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Control of the Catalytic Activity of Tungsten Carbides

II. Physicochemical Characterizations of Tungsten Carbides

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The bulk and surface characterization of tungsten carbide samples, using X-ray diffraction, XPS and chemisorption techniques are described. The aim is to establish links between the preparation factors of tungsten carbides and their catalytic properties. XPS observations have shown that tungsten carbide samples were superficially oxidized as a result of the passivation treatment to which they were submitted in order to prevent them from igniting spontaneously upon exposure to air. According to XPS data, the surface oxide was completely removed by reduction in H_2 at 300°C. No detectable variation of the lattice constants of the carbide samples could be evidenced by X-ray diffraction, which could be ascribed either to the nature of their oxide precursor or to their final composition (W_2C/WC ratio). On the other hand, variations of the surface C/W ratio (as estimated by XPS) versus the conversion to WC have been evidenced and tentatively related to the mechanism of WC formation. The results of H_2–O_2 titration experiments have confirmed the analogy reported previously between the chemisorptive properties of tungsten carbides and noble metal catalysts; they have been interpreted in terms of the surface accessible to gaseous molecules such as H_2 and O_2 (referred to below as "pseudometallic surface"). The extent of the pseudometallic surface has been found to be negligible for carbides prepared in pure CO, and it decreases for increasing conversions to WC of samples prepared in CO–CO_2 mixtures. These observations are correlated with the accumulation of free carbon on the surface of the samples during the progress of the carburization reaction. The pseudometallic surface of tungsten carbides can therefore be interpreted as the fraction of their surface not covered by an impervious layer of pregraphitic carbon.

INTRODUCTION

Physicochemical characterization of the surface of tungsten carbides is essential in order to understand the relationship between their catalytic properties and preparation procedures. Nikolov *et al.* (*1, 2*) have shown that the catalytic activities of carbide samples can be correlated with their surface chemical composition. XPS and Auger spectroscopic observations reported by Ross and Stonehart (*3*) have shown up variations of the surface composition of tungsten carbides depending on their procedure of preparation. Finally, Kojima *et al.* (*4*) have observed a 10-fold increase of the catalytic activity of WC after a thermal treatment resulting in the removal of surface oxygen.

The aim of the present paper is not to make an extensive physicochemical study of tungsten carbides, but rather to gain useful information for interpreting the relationship between the preparation parameters presented previously (*5*) and the catalytic properties of tungsten carbide samples to be described in Part III of this series. Lattice constant measurements will be used to see whether preparation factors can result in bulk deviation of the stoichiometry of carbide samples. The surface composition of the samples (nature of the carbon species, C/W ratio) will be examined by XPS. The effects of a mild oxidation (passivation treatment) and of a subsequent activation treatment in hydrogen will also be reported.

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Finally, the results of H_2–O_2 titration experiments will be presented and tentatively interpreted in the light of the XPS data.

EXPERIMENTAL

Preparation of the Samples

Full details on the preparation of the samples have been presented in Part I (*5*). The conditions of preparation, C/W ratios (as derived from X-ray diffraction data) and specific surface areas of the samples selected for the present study are summarized in Table 1.

It was necessary to submit the samples to a mild oxidation treatment (referred to below as "passivation treatment") in order to prevent them from igniting spontaneously upon exposure to air. The treatment consisted in flowing diluted oxygen (5% O_2 in He, "Accurate Mixture" from Air Liquide) for 2 h at 20°C over the freshly carburized sample. As will be shown in Part III, the catalytic activity of the passivated samples was very low, so that it was necessary to submit them to an activation treatment prior to performing the catalytic tests. To do this, the samples were heated for 2 h at 300°C in the test reactor in a H_2 stream (15 liters/h). Preliminary temperature-programmed reduction experiments have shown that passivated samples exhibited a reduction in the range 300–400°C. Furthermore, the samples activated that way were pyrophoric just like the freshly prepared ones.

