Preparation and Surface Composition of Tungsten Carbide Powders with High Specific Surface Area

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Unsupported tungsten carbide powders of β-W_2C and WC have been prepared with specific surface area of 100 and 30 m^2 g^{-1}, respectively. WC surfaces are equilibrated with a stoichiometric carbide, lack carbon–carbon bonded surface residues, and contain less than 10% of a monolayer of residual oxygen. β-W_2C and WC surfaces chemisorbed CO and H irreversibly with an uptake of 20 and 40% of a monolayer, respectively. Carbide sites chemisorb oxygen and NH_3 strongly: about half of the oxygen desorbed in a TPR as CO at 1150 K and NH_3 desorbed in a TPD as N_2 at 800 and 1200 K.

Introduction

Several reviews of catalysis by transition-metal carbides have been published.[1-3] Early studies were generally made on samples of low specific surface area, e.g., WC[4] and Mo_2C.[5] More recently, techniques have been developed for synthesizing such materials with significantly higher surface areas and, consequently, higher specific catalytic activities. This has raised the level of interest in refractory carbides and nitrides as novel and potentially useful catalysis.

As an example, catalytic properties of high surface area tungsten carbide have recently been investigated for reactions of hydrogen–oxygen,[6] neopentane, methylcyclopentane, and 3,3-dimethylpentane,[7] and of normal alkanes.[8,9] To complement those studies of catalytic properties, we have used selective chemisorption, temperature-programmed reduction, and temperature-programmed desorption experiments to examine the characteristics of the tungsten carbide surface itself. The results reveal interesting features of the surface composition, surface chemistry, and carbonaceous overlayers that may have a significant impact in determining the catalytic behavior of high surface area tungsten carbide.

Experimental Methods

Samples of tungsten carbide powders were prepared from WO_3 powder (99.9994%, Puratronic, Johnson-Matthey). A typical experiment used 0.1–0.3 g of WO_3 spread over a 15-mm fritted quartz disk in a quartz cell in order to carry out sequentially temperature-programmed reduction (TPR) or desorption (TPD), chemisorption, and catalytic experiments without exposing the samples to air. All samples were prepared at atmospheric pressure in flowing He (Liquid Carbonic, 99.995%), CH_4 (Matheson, Matheson Purity), NH_3 (Matheson, anhydrous), or H_2 (Pd-diffused). Helium was passed through a molecular sieve trap at liquid nitrogen (LN_2) temperature and a MnO/SiO_2 oxygen indicator at room temperature. Methane and ammonia were passed through a molecular sieve trap and a MnO/SiO_2 oxygen indicator, both at room temperature.

Chemisorption of H_2 (Pd-diffused), O_2 (Matheson, ultrahigh purity), and CO (Matheson, ultrahigh purity) was measured at room temperature in a constant-volume adsorption system.[10] Isotherms were obtained between 5 and 20 kPa. A second isotherm was measured after evacuation at room temperature for 0.25 h. The difference of gas uptake between the values of both isotherms extrapolated linearly to zero pressure was taken as the amount of gas adsorbed irreversibly. Specific surface areas (S_g), calculated by the BET method, were measured in the same apparatus by N_2 (Matheson, Prepurified) adsorption at LN_2 temperature. Surface coverages of adsorbed species are reported as number density per total BET surface area. The surface area was measured first; then chemisorption uptakes of H_2, CO, and O_2 were measured. After CO or O_2 chemisorption, the specific surface area decreased by ca. 25%. This decrease probably arises from blocking of pores by the adsorbed molecules since a treatment in H_2 at 673 K for 2 h recovered original values of S_g. Thus, it is important to measure surface areas before chemisorption of O_2 and CO. A similar decrease in S_g after O_2 and CO chemisorption on Mo_2N was previously reported.[11]

Fresh samples were exposed to O_2 slowly (leak rate 0.1 μmol s^{-1} g^{-1}) in order to prevent exotherms and bulk oxidation. The passivation was run in the same volumetric system described above. The sample was evacuated, O_2 was introduced up to 30 kPa and the total amount of oxygen adsorbed on the sample was measured. The sample temperature, measured by a thermocouple near the sample, changed by less than 0.2 K during O_2 introduction. These oxidized samples were not exposed further to air.

