ar} = 690$ Torr) with a heating rate of 360 K h^{-1} from room temperature to 1073 K. This last temperature was kept during 30 min. In this figure, the same compounds as previously are observed.

Here again the hydrocarbon participates in the WO_3 reduction process. The main difference with carburization in a 1/4 gas mixture is that only one peak of CO production is observed. The beginning of carbon consumption appears during the production of CO. Then after this one, a large consumption of carbon, associated with the carburization process, occurs before the return of C_2H_4 pressure to its equilibrium value in homogeneous phase (figure 2). A ratio of C/W equal to 2.7 was calculated for this experiment.

3.2.2. C_2H_4/H_2 mixture

A blank experiment is represented in figure 10 where a mixture of C_2H_4/H_2 in Ar ($P_{C_2H_4} = 14$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 686$ Torr) is submitted to a temperature-programmed increase of 720 K h^{-1} from room temperature to 1223 K. In this case, a transformation of C_2H_4 into C_2H_2 appears at 1123 K. At the same temperature, a small production of CH_4 (less than 0.5 Torr) is also observed.

Carburization of WO_3 with a $C_2H_4/H_2 = 1/4$ mixture. The carburization of 100 mg of WO_3 with a 2.7 ℓh^{-1} mixture of C_2H_4/H_2 in Ar ($P_{C_2H_4} = 14$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 686$ Torr) is represented in figure 11 where C_2H_4, CO, H_2O pressures are plotted versus temperature. The beginning of the consumption of C_2H_4, at 973 K, corresponds to the beginning of CO production. At this temperature, a small production of H_2O is also observed. The C_2H_4 consumption abruptly increases at 1050 K and is accompanied by a important production of CO between 1050 and 1173 K and by a decrease of H_2O production. The end of CO production corresponds to the total reduction of WO_3 into W metal (calculated in terms

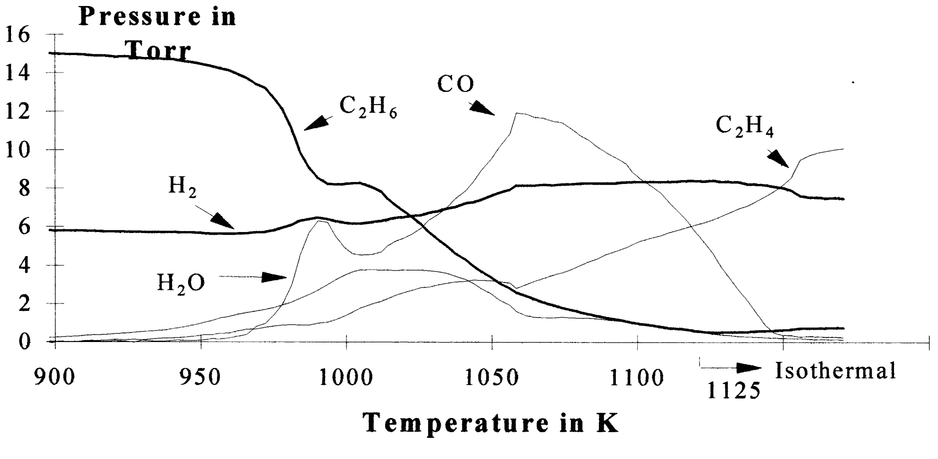

Figure 6. Temperature-programmed reduction/carburization of 60 mg of WO_3 powder with a 2.4 ℓh^{-1} C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 15$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 685$ Torr) at 360 K h^{-1}.

