

ADSORPTION BEHAVIOUR IN THE GAS PHASE OF CARBIDES PREPARED FROM DIFFERENT STARTING MATERIALS

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Summary

The adsorption of H_2 and H_2O from the gas phase on oxidized and non-oxidized tungsten carbide, synthesized from different starting materials, has been investigated. It is shown that non-oxidised WC synthesized from tungsten oxides adsorbs H_2 more strongly and H_2O vapour more weakly than those prepared from tungsten acids. After a partial oxidation of the WC surface the H_2 adsorption increases substantially, while that of H_2O vapour diminishes. The juxtaposition of the H_2O and H_2 adsorption in the gas phase with the catalytic activity of the WC samples in respect of oxidation and evolution of H_2 in H_2SO_4 solutions reveals good correlation. An explanation for the different activities of the carbides studied is proposed.

Introduction

The factors determining the catalytic activity of WC have been discussed in several papers. According to Böhm *et al.* [1] and Ross *et al.* [2] it is determined basically by the chemical composition of the catalyst surface; partial oxidation of the surface results in a substantial increase in the specific activity. Palanker *et al.* [3] assume that the catalytic activity depends only on the surface area, and the increased activity of partially oxidized WC samples is due solely to their higher surface areas.

In two previous papers Nikolov *et al.* [4, 5] pointed out that the specific catalytic activity of WC in regard to the H_2 oxidation and evolution reactions depends on the particle morphology of the WC samples. It was emphasized that this result is not unambiguous, since the different activity could also be due to the different chemical compositions at the surface of the WC samples.

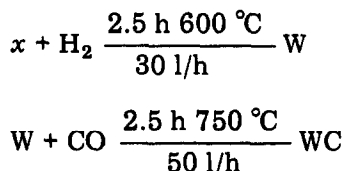
In an investigation of the effect of the method of preparation on the corrosion resistance of WC, the same authors [6] established that as a result of the partial surface oxidation there is an increase not only of the surface

area but also of the specific activity. In some cases WC samples prepared from different starting materials showed similar activities.

The present paper aims at elucidating the factors determining the catalytic activity of WC samples synthesized from different raw materials by studying their adsorption behaviour in H_2 and H_2O vapour atmospheres.

Experimental

The adsorption of H_2 and H_2O vapour on 4 samples of WC was studied. The samples were prepared according to the scheme



where x denotes the starting material — WO_3 , W_4O_{11} , H_2WO_4 (white modification), or H_2WO_4 (yellow modification). The surface areas and chemical compositions of the starting materials have been given in ref. 4.

The WC samples selected for this study had practically similar surface areas (determined by the BET method using low-temperature N_2 adsorption) as well as equal contents of bound and free carbon (determined by a method described in ref. 4), Table 1.

TABLE 1

Surface area (BET) and carbon content of the WC samples studied

Starting material	Surface area (m^2/g)	Carbon content	
		Free carbon (%)	Bound carbon (%)
W_4O_{11}	11.26	0.90	4.98
WO_3	11.55	0.85	4.77
H_2WO_4 (white)	10.81	0.90	4.94
H_2WO_4 (yellow)	11.17	0.90	4.50

The adsorption of H_2 and H_2O vapour was measured by a volumetric adsorption apparatus using the following procedure: the WC samples were evacuated at $350^\circ C$ for 3 h at 10^{-4} Torr (mmHg).

Electron microscope surface analysis (JEOL Super Probe 733) revealed that as a result of this treatment, the surface of the WC samples was free from oxygen.

The adsorption and desorption isotherms of H_2 on the treated samples were recorded at $50^\circ C$ by a method described earlier [7]. The samples were

evacuated once more under the same conditions and the H_2O vapour adsorption and desorption isotherms were recorded.

The surface heterogeneity of two of the samples prepared from W_4O_{11} and H_2WO_4 (white) was assessed by N_2 adsorption isotherms at 77 K by means of a Carlo Erba Sorptomatic apparatus.