Reaction of adsorbed oxygen with H_2 at room temperature was measured in the constant-volume adsorption system by first determining the specific surface area and the H_2 uptake. Then, the sample was heated to 800 K in a vacuum to remove adsorbed hydrogen. Finally, the uptake of O_2 followed by another H_2 uptake (reaction of surface oxygen with H_2) was measured.

TPR studies were carried out in a flowing mixture of 33% H_2 (Linde, prepurified) in He (Linde, high purity) at a total flow rate of 200 μmol s^{-1} g^{-1} and 1 atm. Typically, the sample (0.1 g) was heated from room temperature to 1370 K at a linear rate of 0.24 K s^{-1}. Before contacting the sample, gas mixtures were purified by passage through a molecular sieve trap at LN_2 temperature and a MnO/SiO_2 indicator at room temperature. Reaction products were analyzed by mass spectroscopy using a Hewlett-Packard 5970 mass-selective detector in the scanning mode m/e 10–150 with a scan step of m/e 0.125, and a scan cycle time of 1.5 s. Detection limits were 1 ppm CO and N_2 and 6 ppm H_2O and CH_4. Calibrations for CO, N_2, and CH_4 were obtained by sampling a known amount of these gases after each run. The calibration for water was determined by TPR experiments of NiO samples together with N_2 sampling at the end of the experiment.

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Table I. Preparation Conditions for WC, Specific Surface Area (S_g), and Number Density for Irreversible Chemisorption of CO at Room Temperature (n_{CO})

precursor	carburization	$n_{CO}/10^{15}$ cm^{-2}	S_g/m^2 g^{-1}	ref
tungstic acid	reduction in H_2 at 823 K, followed by carburization in CO up to 1023 K		30	13
tungstic acid	reduction in H_2, followed by carburization in CO/CO_2		30	14
tungstic acid	carburization in CO at 953 K		26	15
tungstic acid	carburization in CO at 973 K		17	16
tungstic acid	reduction in H_2, followed by carburization in CO		12	17
WO_3	carburization in CH_4/H_2/Ar, TPR at 0.042 K s^{-1}; final temp 1200 K	0.4	7	18
WO_3	carburization in CH_4/H_2, isothermal at 1100 K	0.4	30	this work

In this way, the relative signal of H_2O to N_2 was determined, and the amount of H_2O in a given experiment could be calculated by reference to the N_2 signal. The TPR plots will be normalized with the response factor so that the area under the curve will be directly proportional to the amount detected, irrespective of the molecule considered.

Preadsorbed NH_3 was desorbed in pure He (200 μmol s^{-1} g^{-1}) by increasing the temperature at 0.24 K s^{-1} in the same system used for the TPR experiments. Ammonia was adsorbed by continuous flow at room temperature and atmospheric pressure for 0.5 h, and then flushed with He at room temperature for 0.5 h.

Carbide samples were treated in H_2 (100 μmol s^{-1} g^{-1}) at 973 K in order to remove polymeric carbon. Evolved CH_4 was measured by gas chromatography (Hewlett-Packard 5370 A) using a flame ionization detector. The amount of CH_4 was calculated by calibrating CH_4 peak areas with a mixture CH_4–H_2 of known concentration.

The bulk structure of the samples was determined by powder X-ray diffraction (XRD) using Cu Kα radiation. The average size of the crystallites, D_c, was estimated from the Scherrer equation, $D_c = K\lambda/(\beta \cos \theta)$, where λ represents the X-ray wavelength, θ the Bragg angle, and β the peak width at half-maximum corrected for instrumental broadening.[12] The constant K was taken to be unity.