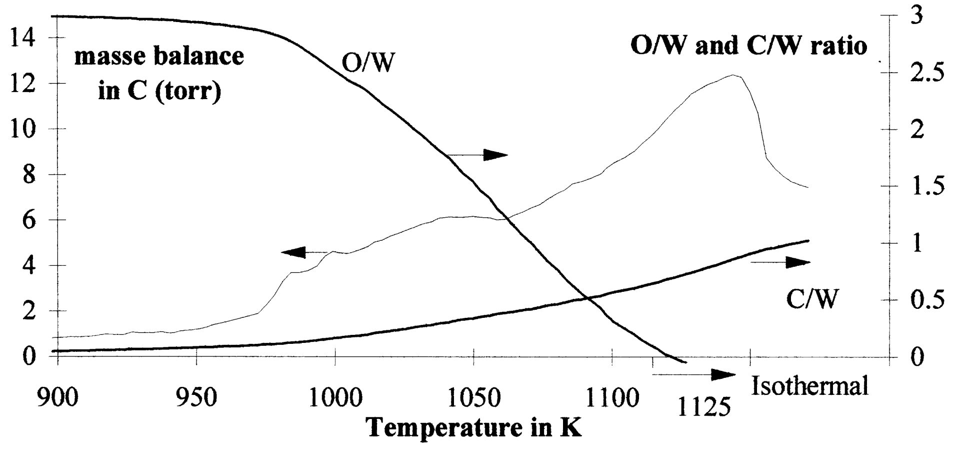

Figure 7. C and O mass balance in C during the carburization.

of mass balance). We observe a carbon consumption only after the top of the peak of CO production. The carburization of the solid appears between 1050 and 1173 K. Then, a carbon deposition, corresponding to that observed in blank experiment (figure 10), takes place. Integration of the peak of carbon consumption leads to a value of C/W ratio equal to 1.5 and the X-ray diffraction pattern is characteristic of only WC.

Carburization of WO_3 with a $C_2H_4/H_2 = 1/1$ mixture. Figure 13 represents the carburization of 100 mg of WO_3 with a 2.7 $\ell\,h^{-1}$ mixture of C_2H_4/H_2 in Ar ($P_{C_2H_4} = 32$ Torr, $P_{H_2} = 35$ Torr, $P_{Ar} = 693$ Torr) during a linear increase of the temperature of 360 K h^{-1} from room temperature to 1223 K. The beginning of C_2H_4 consumption is still observed at 973 K and corresponds to the beginning of CO production and a small production of H_2O. The C_2H_4 consumption increases at 1023 K together with the production of CO. This occurs mainly between 1023 and 1163 K. During CO production, the C_2H_4 pressure remains quite high and follows the CO production. Nevertheless, at this moment, the consumption of hydrocarbon is higher than the production of CO. This indicates that a small amount of carbon is retained by the solid. This amount increases between 1100 and 1163 K. After this temperature, the consumption of carbon decreases to a given value proportional to the C_2H_4 degradation in homogeneous phase (figure 10). In this case, it is difficult only by the means of TPR experiments to say when exactly the carburization process occurs.

The integration of the peak of carbon consumption provides a value of C/W ratio equal to 4.5 and the X-ray diffraction pattern is characteristic of WC.

4. Discussion

For several years, different works concerning the intention to use tungsten carbide in catalysis have been