Determination of Lattice Constants

X-Ray diffraction patterns were obtained with a Norelco-Philips diffractometer (PW 43090) equipped with a diffracted-beam graphite monochromator (Cu$K\alpha$ radiation $\lambda = 1.5418$ Å). The interplanar spacings d corresponding to the following sets of indices were accurately determined: (100),

TABLE 1

Conditions of Preparation, Composition, and Specific Surface of Tungsten Carbide Samples[a]

Sample[b]	Carburizing conditions		Composition		S_{BET} (m^2/g)
	Gas CO_2/CO	Time (h)	$WC/(WC + W_2C)$[c]	C/W[d]	
Wh-W_2C-wc[e]	0.5	24	0	0.50	36
Wh-W_2C-ic[e]	0.1	0.5	0	0.50	33
Wh-WC-14	0.1	1	14	0.54	32
Wh-WC-55	0.1	6	55	0.69	30
Wh-WC-72	0.1	10	72	0.78	29
Wh-WC-76	0.1	10.5	76	0.81	31
Wh-WC-100	0.1	13	100	1.00	28
Ye-WC-100	0.1	13	100	1.00	20
Wh-WC-CO	0.0	24	100	1.00	47

[a] The samples were first reduced in hydrogen and then carburized at 780°C (gas flow rate = 31 liters/h) (*5*).

[b] The oxide precursors were respectively $WO_3 \cdot \frac{1}{3}H_2O$ and $WO_3 \cdot 2H_2O$, for samples Wh-W_2C-n and Ye-WC-100.

[c] Determined from X-ray diffraction (see Experimental Section).

[d] Taking x as the molar fraction of WC in the carbide mixture, $(C/W) = 1/(2 - x)$ (*5*).

[e] wc, well-crystallized; ic, ill-crystallized. Details about the nomenclature are given in (*5*).

(101), and (110) for W_2C and (001), (100), and (110) for WC. Each line was recorded in the step-scanning mode (angular increment = 1/100° 2θ and counting time = 1 min) and the peak angle was taken as a measure of its position. The lattice constants were calculated using the following equation, valid for the hexagonal system (*6*):

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{3a^2 \times 1}{4c^2}.$$

The molar fraction x of WC in a W_2C–WC mixture was calculated from the X-ray diffraction patterns as

$$x = h_1/(h_1 + h_2),$$

where h_1 and h_2 are the peak heights of the most intense reflections of WC ($d = 1.88$ Å) and W_2C ($d = 2.28$ Å), respectively.

The X-ray measurements have been made on passivated samples. Lines corresponding to oxidized tungsten phases were never detected on the diffraction patterns, indicating that the passivation treatment did not affect the results.

XPS Analysis

XPS spectra were recorded with a Vacuum Generators ESCA 3 spectrometer equipped with a Tracor Northern NS560 signal averager (A1 anode, $h\nu = 1486$ eV, operated at 14 kV, 20 mA; residual pressure in the analysis chamber = 1.32×10^{-7} Pa).

In situ activation treatment. Early attempts to analyze activated samples by XPS consisted in transferring them from the reactor to the spectrometer via a glovebox purged with nitrogen. However, this technique did not prevent the samples from suffering surface oxidation. Therefore, the samples were submitted to an activation treatment in the preparation chamber of the spectrometer. The following conditions were found to simulate satisfactorily the standard activation treatment used prior to the catalytic test: the sample was maintained for 16 h at 300°C in a 50% H_2 in Ar mixture (due to its high thermal conductivity, the use of pure H_2 did not allow the desired temperature to be reached in the spectrometer).

Quantitative treatment of XPS data. Carbon/tungsten ratios were estimated using the formula (*7*)

$$\frac{C_x}{C_y} = \frac{I_x i_y}{I_y i_x},$$

where I_x and I_y are the peak intensities corresponding in the present case, respectively, to C and W, and i_x and i_y are the corresponding sensitivity factors of Wagner *et al.* (*8*).

The C 1*s* peaks were decomposed using a computer program developed by Debatty and Genet (*9*), assuming three carbon species, viz. pregraphitic carbon ($E_B = 285 \pm 0.1$ eV), carbidic carbon ($E_B = 382.7 \pm 0.5$ eV) and carbonate ($E_B = 288$ eV) (*10*). All the carbon species were assumed to have the same sensitivity factor. Their sum will be referred to below as C_{total}.