Adsorption measurements of H_2 and H_2O vapour were also carried out after a partial oxidation of the samples (48 h at 20 °C in 4.5N H_2SO_4). The X-ray diffraction patterns obtained after this treatment revealed that the samples contained WO_2 . The content of the latter, determined by chemical analysis, was 3 - 5%.

Results

The adsorption-desorption isotherms of H_2 on the three WC samples are given in Fig. 1. As can be seen, the shape of the isotherms is similar but the amount of the adsorbed H_2 at saturation is quite different.

(i) The sample prepared from H_2WO_4 (yellow) exhibits a complete reversibility of the adsorption-desorption cycle at 50 °C (Fig. 1(A)). In this case it is possible to calculate the isosteric heat of adsorption of H_2 by the Klausius-Klapeyron equation using the isotherms taken at 30 and 50 °C. A value of 5.8 kcal/mol was calculated.

(ii) The samples prepared from H_2WO_4 (white) and W_4O_{11} revealed only a partial reversibility in the adsorption-desorption cycle (Fig. 1(B)). Only part of the adsorbed H_2 is desorbed at 50 °C. The rest of the H_2 can be desorbed at temperatures as high as 250 - 350 °C.

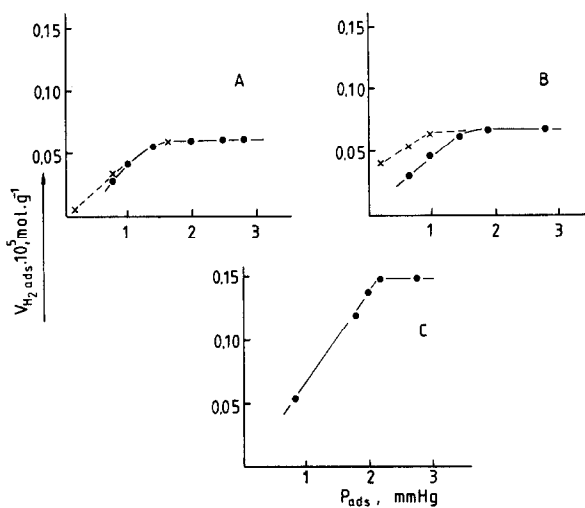


Fig. 1. Adsorption-desorption isotherms of hydrogen on WC synthesized from different starting materials. A, H_2WO_4 (yellow); B, H_2WO_4 (white); C, WO_3 .

TABLE 2

Amounts of adsorbed and chemisorbed hydrogen on WC prepared from different starting materials

Starting materials	$V_{H_2, ads.} \times 10^5 \text{ mol/m}^2$ ($P_{max} = 2.5 \text{ mmHg}$)	$V_{H_2, chem.} \times 10^5 \text{ mol/m}^2$ ($P_{max} = 2.5 \text{ mmHg}$)
WO_3	0.0130	0.0130
W_4O_{11}	0.0110	0.0090
H_2WO_4 (white)	0.0064	0.0039
H_2WO_4 (yellow)	0.0057	—

(iii) A complete irreversibility of the adsorption-desorption cycle is observed for samples prepared from WO_3 (Fig. 1(C)). The desorption of H_2 occurs at 300 - 350 °C.

Table 2 presents the total amount of adsorbed and chemisorbed H_2 per m^2 . The difference in the adsorption of H_2 for the various WC samples reveals that the number and type of the adsorption sites depends on the starting material used in the WC synthesis. A similar dependence was observed in the case of H_2O vapour adsorption (Fig. 2). As shown in Fig. 2A, two types of adsorption are also observed in this case.