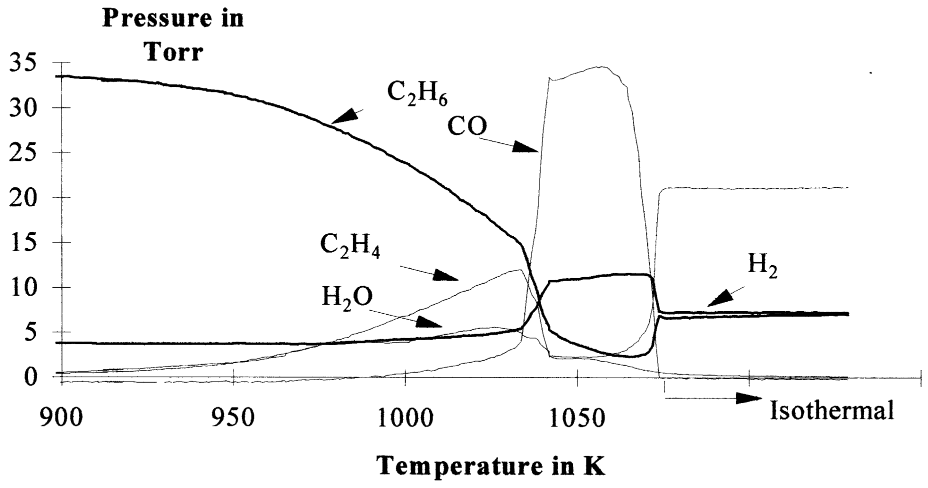

Figure 8. Temperature-programmed reduction/carburization of 100 mg of WO_3 powder with a 2.7 $\ell\,h^{-1}$ C_2H_6/H_2 mixture in Ar ($P_{C_2H_6} = 35$ Torr, $P_{H_2} = 35$ Torr, $P_{Ar} = 690$ Torr) at 360 K h^{-1}.

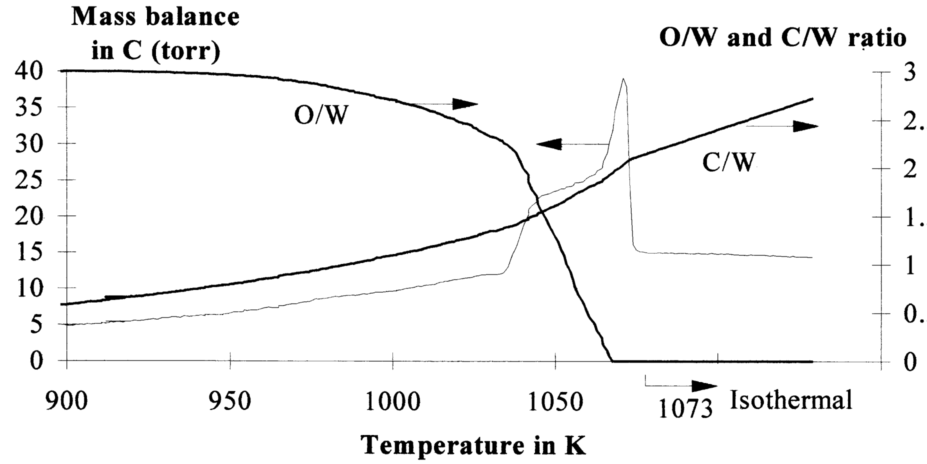

Figure 9. C and O mass balance during the carburization.

made. Many of these works were focused on the improvement of the value of the surface area for these carbides, using different preparation procedures as well as, for example, the choice of WO_3 as precursor. It is surprising that a lot of these works mention an increase of the value of surface area since the catalytic properties of the tungsten carbide depend mainly on the surface state (oxygen contents, the porous system, surface composition, ...). Moreover, it has been shown that the high value of the surface area for these catalysts is due for a large part to the presence of micropores, which are interesting for only few reactions in catalysis [22].

Unfortunately, only few works have been devoted to a systematic study of the preparation procedures for WC, the influences of the gas used, their ratios in the gas phase, the temperature used in order to put in evidence the mechanism(s) of carburization and their influences on the catalysts obtained. Under these conditions, we felt obligated to prepare ourselves a reference catalyst using CH_4 as carburizing agent.

The important stability of CH_4 is well known and can be responsible for the high temperature of reduction and carburization of WO_3 (figure 1). This high temperature has been shown by Vermaire et al. [23] to be responsible for the formation of tungsten aluminates that are very difficult to reduce. Moreover, under our carburization conditions, the total reduction of WO_3 into metallic W must be reached before observing a consumption of CH_4 responsible for the carburization. This process appears at 1273 K. Such temperature, needed to obtain the complete carburization, can be responsible for the small surface area obtained for this catalyst. Furthermore, no previous reduction of the WO_3 due to methane is observed. In this case, H_2 reduces WO_3 to a stoichiometry corresponding to WO_2. Then the hydrocarbon participates in the reduction and CO is produced quantitatively until a stoichiometry equal to W metal is reached. The following consumption of the hydrocarbon corresponds to the carburization.

To enhance the interaction between the hydrocarbon and the solid at lower temperature, other carburizing agents, like C_2H_6 and C_2H_4, have been used in this work.