The W 4*f* doublet ($E_B = 34$ eV) of W^{VI} is shifted by about 4 eV toward higher energies as compared with W^0. The $I(W^{VI})/I(W^0)$ experimental ratios have been interpreted using an extension of the model proposed by Kerkhof and Moulijn (*11*) for supported catalysts. In the present case, the passivated examples have been modelled as cubic particles covered by a uniform layer of WO_3. In this case, it can be demonstrated that the experimental intensity ratio of the W^{VI} and W^0 peaks is given by the formula

$$\left(\frac{I_y}{I_x}\right)_{\text{exp}} = \left(\frac{n_y}{n_x}\right)_{\text{bulk}} \left(\frac{b}{a}\right) \frac{1 - \exp(-a)}{1 + \exp(-a)} \frac{2 - f(1 - \exp(-b))}{1 - \exp(-b)},$$

where I_x and I_y are the experimental intensities assigned, respectively, to W^0 and W^{VI}; n_i is the bulk atomic concentration of species i (atoms/cm^3); $b = c/l_x$ and $a = t/l_y$, where c is the edge of the model particle of W_xC, t is the thickness of the oxide layer, l_x and l_y are the mean free path of the W 4*f* photoelectrons, respectively, through W_xC and WO_3; $f = t^2/(c + 2t)^2$ is the ratio of the surface of the W_xC core to the outer surface of the oxide layer.

$$\left(\frac{n_y}{n_x}\right)_{\text{bulk}} = \frac{(c + 2t)^3 - c^3}{c^3} \times \frac{\nu_y \rho_y M_x}{\nu_x \rho_x M_y}$$

where ν_i is the stoichiometric coefficient of W in the formula of species i (x and y standing respectively for W_xC and WO_3), ρ_i is its density, and M_i its molecular weight. Estimates of the l_i have been calculated using the method of Seah and Dench (*12*): l_x = 1.85 and 1.75 nm, respectively, for W_2C and WC, and l_y = 3.31 nm for WO_3. The procedure used for estimating t from the experimental data consisted in calculating the $(I_y/I_x)_{\text{exp}}$ expected for various values of t and for a given set of the parameters, using the equations above, and then interpolating the value of t corresponding to the observed (I_y/I_x) ratio.

Hydrogen–Oxygen Titrations

The H_2–O_2 titration method proposed by Benson and Boudart (*13*) for estimating the metallic surface of noble metal catalysts have been found to be ineffective for tungsten carbides when it was carried out at 20°C. Therefore, a temperature-programmed titration (TPT) procedure, similar to that used previously by Blanchard *et al.* (*14*), has been developed. The present method differed from that of the cited authors in that the titration reaction was monitored by measuring the amount of water produced rather than that of hydrogen consumed.

About 0.1 g of passivated sample previously stored in air was placed in the reactor of a temperature-programmed reduction (TPR) apparatus similar to that of Robertson *et al.* (*15*). After purging with Ar, a pure H_2 flow (25 ml/min) was established. The temperature was raised to 300°C at a rate of 10°C/min and the cycle was continued isothermally. After the reduction of the sample was complete, the reactor was purged with Ar and cooled to room temperature (Cycle I). At the end of this first titration cycle, the sample was contacted with the passivating gas mixture for a fixed time; a second titration cycle (Cycle II) was then performed in exactly the same conditions as Cycle I. The complete passivation–titration cycle was repeated once more in the same conditions (Cycle III).

The amount of H_2O evolved during the titration (corresponding to the amount of O_2 fixed by the sample upon contacting it with the O_2–He mixture) was estimated from the area under the TPT pattern. The recorder response was calibrated by submitting a known amount of WO_3 (calcined beforehand for 16 h at 500°C in air) to a TPR cycle in pure H_2 until there was complete reduction (flow rate = 25 ml/min, temperature rise = 10°C/min). The area under the recorded TPR pattern was thus proportional to the amount of water evolved which can be calculated using the stoichiometry of the reaction of reduction.

In view of the present lack of data concerning the stoichiometries of oxygen and hydrogen adsorption on tungsten carbides, the interpretation of the H_2–O_2 titration data in terms of carbide areas exposed to the gaseous reactants (referred to below as "pseudometallic" surface, by analogy with the metallic surface of Pt and noble metals) will be taken up in the Discussion Section.

RESULTS

Determination of the Lattice Constants

All the carbide samples considered in this work presented a value of the lattice constant a equal to that reported in the literature ($a = 2.18 \pm 0.01$ Å) (*15*). The values of the lattice constant c are presented in Table 2. In the case of W_2C samples, the value of c was found to decrease with an increase of their degree of crystallinity, as indicated by the sharpening of their diffraction lines. In the case of the WC samples, the observed c values did not differ significantly from the theoretical one, except for sample Wh-WC-100, for which c was slightly smaller than expected.

