JOURNAL OF CATALYSIS 39, 298-301 (1975)

Surface Characterization of Catalytically Active Tungsten Carbide (WC)

Levy and Boudart (*1*) have reported previously that tungsten carbide exhibits platinum-like behavior for hydrogen chemisorption and isomerization of 2,2-dimethylpropane. Tungsten carbide is also known to act as a hydrogenation catalyst in the liquid-phase for aromatic nitro compounds (*3*) and can act in a similar manner to platinum for oxidation of hydrogen, hydrazine, aldehydes, formic acid and carbon monoxide (*4–10*) at porous fuel cell electrodes in acid electrolyte, but it is necessary to "activate" the tungsten carbide prior to reaction. Levy and Boudart postulated that the Pt-like behavior of tungsten carbide was due to the donation of electrons from carbon to the W 5*d* band, resulting in an electronic structure similar to that of Pt. However, recent studies using soft X-ray appearance potential spectroscopy indicated (*2*) that the width of the unfilled portion of the *d* band *increases* on going from tungsten to tungsten carbide, rather than decreasing as expected for a band-filling picture of bonding in WC. In the work described here, a unique relationship is shown between the Pt-like behavior of WC for hydrogen chemisorption and the surface composition of the WC determined by Auger electron spectroscopy (AES).

Tungsten carbide powders used for this study were obtained from different sources. Commercially available ultrahigh purity WC was obtained from Ventron, Materials Research Corp. and Hermann C. Starck Co. (Berlin, Germany). These were examined by X-ray diffraction and found to be single-phase with hexagonal lattice parameters $a = 2.906$ Å, $c = 2.836$ Å, identical to the usually accepted values (*11*). A tungsten carbide identical to that used by Levy and Boudart was obtained from the laboratory of Dr. H. Böhm (AEG-Telefunken, Frankfurt, Germany) and X-ray diffraction indicated hexagonal parameters of $a = 2.900$ Å, $c = 2.843$ Å. The deviation from the usually accepted values indicates a slight carbon deficiency in the bulk lattice. High surface area tungsten carbide was prepared in our laboratory by carburizing WO_3 with carbon monoxide and X-ray diffraction indicated a single-phase with the ideal hexagonal lattice parameters. Commercially available ditungsten carbide, W_2C, was obtained from Atomergic Chemical Co., and was found to be two-phase, a major α-W_2C phase with a minor WC phase. A dc-arc emission spectrographic analysis indicated that no Pt, Ir, Rh, or Pd was present in any of these materials above the lowest limit of detection (2 ppm).

BET surface areas of tungsten carbide powders were obtained using a sorptometer. After surface area determinations, the powders were placed into a gas volumetric adsorption apparatus such that 1–5 m^2 of powder surface was available for each sample. Pretreatment sequences used for the samples and the volumetric quantity of hydrogen adsorbed following the pretreatments are shown in Table 1. These results clearly indicate that only the AEG-Telefunken "WC" and the commercial W_2C chemisorbed hydrogen when oxygen had been preadsorbed, the chemisorbed hydrogen being removed by titration with oxygen at 25°C. Approximately 20% of the AEG-Telefunken "WC" surface and 5% of the W_2C surface participates in the formation of water at 25°C. The other WC catalysts adsorb hydrogen

TABLE 1

Hydrogen Adsorption on Tungsten Carbide Following Pretreatment

Sequence	Pretreatment
1	Original sample (exposed to air) evacuated at 150°C for 1 hr
2	After (1) and hydrogen adsorption, evacuation at 150°C for 1 hr
3	After (2) and hydrogen adsorption, exposure to 400 Torr O_2 at 25°C 1 hr, evacuation at 150°C

Sample	BET area (m^2/g)	Hydrogen uptake (μmol/BET m^2)		
		1	2	3
Ventron WC	1.6	0.2	0.2	0.3
MRC WC	0.2	0.2	0.1	0.2
Starck WC	1.0	0.2	0.2	0.2
PWA WC	15	0.7	0.2	0.7
AEG WC	5	7.0	0.2	7.0
Atomergic W_2C	0.1	1.7	0.1	3.4

very weakly, probably only by physical adsorption.