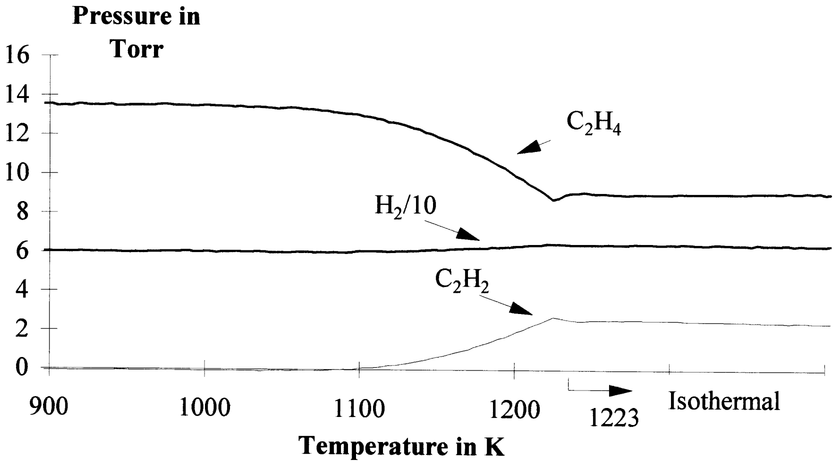

Figure 10. Blank experiment with a mixture of 2.4 ℓ h^{-1} C_2H_4/H_2 in Ar ($P_{C_2H_4} = 14$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 686$ Torr) at 720 K h^{-1}.

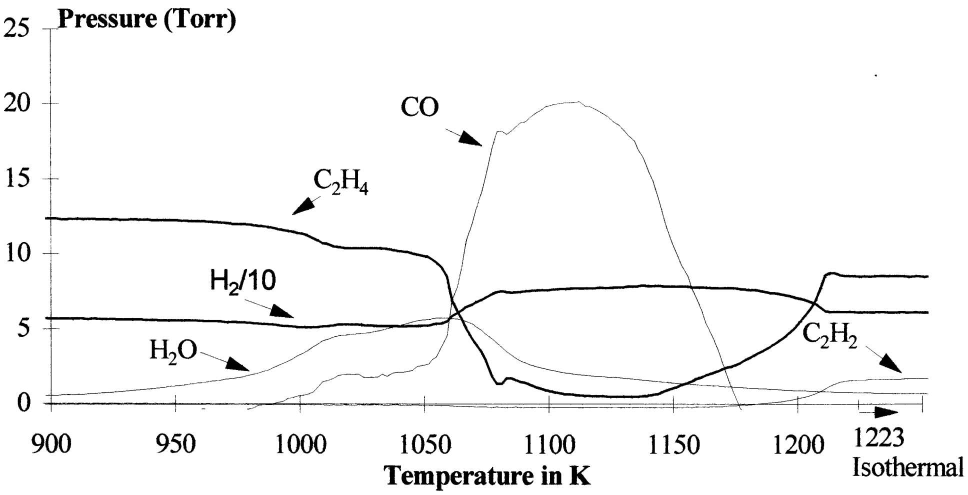

Figure 11. Temperature-programmed reduction/carburization of 100 mg of WO_3 with a 2.7 $\ell\,h^{-1}$ mixture of C_2H_4/H_2 in Ar ($P_{C_2H_4} = 14$ Torr, $P_{H_2} = 60$ Torr, $P_{Ar} = 686$ Torr) at 360 K h^{-1}.

It should be noticed that the C–H bond in these compounds is less strong than in CH_4. Moreover, rupture of the C–C bond can also appear and then can intervene in the carburization process. One can verify this difference in reactivity by comparing the temperature of the reduction of WO_3 on figures 1 and 5. This temperature is 150 K lower using C_2H_6 as carburizing agent. Another important difference in reactivity is that C_2 hydrocarbons participate in the reduction more than CH_4.