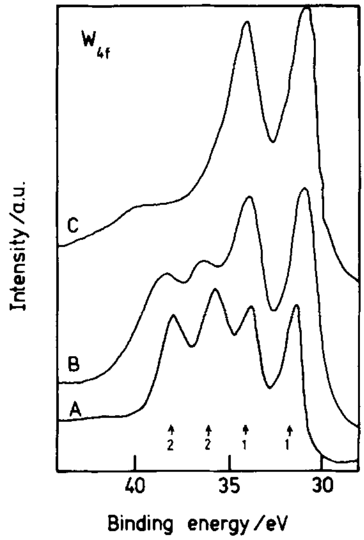

FIG. 1. W 4*f* XPS spectra of tungsten carbide samples. Wh-W_2C-wc passivated (A), Wh-WC-100 passivated (B), and activated (C). The arrows show the positions of the peaks corresponding to W^0 (1) and W^{VI} (2).

TABLE 2

Variation of the Lattice Constant *c* of Tungsten Carbide Samples

Sample	Constant *c* or 2*c*[a] (nm)
W_2C[b]	0.472 ± 0.001
Wh-W_2C-wc	0.475 ± 0.002
Wh-W_2C-ic	0.502 ± 0.002
Wh-WC-14	0.570 ± 0.004
Wh-WC-55	0.570 ± 0.004
Wh-WC-76	0.568 ± 0.004
Wh-WC-100	0.564 ± 0.004
Ye-WC-100	0.568 ± 0.004
WC[b]	0.567 ± 0.001

[a] The unit cell of the W_2C lattice can be seen as the superimposition of two unit cells of the WC lattice from which half of the carbon atoms have been removed. To make the comparison easier, the lattice constants *c* of the WC samples have been multiplied by 2.

[b] Theoretical values.

XPS Analysis

Study of passivated and activated samples. The W 4*f* spectra of two representative passivated samples (Wh-W_2C-wc and Wh-WC-100) are presented in Fig. 1. Both spectra indicate that a significant amount of tungsten atoms are in the W^{VI} state. The figure shows also that the W^{VI}/W^0 ratio is higher for W_2C (spectrum A) than for WC (spectrum B). Spectrum C shows that the zero oxidation state is restored for all the tungsten atoms as a result of the activation treatment.

Change in the C/W ratio. The overall C_{tot}/W ratios estimated from XPS data are plotted in Fig. 2 versus the conversion to WC (mol%) deduced from X-ray diffraction data (see also Table 1). The dotted line corresponds to the theoretical variation that should be observed if the bulk and surface compositions of the samples were equal. The figure shows that the experimental points are very close to the theoretical line for bulk C/W ratios comprised between 0.6 and 0.8. Table 3 shows that $(C_{carbide}/C_{total})$ ratio of the samples do not vary significantly according to their degree of carburization.

Hydrogen–Oxygen Titrations

Figure 3 shows no observable variation of the amount of water evolved upon H_2–O_2

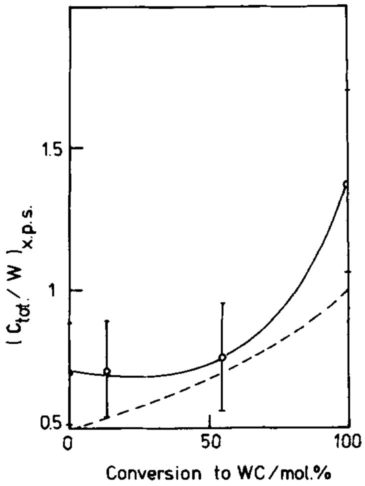

FIG. 2. Variation of the $(C_{total}/W)_{XPS}$ ratio versus the conversion to WC as derived from X-ray data. The dotted line indicates the theoretical variation when bulk and surface compositions are equal.

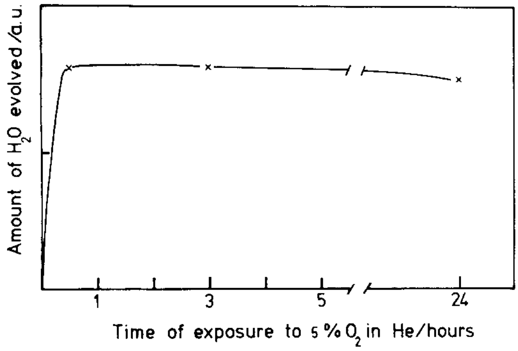

FIG. 3. Influence of the time of passivation on the amount of water evolved during a H_2–O_2 titration at 300°C.