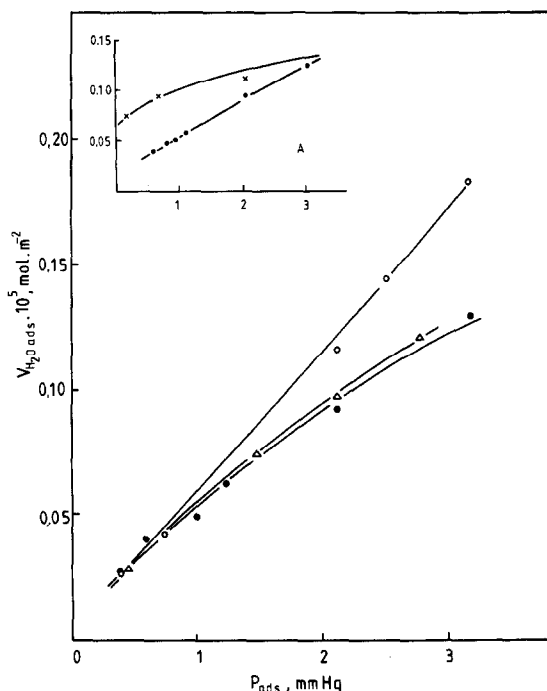


Fig. 2. Adsorption isotherms of water vapour on WC synthesized from different starting materials: \circ , H_2WO_4 (yellow); \bullet , W_4O_{11} ; \triangle , WO_3 . A, Adsorption-desorption isotherms of water vapour on WC synthesized from W_4O_{11} .

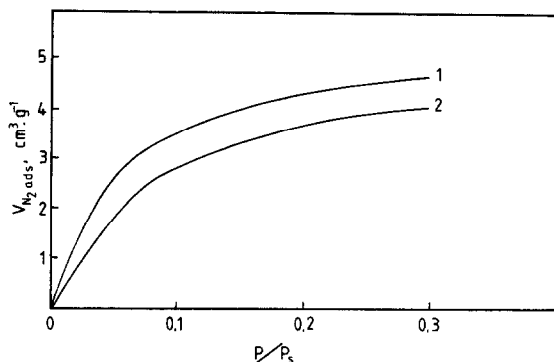


Fig. 3. Adsorption isotherms of nitrogen up to $p/p_s = 0.3$ on WC synthesized from different starting materials: 1, W_4O_{11} ; 2, H_2WO_4 (white).

As demonstrated earlier [4], the particles of the WC samples studied show different morphology. It might be supposed that the particle morphology could determine a different surface heterogeneity, *i.e.*, different energy states on the catalyst surface. Additional information in this respect was obtained through the study of the carbide surface by physical adsorption of N_2 at 77 K.

Figure 3 illustrates the experimental adsorption isotherms of N_2 on two samples in the range of low relative pressures ($p/p_s = 0.3$). The experimental data were treated by the generalized isotherm of Cavalotti [8] for physical adsorption at low coverage and the simplified BET isotherm for monolayer coverage [9]. The expression for the first isotherm is:

$$\ln \theta = \ln \frac{V}{V_m} = -B \ln \left(\frac{P}{P_m} \right) \ln \left(\frac{P}{P_s} \right) + \ln \left(\frac{P_s - P_m}{P_s - P} \right) \quad (1)$$

where V_m is the adsorbate volume for a monolayer coverage, P_m the adsorbate pressure at a monolayer coverage, P_s the pressure of saturated vapours, and B is a constant associated with the shape of the distribution function of the adsorption energy.

The simplified BET isotherm for monolayer coverage is:

$$\frac{P}{V(P_s - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \frac{P}{P_s} \quad (2)$$

where $C = \exp[(q - l)RT]$, q is the heat of adsorption and l the latent heat of condensation.

The constant C and the volume of the adsorbate were obtained by a computer treatment of the experimental data. The adsorbate pressure for a monolayer coverage (P_m) was estimated from the experimental isotherms, after which the isotherm (1) was used to estimate the values of the constant B . Table 3 presents the values of these parameters.

These data reveal that WC synthesized from W_4O_{11} has, on average, a higher surface heterogeneity and higher adsorption energy. This result correlates well with the data for H_2 adsorption.