By examining figures 4, 6 and 8 one sees an effect of the partial pressure in carburizing agent. For a 1/9 C_2H_6/H_2 mixture (figure 4), the first step of the reduction is associated with H_2 consumption and H_2O production. When a stoichiometry close to WO_2 is obtained, the carburizing agent intervenes in the reduction process, which results in a CO production. All the carbon consumed from ethane quantitatively appears in the form of CO. After quasi-total reduction of WO_3 into tungsten metal, the carburization process starts.

On the other hand, by using higher partial pressures of C_2H_6 (figures 6 and 8), one observes an increase of the production of CO. Moreover, as can be seen in figure 5 the reduction of WO_3 starts with the production of CO. The mass balance analysis shows that the H_2O produced during these experiments can be due to the reaction between the hydrogen produced by the reaction $C_2H_6 \rightarrow C_2H_4 + H_2$ and the tungsten trioxide. Nevertheless, in these experiments, the carbon consumption starts during the CO production and thus before complete reduction of WO_3 into metal and increases when the reduction of WO_3 is nearly finished. In this case, it is difficult to determine the step at which the carburization occurs.

By increasing the partial pressure of C_2H_6, we also observe that the reduction of WO_3 starts at lower temperature than the experiments using CH_4 as carburizing agent . This is in agreement with the results using CH_4 mixtures published by Frennet et al. [11,12].

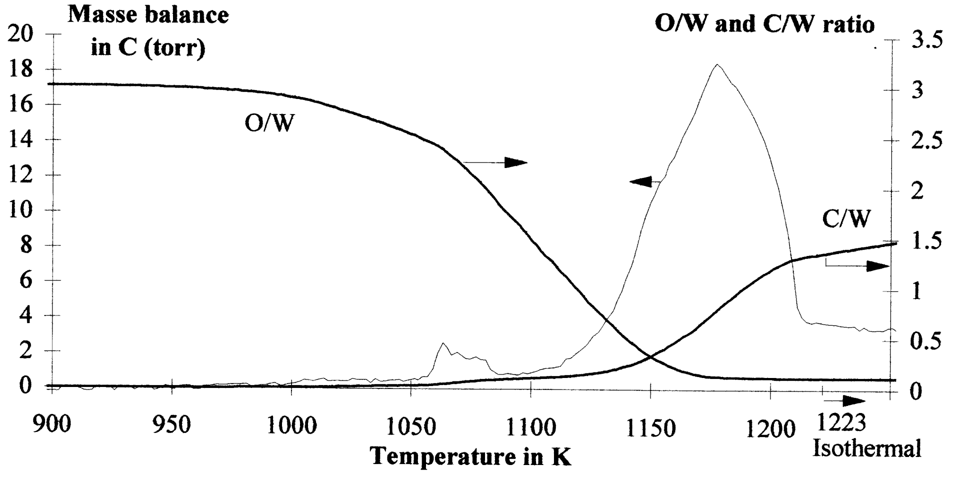

Figure 12. C and O mass balance during the carburization.