TABLE 4

Influence of the Sample Composition on the Amount of Water Evolved as a Result of Successive Titration Cycles

Sample	Amount of H_2O evolved (10^{-3} mol/g)		
	Cycle I	Cycle II	Cycle III
Wh-W_2C-wc	0.73	0.44	0.43
Wh-W_2C-ic	1.59	0.72	0.72
Wh-WC-14	1.59	0.57	0.58
Wh-WC-55	1.15	0.53	0.52
Wh-WC-72	0.72	0.55	0.55
Wh-WC-76	0.71	0.57	0.56
Wh-WC-100	1.03	0.24	0.23
Wh-WC-CO	0.0	0.0	0.0

titrations for passivation times longer than 30 min. Therefore all the samples considered below have been passivated for at least 3 h before titration. The results of the three titration cycles are presented in Table 4. The amount of water evolved is generally much higher (2 to 4 times according to samples) for Cycle I than for the subsequent cycles. No evolution of water was observable in the case of sample Wh-WC-CO, whatever the titration cycle considered.

DISCUSSION

Stoichiometry of the Carbides

X-Ray diffraction. Only the lattice constants of sample Wh-W_2C-ic and Wh-W_2C-wc appear to be affected by the preparation conditions. The constant *c* of sample Wh-W_2C-ic (carburized for the shortest time) is significantly higher than the theoretical value, as shown in Table 2. Although the data available presently do not allow a definitive interpretation of these results to be made, they can be tentatively explained as follows. An increase of the carburization time could possibly result in some ordering of the interstitial carbon atoms in the W_2C structure; a similar phenomenon has been reported by Pearson (*16*) and by Storms (*17*) in the case of metallic nitrides and carbides. The semicarbide Wh-W_2C-ic could thus be considered as a hexagonal lattice in which carbon atoms are randomly distributed between the adjacent basal planes of tungsten atoms. The lattice constant *a* (parallel to the basal planes) would thus not be affected by the distribution of the carbon, in contrast to constant *c* (perpendicular to the basal planes). A reordering of the carbon atoms brought about by recrystallization would then enable adjacent planes to come into closer contact, resulting in a decrease of *c*.

TABLE 3

Distribution of Carbon Species in Tungsten Carbide Samples, According to XPS Measurements

Sample	$(C_{carbide}/C_{tot})_{XPS}$
Wh-W_2C-wc	0.6
Wh-WC-14	0.6
Wh-WC-55	0.5
Wh-WC-100	0.6
Ye-WC-100	0.7

No effect on the lattice constants of WC, either of the nature of the starting precursor or of the final carbide composition has been observed in the present work, in contrast to previous results reported by Ross and Stonehart (*18*).

XPS results. The approximation affecting the estimate of the sensitivity factors of Wagner (±30%) and the additional error brought about by the decomposition of the C 1*s* peak (±30%) make it hazardous to discuss the absolute values of C_{tot}/W and the distribution of carbon among different species as deduced from XPS data. Therefore only the variations of these parameters will be considered below. The minimum difference between $(C_{tot}/W)_{xps}$ and the theoretical value deduced from X-ray diffraction data (Fig. 2), observed at about 50% conversion to WC, indicates that the amount of excess carbon present at the surface of the particles is less at intermediate conversions. According to the reaction scheme presented in Part I (*5*) for the transformation of W_2C to WC, the preceding observation would correspond to a faster formation of WC through the reaction $W_2C + C_{at} \rightarrow 2WC$, and, consequently, a more efficient removal of the free carbon formed at the surface of the solid as a result of the Boudouard reaction: $2CO \rightarrow C_{at} + CO_2$. The question as to whether the influence of the conversion to WC on the catalytic activity of the samples supports this interpretation will be considered in Part III. According to Table 3, the distribution of carbon among carbidic and noncarbidic (mainly pregraphitic) species is not sensitive to the conversion of the samples to WC. As XPS is more sensitive to the surface composition of the solid, this result indicates that the change with time of the accumulation of free atomic carbon goes parallel with that of the carbon dissolved in the surface layers of the reacting particles. This is in agreement with the concept presented previously (*5*), according to which the mechanism of WC formation involves the successive deposition of free atoms of carbon on the surface of the reacting solid and their diffusion into the bulk.