TABLE 3

Values of the parameters characterizing the energy states at the surface of two WC samples

Starting material	S (m^2/g)	C	P_m (Torr (mmHg))	B
W_4O_{11}	11.26	50.23	78.11	0.112
H_2WO_4 (white)	10.81	25.57	127.75	0.068

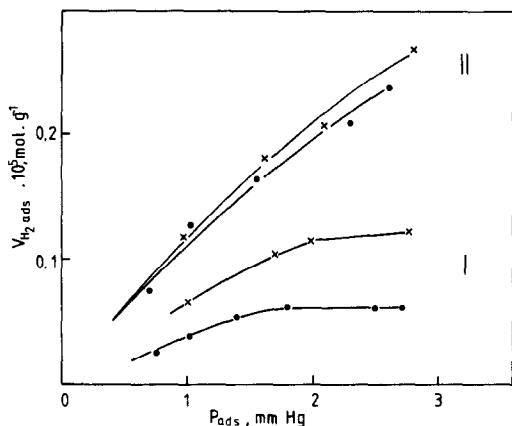


Fig. 4. Adsorption isotherms of hydrogen on WC synthesized from different starting materials: \times , W_4O_{11} ; \bullet , H_2WO_4 (yellow). I, Before oxidation; II, after oxidation.

The adsorption of H_2 and H_2O vapour was also measured after partial oxidation of the surface of the samples under investigation.

Figure 4 shows the adsorption isotherms of H_2 on carbides synthesized from yellow tungsten acid and W_4O_{11} prior to, and after, partial oxidation of the samples. It can be seen that as a result of the occlusion of oxygen in the surface layers of the carbides, their hydrogen adsorptivity increases significantly. The difference in the amounts of H_2 adsorbed on the two carbides prepared from different sources is insignificant.

The adsorption measurements in H_2O vapour (Fig. 5) show that the adsorptivity of water strongly decreases as a result of the oxidation. The water molecules, as seen from Table 4, are only physically adsorbed.

Discussion

According to current models, the reactions of hydrogen ionization and evolution have an adsorption stage. When the reactions occur in an aqueous electrolyte solution the adsorption of water competes with that of hydrogen. Comparison of the data in Tables 2 and 4 reveals that the adsorptivity of

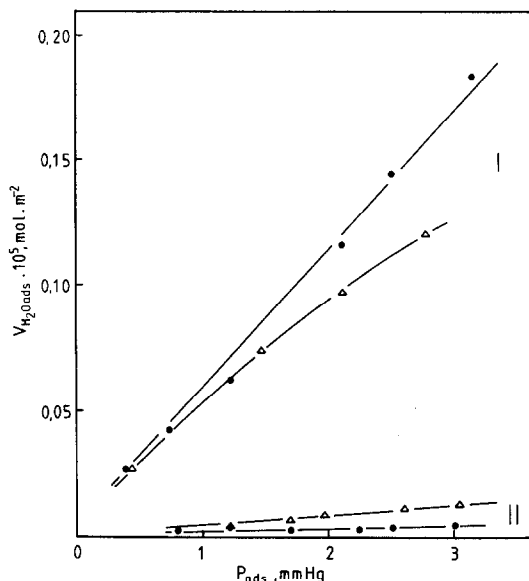


Fig. 5. Adsorption isotherms of water vapour on WC synthesized from different starting materials: \triangle , WO_3 ; \bullet , $\text{H}_2\text{WO}_4(\text{yellow})$. I, Before oxidation; II, after oxidation.

TABLE 4

Amount of adsorbed and chemisorbed water on unoxidized and oxidized carbides obtained from different starting materials

Starting material	Unoxidized WC		Partially oxidized WC	
	$V_{\text{H}_2\text{O}_{\text{ads}}} \times 10^5 \text{ mole/m}^2$ ($P_{\text{max}} = 2.5 \text{ mmHg}$)	$V_{\text{H}_2\text{O}_{\text{chem}}} \times 10^5 \text{ mole/m}^2$	$V_{\text{H}_2\text{O}_{\text{ads}}} \times 10^5 \text{ mole/m}^2$ ($P_{\text{max}} = 2.5 \text{ mmHg}$)	$V_{\text{H}_2\text{O}_{\text{chem}}} \times 10^5 \text{ mole/m}^2$
WO_3	0.112	0.086	0.0078	—
W_4O_{11}	0.106	0.076	0.0042	—
$\text{H}_2\text{WO}_4(\text{yellow})$	0.145	0.132	0.0028	—

water on all unoxidized samples studied considerably exceeds that of hydrogen. This result is in accordance with the data of Sandst de [10] obtained on transition metals and Pt. The data in Fig. 4 and Table 4 reveal that the chemisorption of water is stronger on carbides prepared from tungsten acids. The amounts of water vapour chemisorbed at $p_{\text{max}} = 2.5 \text{ mmHg}$ on the various carbides are compared with the respective amounts of chemisorbed hydrogen at the same pressure in Fig. 6. It is evident that these two amounts are inversely proportional.