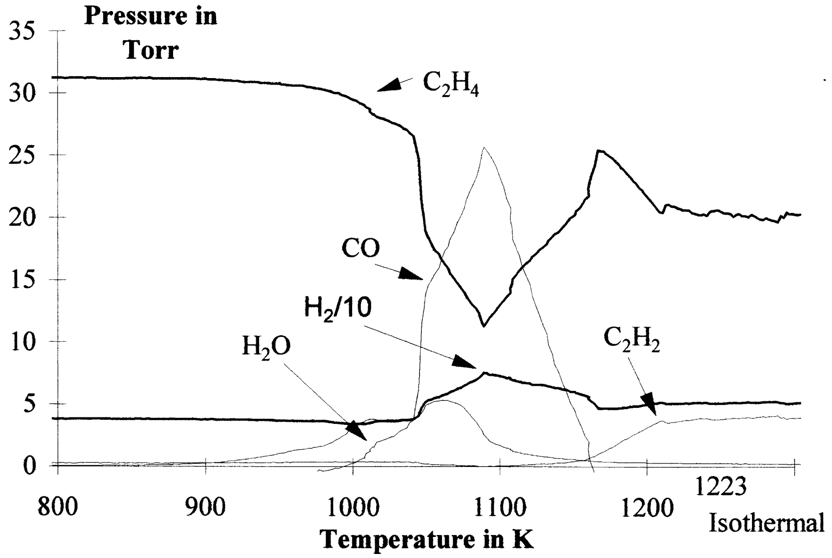

Figure 13. Temperature-programmed reduction/carburization of 100 mg of WO_3 with a 2.7 ℓ h^{-1} mixture of C_2H_4/H_2 in Ar ($P_{C_2H_4} = 32$ Torr, $P_{H_2} = 35$ Torr, $P_{Ar} = 693$ Torr) at 360 K h^{-1}.

Nevertheless, let us mention that when the P_{Hc}/P_{H_2} ratio increases in fact the pressure of the hydrocarbon increases but also the pressure of hydrogen decreases since the partial pressure of the total reactants remains equal to 10% of the atmospheric pressure. Then, when this ratio is high, the conditions are more unfavorable for the reduction of WO_3 by H_2 since its amount is low in the gas phase. This fact must be taken into account and can be responsible for the participation of the hydrocarbon in the reduction of WO_3, instead of participation of hydrogen.

To summarize, a partial pressure effect in carburizing agent is observed during reduction of WO_3. If the hydrocarbon partial pressure is not high enough (7.5 Torr, figure 4), the reduction of WO_3 occurs by the action of hydrogen included in the C_2H_6/H_2 mixture and corresponds to a production of H_2O. After WO_2 formation, the carburizing agent participates in the reduction process. If the partial pressure is high enough (15 Torr figure 6, 35 Torr figure 8), the reduction is associated with some production of CO and the H_2O formed during this step may be due (in term of mass balance) to the reduction of WO_3 by the hydrogen formed during the dehydrogenation of C_2H_6 into C_2H_4.

During the reduction of WO_3, a competition takes place between the rate of diffusion of the metallic tungsten created at the surface and the reduction by hydrogen:

– At high hydrogen pressure, this reduction is rapid and the temperature is relatively low and thus the diffu-

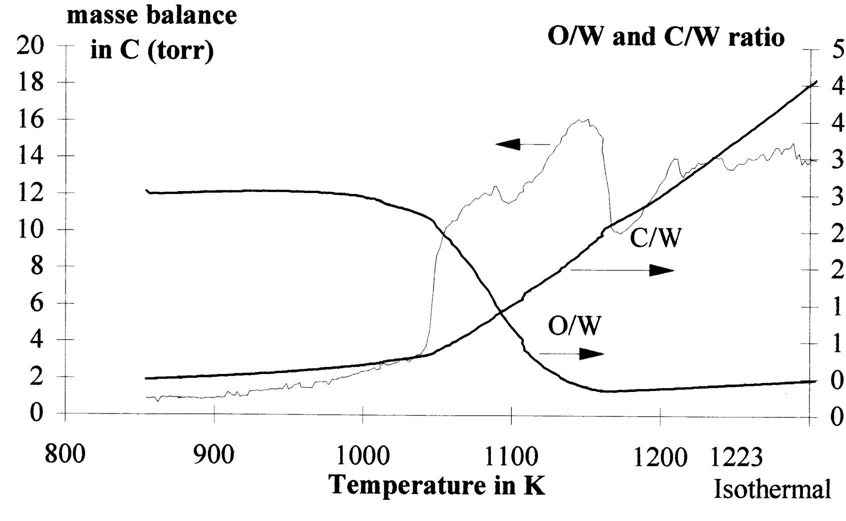

Figure 14. C and O mass balance during the carburization.

sion rate is low. This would allow the reaction of the alkane with the surface W metal before its diffusion in the bulk of the solid. As the alkane pressure is also high, large amounts of carbon react with the surface and contribute simultaneously to the reduction and to the actual carburization.