TABLE 5

Calculated Surface Area per Surface W Atom for Different Crystallographic Planes of Tungsten Carbides

Compound	Crystallographic plane	Area/W (nm^2)	Average[a] area (nm^2)
WC	(001)	0.1457	
	(100)	0.1642	0.1460
	(111)	0.1317	
W_2C	(001)	0.1538	
	(100)	0.1404	0.1593
	(111)	0.1920	

[a] Average area calculated assuming an equiprobable distribution of the atoms among the three crystallographic planes.

Effect of Passivation and Activation Treatments

Hydrogen–oxygen titrations. The discrepancies observed in Table 4 between the titration values of Cycle I and those of the subsequent cycles suggests that the surface state of the carbides has been modified irreversibly as a result of the first titration experiment. Similar observations reported by Prasad *et al.* (*19*) in a study of the H_2–O_2 titration of supported Pt catalysts were attributed to the lack of reproducibility of freshly reduced catalysts. Later on, Menon and Froment (*20*) observed that the stronger chemisorption of H_2 occurring on Pt at higher temperatures depressed the reactivity of a fraction of the surface Pt atoms in such a way that they could not react with H_2 and O_2 at room temperature. The similar behavior of Pt and tungsten carbides with respect to H_2–O_2 titration experiments suggests that some kind of strong hydrogen adsorption could also take place on tungsten carbide samples during the very first activation treatment, resulting in a decrease of the adsorption capacity for oxygen of the carbide surface upon further passivation treatments.

The original purpose of H_2–O_2 titration was to allow an estimation to be made of the active, i.e., presumably the metallic, surface of supported metal catalysts. In the following discussion, the surface of the carbide samples actually exposed to the gas phase, referred to below as "pseudometallic surface," will be tentatively estimated from the titration data presented in Table 4. In order to do so, the area occupied per surface tungsten atom, and the stoichiometry of adsorption need first to be estimated. Values of the area occupied per surface tungsten atom have been computed for W_2C and WC on the basis of crystallographic data and are presented in Table 5. Since no information on the stoichiometry of adsorption of H_2 or O_2 on tungsten carbides are available presently in the literature, reasonable values will be tentatively deduced from the present data. The titration reaction can be expressed by the equation

$$W_s{-}xO + (x + y/2)H_2 \rightarrow W_s{-}yH + xH_2O$$

where W_s stands for a surface W atom, x and y being the stoichiometries of oxygen and hydrogen adsorption, respectively. If this equation is correct, the number of H_2O molecules evolved during the titration cycle is equal to the number of oxygen atoms adsorbed initially. Table 6 presents the apparent adsorption stoichiometries derived from the data of Tables 4 and 5. Maximum values of 4.8 and 2.1 are observed, corresponding, respectively, to Cycle I (sample Wh-WC-14) and Cycle II (sample Wh-W_2C-ic). The lower values observed for the remaining samples can be explained either by a decrease of the fraction of the W atoms actually exposed to the gas phase, or to changes in the stoichiometry of adsorption. For the sake of clarity, the results corresponding to Cycles I and II will now be discussed successively.

TABLE 6

Apparent Stoichiometries of H_2–O_2 Titrations

Sample	Number of surface W[a] (10^{20} at./g)	x_A, Apparent stoichiometry of O_2 adsorption[b]	
		Cycle I	Cycle II
Wh-W_2C-wc	2.26	4.6	1.2
Wh-W_2C-ic	2.07	4.6	2.1
Wh-WC-14	2.00	4.8	1.7
Wh-WC-55	1.98	3.5	1.6
Wh-WC-72	1.94	2.2	1.7
Wh-WC-76	1.88	2.0	1.1
Wh-WC-100	1.92	3.2	0.8

[a] $N = 10^{16}\, S_{\mathrm{BET}} \left(\frac{\%\mathrm{WC}}{0.146} + \frac{100 - \%\mathrm{WC}}{0.159}\right)$, where S_{BET} is expressed in m^2/g.

[b] $x_A = 6.021 \times 10^{23}\, Q/N$ where Q(mol/g) is the amount of H_2O evolved, extracted from Table 4.