In order to identify the surface properties of tungsten carbide leading to Pt-like chemisorption of hydrogen, the surface compositions were analyzed by Auger electron spectroscopy, using a Physical Electronics Industries Model 5000 spectrometer. Thick coatings of the powders were pressed in Al substrates and a 3 keV, 30 μA normal incidence electron beam was used as the excitation source. The electron beam and cylindrical mirror analyzer were at normal incidence to the samples to minimize the effects of surface roughness. Calculations of the surface compositions were based on the peak to peak heights of the derivative spectra and the relative sensitivities of the Auger transitions determined for the pure elements (*12*). The *KLL* transitions in C at 270 eV, O at 505 eV, and the W $N_{v}OO$ transition at 163 eV were selected for this calculation. These transitions should correspond to essentially identical escape depths of 5–10 Å (*13*) for the C and W Auger electrons. Spectra were recorded at a base line pressure of 5×10^{-10} Torr, for untreated samples and after argon ion bombardment at 1 keV, 30 mA. The C *KLL* transition derivative spectrum typical of tungsten carbide indicated there were small variations in lineshape with some of the untreated tungsten carbides but significant differences were observed between the untreated and the ion-bombarded surface. The primary effect of ion bombardment on the C *KLL* transition spectrum was to increase the peak to peak height at 268 eV and to sharpen the fine structure at 270 eV, these changes resulting from the removal of carbon contamination from the surface.

The surface compositions of the tungsten carbides examined are shown in Table 2 both for the untreated samples, and following 10 min Ar ion bombardment. The untreated surfaces of PWA, MRC, Starck and Ventron tungsten carbide all contained an excess of carbon relative to the bulk stoichiometry. This excess carbon is primarily a surface contamination characteristic of an untreated metal surface in vacuum, as for example, the carbon line seen on pure W powder (0.2 m^2/g). Removal of the carbon contamination from these sur-

TABLE 2

Surface Composition by AES of Tungsten Carbides, Before and After Surface Cleaning by Ar Ion Bombardment

Sample	Untreated (atomic%)				Cleaned (atomic%)		
	W	C	O	Bal.[a]	W	C	O
Ventron WC	15	73	2	10	54	46	Tr
MRC WC	14	66	6	14	56	44	Tr
Starck WC	29	48	7	16	48	52	Tr
PWA WC	14	85	1	—	49	51	Tr
AEG WC	41	45	14	—	65	25	10
Atomergic W_2C	44	26	26	5	65	33	2
Fansteel W	57	13	28	2	88	11	1

[a] Typically S, Fe, and Ni, entirely removed by ion-bombarding.

faces by Ar ion bombardment resulted in a surface W/C stoichiometry exactly identical to the bulk. Further evidence that ion bombardment selectively removed *carbon contamination* and not carbon from the carbide lattice is the variation of initial surface excess of carbon with surface area of the sample, which increased with increasing surface area.

The surface composition of the AEG-Telefunken "WC" was completely different from that of the other carbides of the WC stoichiometry. On both the untreated and ion bombarded surface the W/C ratio was significantly larger than that of the other samples of bulk WC stoichiometry, and the surface composition following ion bombardment was essentially identical to that of commercial ditungsten carbide (W_2C). These two carbides were also the only tungsten carbides observed to chemisorb hydrogen on a surface previously exposed to oxygen. There is, therefore, an apparent correlation of a surface excess of W on a WC surface and the Pt-like chemisorption of hydrogen.

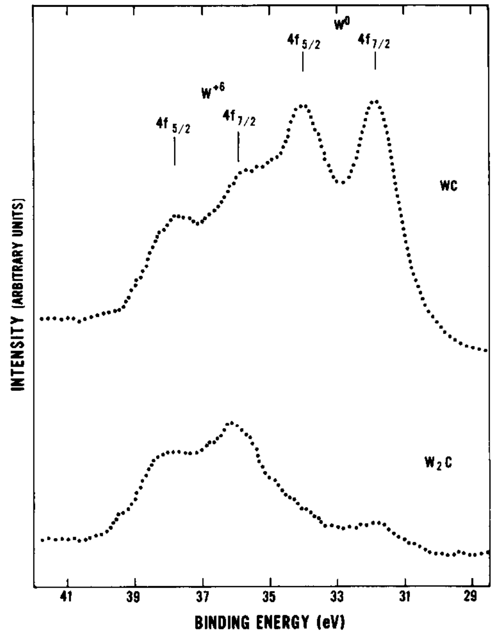

FIG. 1. X-Ray photoelectron spectra of untreated (prolonged exposure to air) AEG-Telefunken "WC" and W_2C. Two valence states of tungsten are evident, W^{6+} and W^0. Binding energy scale is referenced to carbon 1*s* line in graphite (284 eV).