Hence it may be concluded that, in aqueous solutions, the adsorption of hydrogen on carbides synthesized from oxides will be stronger, and consequently their activity will be higher.

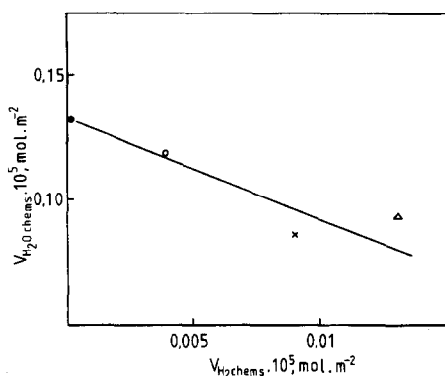


Fig. 6. Comparison of the amount of chemisorbed water vapour with that of hydrogen at $p = 2.5$ mmHg on WC synthesized from different starting materials: ●, $\text{H}_2\text{WO}_4(\text{yellow})$; ○, $\text{H}_2\text{WO}_4(\text{white})$; △, WO_3 ; ×, W_4O_{11} .

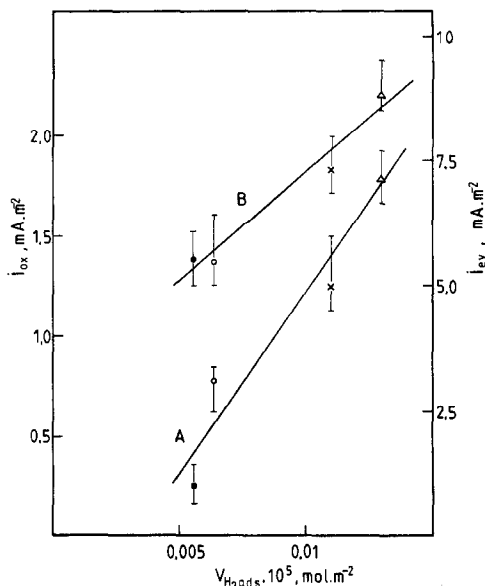


Fig. 7. Dependence between the specific catalytic activity and the amount of adsorbed hydrogen on WC synthesized from different starting materials: ●, $\text{H}_2\text{WO}_4(\text{yellow})$; ○, $\text{H}_2\text{WO}_4(\text{white})$; △, WO_3 ; ×, W_4O_{11} . A, Hydrogen oxidation; B, hydrogen evolution.

Figure 7 presents the relations between the amounts of adsorbed hydrogen and specific catalytic activity of the carbides under investigation with respect to the hydrogen ionization, (A), and the hydrogen evolution reaction (B). The activities are expressed as c.d. at 80 mV (SHE) and at -80 mV (SHE). The true surface areas of the electrodes were assessed electrochemically [4, 5]. As seen from the plots in Fig. 7, there is, in both cases, a direct proportionality between the juxtaposed values. It is noteworthy that this proportionality also holds true for the BET catalyst surface area of the electrodes, provided that its weight does not exceed 2 mg/cm² for the anodic measurements [6] and 20 mg/cm² for the cathodic measurements. Similar relations are observed between the amounts of chemisorbed hydrogen on the various carbides and their activities with respect to the hydrogen reactions (Fig. 8).