Considering that the first passivation treatment was performed *in situ* on the freshly prepared carbides, the results of the first H_2–O_2 titration cycle are most likely to reflect accurately the genuine surface state of the samples. It has been shown previously (*5*) that carbon formation was proportional to the carburization time of the samples. Hence, the fraction of their surface covered by free carbon is expected to increase with their degree of conversion to WC, affecting thereby the fraction of W atoms available for oxygen adsorption. On the other hand, no indication exists that the presence of free carbon would affect the stoichiometry of adsorption of oxygen on the W atoms exposed at the surface of freshly prepared carbides. Therefore, the rounded maximum stoichiometry observed in Table 6, i.e., $x = 5$, will be taken as a reasonable value in the titration reaction presented above. The pseudometallic surface/total surface ratio of a given sample will then be given by

$$(S_{\mathrm{met}}/S_{\mathrm{BET}})_{\mathrm{I}} = x_A/5,$$

where x_A is the apparent stoichiometry extracted from Table 6 (column 3). The change of $S_{\mathrm{met}}/S_{\mathrm{BET}}$ corresponding to Cycle I is plotted versus the percent conversion to WC in Fig. 4 (curve A). The trend observed is consistent with the hypothesis made above concerning the progressive contamination by free carbon of the surface of the carbide samples during their preparation. It is further supported by the complete absence of oxygen adsorption on sample Wh-

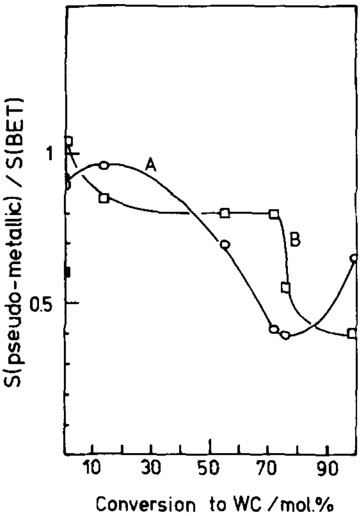

FIG. 4. Variation of the S_{met}/S_{BET} ratio versus the conversion to WC of carbide samples, as deduced from titration Cycle I (curve A, open circles) and Cycles II or III (curve B, open squares). The black circle and square correspond, respectively, to Cycles I and II sample Wh-W_2C-wc.

WC-CO, which was proven previously to be covered extensively by free carbon (5). It confirms that the pseudometallic surface of tungsten carbides can be estimated by titrating the oxygen fixed during the very first passivation treatment. The case of sample Wh-WC-100, for which an abnormally high S_{met}/S_{BET} value is observed, is not yet fully understood. One possible explanation is that some sintering of the carbon layer can take place upon prolonged reaction times, so that a higher fraction of the surface W atoms would be exposed to the gas phase. This interpretation will be reconsidered in Part III of this study, in the light of the catalytic properties of the samples.

Reasoning along similar lines as above on the results of the second titration cycle leads us to adopt $x = 2$ as a reasonable stoichiometry of O_2 adsorption in that case. Hence,

$$(S_{met}/S_{BET})_{II} = x_A/2,$$

where x_A is the apparent stoichiometry taken from Table 6 (column 4). The corresponding change on S_{met}/S_{BET} versus the conversion to WC shown in Fig. 4 (curve B) differs markedly from that observed for the fresh samples. Such a difference is difficult to interpret on the basis of the present data. However, the fact that the change for repassivated samples is not compatible with their probable state of contamination confirms that an irreversible modification of the carbide surface has taken place during the first titration cycle. Moreover, the results indicate that the stoichiometry of oxygen adsorption is affected differently by previous hydrogen adsorption according to the degree of conversion to WC of the samples. The relevance of these two methods of pseudometallic surface estimation will be discussed further in Part III in the light of the catalytic activities of the samples.

XPS results. The presence of a W^{VI} component in the XPS spectra of the passivated carbides indicates that the passivation treatment actually results in a surface oxidation of the samples (see Fig. 1, curves A and B). The absence of detectable amounts of W^{VI} in the spectrum of the activated carbide indicates that an extensive removal of oxygen has been brought about by the activation treatment in hydrogen. This result is in agreement with the pyrophoric character of the activated samples.