– At lower hydrogen pressure, the rate of reduction by hydrogen is lower. This would induce a shift of this process to higher temperature and to higher diffusion rates of tungsten within the oxide structure. The residence time of such metallic tungsten at the surface of the carbide is therefore shorter and limits the reaction with ethane. However, around 973 K, ethane is homogeneously activated and the reactive radicals may therefore take over the reduction, which is, in this case, characterized by CO production.

The blank experiment of C_2H_6/H_2 mixture (figure 3) shows that the production of C_2H_4 increases with the increase of temperature. Moreover, it has been shown in our experiments that the participation of the hydrocarbon in the WO_3 reduction occurs when the amount of C_2H_4 in the system is sufficient.

At this point it can be questioned which of C_2H_6 or C_2H_4 is the carburizing agent.

During these experiments, the partial pressure of C_2H_4 in the system allows the quantitative production of CO during the reduction of WO_3, and the behavior of the production of C_2H_4 in parallel with the production of CO allows us to say that C_2H_4 is the carburizing agent and not C_2H_6. Moreover, it appears from figure 8 that at the moment corresponding to the production of CO and by extrapolating the C_2H_6 consumption to its end value at 1073 K, the amount of C_2H_6 remaining in the system is not sufficient to be responsible for the complete production of CO.

The experiments using C_2H_4/H_2 mixtures (figures 11 and 13) show that the transformation of C_2H_6 into C_2H_4 is not a limiting step responsible for the decrease of the temperature of the reduction of WO_3. By using the same ratio of C_2H_6 (figures 6 and 8) or C_2H_4 (figures 11 and 13) in the carburizing mixture, the temperature at which the reduction of WO_3 starts remains unchanged. In figures 11 and 13 the H_2O produced can be due to the reaction between WO_3 and H_2 produced by C_2H_4 dehydrogenation ($C_2H_4 \rightarrow C_2H_2 + H_2$).

Let us notice that this reaction appears in the blank experiment for a mixture 1/4 C_2H_4/H_2 (figure 10) at 1100 K while in presence of WO_3 (figure 11) it appears at 973 K. This indicates a possible effect of the solid on the temperature of C_2H_4 dehydrogenation.

5. Conclusion

The study of the carburization of bulk WO_3 by means of C_2H_6/H_2 and C_2H_4/H_2 mixtures has given the following interesting information.

When using a C_2H_6/H_2 mixture, the results suggest that C_2H_4, formed by the dehydrogenation of C_2H_6 in homogeneous phase, is the carburizing agent and not C_2H_6. The carburization process only occurs when C_2H_4 is present in a sufficient amount. During WO_3 reduction, ethylene consumption is observed and corresponds quantitatively to the production of CO. After carburization, ethylene pressure returns to an equilibrium value which depends on the temperature.

We have shown that the use of C_2H_6 or C_2H_4 instead of CH_4 induces a decrease of 150 K in the temperature needed for the total reduction of WO_3. Nevertheless, C_2H_6/H_2 and C_2H_4/H_2 mixtures lead to a large excess of free carbon deposited on the WC surface as compared to CH_4-based mixtures. This free carbon can, however, be removed by means of an activation process with hydrogen [22]. This decrease of the temperature of reduction of WO_3 may be interesting for the preparation of supported tungsten carbide by avoiding the formation of irreducible species resulting from the reaction of WO_3 with a support.

These results also show a large pressure effect of the carburizing mixture on the tungsten trioxide reduction. Let us mention that two WO_3 reduction process have been observed.

– When the reduction begins by means of hydrogen, which is responsible for the production of water, a stoichiometry close to WO_2 is needed before the carburizing agent reacts with the solid phase.

– If the partial pressure in carburizing agent is sufficient, leading to a low partial pressure of H_2, the reduction begins with hydrocarbon consumption, which quantitatively reappears in the form of CO. The H_2O produced during this experiment can be due to the reaction between WO_3 and H_2 resulting from the dehydrogenation of the hydrocarbon.

Total surface areas obtained for samples prepared using ethane as carburizing agent are close to 25 m^2/g instead of 10 m^2/g for those prepared under the same conditions but using methane as carburizing agent.

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