The experimental data presented so far reveal that there is a good correlation between the adsorptivity of the carbides studied and their catalytic activity with respect to the ionization and evolution of hydrogen, as previously established [4, 5]. The higher catalytic activity of the carbides synthesized from tungsten oxides is due to the stronger adsorption of hydrogen and weaker adsorption of water molecules, respectively. These adsorption properties are most probably associated with the morphology of the particles of the carbides studied, as previously established [4]. It is also possible that

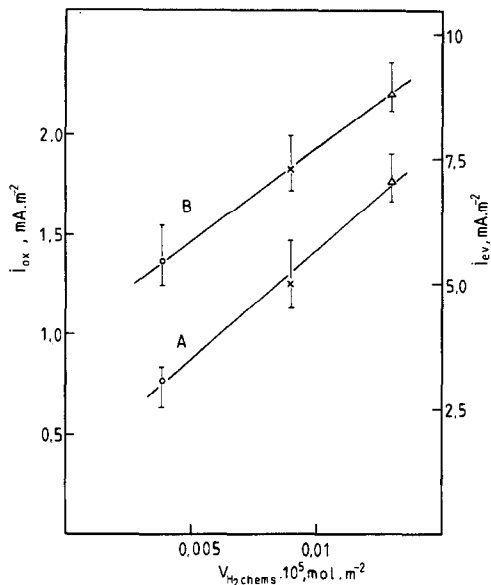


Fig. 8. Dependence between the specific catalytic activity and the amount of chemisorbed hydrogen on WC synthesized from different starting materials: ○, H_2WO_4 (white); △, WO_3 ; ×, W_4O_{11} . A, Hydrogen oxidation; B, hydrogen evolution.

the differences in the adsorption properties could be due to small differences in the oxygen content in the surface layers of the carbides. This would not be shown by the method of oxygen determination described in the Experimental section which has a sensitivity of only *ca.* 1%. There is also an indirect influence of the morphology of the particles, since at approximately equal contents of bound carbon in the crystal lattice of the carbides, the inclusion of oxygen in the surface layers will be controlled by the morphology of their particles.

It may be expected that resulting from the different adsorptivities of water and hydrogen on the partially oxidized surfaces their catalytic activities will be changed. The adsorption and catalytic properties of the carbides studied after a partial oxidation are compared in Table 5 where it can be seen that the specific activities of all carbides increase after partial oxidation, and reach almost the same value. This result is in accordance with those of the adsorption measurements.

The significant increase in the activity is obviously due not only to the increase in the number of active sites which adsorb hydrogen, as suggested by Böhm [1], but also to the diminished adsorptivity of water on the partially oxidized surfaces.

The differences in the adsorption of water on unoxidized and oxidized carbides observed in the present study are in accord with the ideas for the hygrophilicity of metals. Tungsten carbide has a hexagonal lattice and the W atoms at the corners of the lattice retain, to great degree, the properties of

TABLE 5

Comparison of the adsorption and catalytic properties of the carbides studied prior to and after partial oxidation

Starting material	$V_{\text{H}_2, \text{chem.}} \times 10^5 \text{ mole/m}^2$ $P_{\text{max}} = 2.5 \text{ mmHg}$		$V_{\text{H}_2\text{O ads.}} \times 10^5 \text{ mole/m}^2$ $P_{\text{max}} = 2.5 \text{ mmHg}$		$i, \mu\text{A/m}^2$ 20 °C 4.5N H ₂ SO ₄ $\phi = 100 \text{ mV(HE)}$	
	Unoxid.	Oxid.	Unoxid.	Oxid.	Unoxid.	Oxid.
WO ₃	0.013	0.0174	0.112	0.0078	3340	4320
W ₄ O ₁₁	0.009	0.0176	0.106	0.0042	2470	3990
H ₂ WO ₄ (yellow)	0	0.0162	0.145	0.0028	550	4040

Data for hydrogen evolution is not presented in this Table since the increased cathodic current can also be due to the reduction of the oxides.

transition metals [11], which possess a strong hygrophilicity [12]. This explains the considerably higher adsorptivity of water molecules on unoxidized surfaces. According to Trasatti [12] W-O bridges are formed on the surface during the adsorption of water. The oxygen groups obtained after oxidation hamper this process. This is in accordance with the observed reduction of the adsorptivity of water following the partial oxidation of the carbides under investigation. On the other hand, the inclusion of oxygen in the surface layers during oxidation should enhance the acceptor properties of the carbides. This, in turn, will lead to the formation of new adsorption sites and increase the energy of hydrogen adsorption on the catalyst, which is confirmed by the present experimental results.

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