We will now attempt to interpret the above XPS results more quantitatively, in order to evaluate the extent to which the oxidation brought about by the passivation treatment is actually restricted to the surface of the samples, and to see whether the XPS data are consistent with the H_2–O_2 titration results. Table 7 presents the results computed with the help of the model presented in the experimental section. The experimental (I_y/I_x) values have been estimated from the spectra of Fig. 1, using the same deconvolution program as before (9). Next, the number of oxide layers and the atomic ratios (W^{VI}/W_{tot}) have been estimated using the procedure described in the experimental section. Finally, the ratio $(W^{VI}/W_{surface})$ of the number of oxidized W

TABLE 7

Quantitative Interpretation of the XPS Spectra of Passivated Tungsten Carbides[a]

	Sample	
	$Wh\text{-}W_2C\text{-}wc$	Wh-WC-100
$(I_y/I_x)_{obs}$	0.7 ± 0.1	0.3 ± 0.1
c (nm)	9.8 ± 3	13.7 ± 0.6
t (nm)	0.8 ± 0.1	0.4 ± 0.1
Number of oxide layers	2.2 ± 0.2	1.0 ± 0.3
(W^{VI}/W_{tot})	0.18 ± 0.02	0.07 ± 0.02
(W^{VI}/W_{surf})	2.2 ± 0.2	1.1 ± 0.3
$(O/W_{surf})_{XPS}$[b]	6.6 ± 0.6	3.3 ± 0.9

[a] See text. The molecular weights and densities of the different phases (WO_3, W_2C, and WC) were taken from Ref. (*21*).

[b] Each W^{VI} has been assumed to fix 3 oxygen atoms.

atoms over the number of W atoms exposed initially at the surface of the carbide has been estimated using the formula

$$(W^{VI}/W_{surface}) = \frac{(W^{VI}/W_{tot})}{(W_{surface}/W_{tot})},$$

where $(W_{surface}/W_{tot})$ is the ratio of surface over total W atoms in a cube of edge c, calculated using the formula

$$(W_{surface}/W_{tot}) = 6M/caxN\rho,$$

where M is the molecular weight of W_xC, c is the edge of the elementary cubic particle, a is the average area per surface W atom extracted from Table 6, x is the stoichiometric coefficient of W in the carbide molecule, N is the Avogardro constant, and ρ is the density of the carbide under consideration. The values of c have been deduced from the BET surface of the samples using the formula

$$c = 6/\rho S_{BET},$$

where the symbols have their usual meaning. Finally, the stoichiometry of oxygen adsorption $(O/W_{surface})_{xps}$ has been calculated assuming 3 oxygen atoms fixed per W^{VI} atom.

Table 7 shows that about 2 layers of oxide are formed on the surface of sample $Wh\text{-}W_2C\text{-}wc$ as a result of the passivation treatment, corresponding to an adsorption stoichiometry of 6 oxygens per surface W atom. These values are twice those observed for sample Wh-WC-100. These results agree well with the corresponding apparent stoichiometries of oxygen adsorption deduced from the H_2–O_2 titration data (compare with Table 6). Furthermore, when allowance is made for the conclusions drawn from the titration results, namely that 64% of the surface of sample Wh-WC-100 contributes actually to the adsorption of oxygen (see Fig. 4, curve A) one can see that the stoichiometry of oxygen adsorption on the *fraction of the surface actually exposed to the atmosphere* would be (3.3 ± 0.9)/0.64 = 5.2 ± 1.4, which is not significantly different from the value of found for sample $Wh\text{-}W_2C\text{-}wc$.

CONCLUSIONS

The present work has shown that the lattice constants of WC in samples prepared in CO–CO_2 mixtures were not significantly affected by their degree of carburization, and that their (C/W) atomic ratios could be merely related to their (W_2C/WC) phase composition and the amount of excess free carbon present.

According to H_2–O_2 titration and XPS results, the passivation treatment of freshly prepared carbides results in the formation of a surface oxide about 2 molecular layers thick. The surface oxide is completely reduced as a result of an activation treatment in H_2 at 300°C. Furthermore, the first activation treatment of tungsten carbides brings about an irreversible modification of their surface, similar to that observed when Pt is submitted to a heat treatment in H_2 at elevated temperature, which results in a marked decrease of their capacity to fix O_2 at ambient temperature. The amount of oxygen fixed during the first passivation treatment allows one to estimate the extent of the pseudometallic surface of tungsten carbides, i.e., the fraction of their surface which is not covered by an excess of free carbon. The results show that the surface of carbides prepared in pure CO is made completely inaccessible to gaseous molecules as a result of its extensive coverage by free carbon, while the degree of coverage of samples prepared in CO–CO_2 mixtures increases with the time of carburization.

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