Although the results in Tables 1 and 2 indicate that W_2C is the "active" form of tungsten carbide, examination of the W_2C and AEG-Telefunken "WC" surfaces by X-ray photoelectron spectroscopy (XPS) indicated significant differences in the surface chemistry. An example of this is the valence state of W at the surface of these two materials in the untreated state (i.e., after prolonged exposure to air). Figure 1 shows a comparison of the 4*f* electron photoemission spectra of W_2C and AEG-Telefunken "WC," with the proportion of W^{6+} to W^0 clearly much greater in the case of W_2C (66% W^0 in AEG-Telefunken to 15% W^0 in W_2C). The notation W^0, or zero-valent W, is used here to denote the oxide-free state of W in WC where the 4*f* binding energy is very close to that for metallic W (*14*). This fourfold difference in the surface concentration of zero-valent W is approximately the difference observed in the fraction of the surface that participates in the formation of water at 25°C on titration with hydrogen. The number of sites for activated (dissociative) chemisorption of hydrogen on tungsten carbide is probably proportional to the number of oxide-free W atoms on the carbide surface, since tungsten metal is well known for an ability to dissociate hydrogen at room temperature. The active sites on AEG-Telefunken "WC" are probably tungsten atoms that chemisorb oxygen in a form that is readily reducible by hydrogen. This is a unique property of this material because both stoichiometric WC and pure W react strongly with oxygen to form a passive surface oxide. The coordination of carbon atoms around tungsten atoms is obviously a critical factor in determining the interactions between the surface excess tungsten atoms and both oxygen and hydrogen molecules. The critical surface coordination of carbon around tungsten at the active sites is not known, but a WC surface that is carbon deficient must contain a high proportion of such active sites.

The dependence of the catalytic properties of WC for hydrogen dissociative chemisorption on the surface composition is not unexpected in the light of the electrochemical results of Böhm *et al.* (*4,5,8*) and Binder *et al.* (*6,7,10*). Stoichiometric WC synthesized by carburizing W or WO_3 is inactive for electrochemical hydrogen chemisorption or hydrogen molecule oxidation in acid electrolyte but when electrochemically "activated" (electrochemically oxidized in the presence of hydrazine) CO_2 is evolved (*15*) and the tungsten carbide becomes an active electrocatalyst for hydrogen molecule oxidation. Böhm (*8*) has identified the electrochemical rate determining step on activated "WC" for hydrogen molecule oxidation as the dual site dissociative chemisorption of the hydrogen molecule. Ross and Stonehart (*16*) have shown that this rate determining step also occurs on platinum under the same conditions, which shows in part the platinum-like behavior of "WC."

Whereas the results of Levy and Boudart (*1*) are not incorrect, the material they used was an atypical tungsten carbide. The surface composition of activated "WC" is clearly not the same as the bulk composition and is certainly carbon deficient.

REFERENCES

1. Levy, R. B., and Boudart, M., *Science* **181**, 547 (1973).
2. Houston, J. E., Laramore, G. E., and Park, R. L., *Science* **185**, 258 (1974).
3. Horányi, G., and Vértes, G., *Z. Phys. Chem. NF.* **83**, 322 (1973).
4. Böhm, H., and Pohl, F. A., *Wiss. Ber. AEG-Telefunken* **41**, 46, (1968).
5. Pohl, F. A., and Böhm, H., "Troisième Journées Internationales D'Etude des Piles à Combustible," pp. 183. Presses Academiques Europeennes, Brussels, 1969.
6. Binder, H., Köhling, A., Kuhn, W., and Sandstede, G., *Angew. Chem. Int. Ed.* **8**, 757 (1969).
7. Binder, H., Köhling, A., Kuhn, W., Lindner, W., and Sandstede, G., *Energy Convers.* **10**, 25 (1970); *Nature* (*London*) **224**, 1299 (1969).
8. Böhm, H., *Electrochim. Acta* **15**, 1273 (1970).
9. Baresel, D., Gellert, W., Heidemeyer, J., and Scharner, P., *Angew. Chem.* **83**, 213 (1971).
10. von Benda, K., Binder, H., Köhling, A., and Sandstede, G., *in* "From Electrocatalysis to Fuel Cells" (G. Sandstede, Ed.), p. 87. Univ. of Washington Press, Seattle, London, 1972.
11. Pearson, W. B. (Ed.), "Handbook of Lattice Spacings and Structures of Metals," Vol. 2, p. 439. Pergamon, 1967.
12. "Handbook of Auger Electron Spectroscopy." Palmberg, P. W., Reach, G. E., Weber, R. E., and MacDonald, N. C. (Eds.), Physical Electronics Industries, Edina, MN, 1972.
13. Jacobi, K., and Hoelzl, J., *Surface Sci.* **26**, 54 (1971).
14. Ramquist, L., Hamrin, K., Johansson, G., Fahlman, A., and Nordling, C., *J. Phys. Chem. Solids* **30**, 1835 (1969).
15. Voorhies, J. D., *J. Electrochem. Soc.* **119**, 219 (1972).
16. Ross, P. N., Jr., and Stonehart, P., *J. Res. Inst. Catal.* (Hokkaido) **22**, 22 (1974).

PHILIP N. ROSS, JR.
PAUL STONEHART

Materials Engineering & Research Laboratory
Pratt & Whitney Aircraft
Middletown, Connecticut 06457
Received February 14, 1975