Results and Discussion

Sample Preparation. The preparation of high specific surface area β-W_2N and β-W_2C was described previously.[11] The specific surface area (S_g) reported earlier[11] for β-W_2C was 55 m^2 g^{-1}; here, a lower heating rate during the carburization of β-W_2N to β-W_2C gave samples with a higher S_g (100 m^2 g^{-1}). First, β-W_2N was prepared by temperature-programmed reaction of WO_3 with NH_3 (300 μmol s^{-1} g^{-1}) by heating from 700 to 1000 K at 8.3 × 10^{-3} K s^{-1}. β-W_2C was then prepared by carburization of β-W_2N in a 80 mol % CH_4/20 mol % H_2 mixture (500 μmol s^{-1} g^{-1}) using the same temperature heating rate as in the nitride preparation but with a final temperature of 1150 K.

WC was prepared by carburization of WO_3 in CH_4/H_2 mixtures. A mixture of WC and β-W_2C was obtained with S_g of 49 m^2 g^{-1} when WO_3 was heated slowly (8.3 × 10^{-3} K s^{-1}) from room temperature to 1150 K in 80 mol % CH_4 in H_2 or pure CH_4. Oxygen adsorbed on this sample did not react with H_2 at room temperature. After carburization, the sample was kept in the CH_4/H_2 mixture for 4 h at 1150 K, but the metastable β-W_2C did not convert to the thermodynamically stable WC phase. WC or a mixture of WC and β-W_2C were formed when fast heating rates were used (0.6 K s^{-1}). Preheating WO_3 in He to 1100 K and then contacting the oxide with the carburizing mixture (80 mol % CH_4 in H_2) for 6 h at 1100 K led to reproducible formation of WC.

The surface of these samples was covered with polymeric carbon; it prevented strong chemisorption of CO, H_2, or O_2 at room temperature. Here, polymeric carbon means surface carbon in amorphous, graphitic, "coke", or other

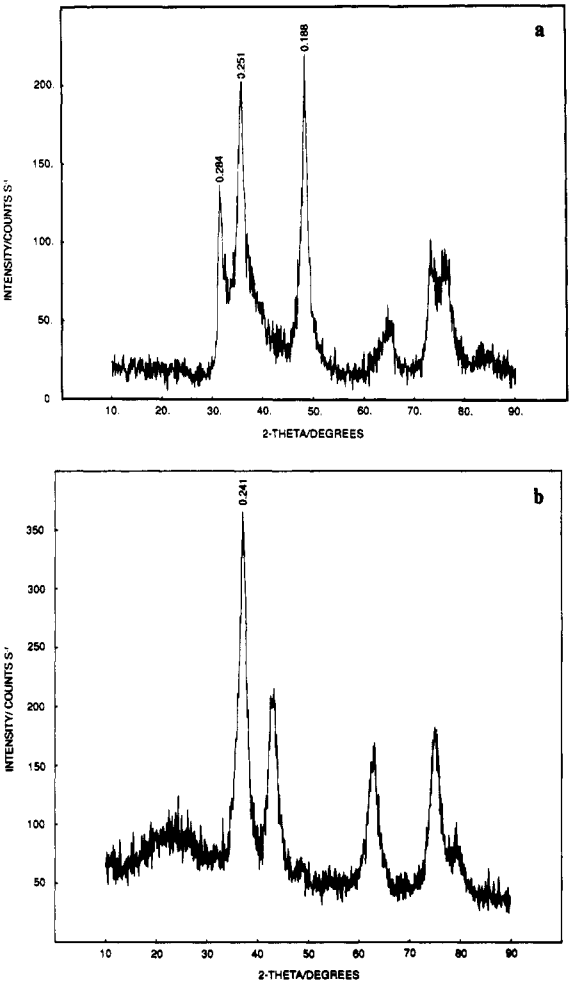

Figure 1. XRD pattern on tungsten carbides. The values for the d spacings (nanometers) on the most intense peaks are also given: (a) WC; (b) β-W_2C.

aggregate form. A H_2 treatment at 973 K for 0.8–1.5 h removed this carbon as methane from β-W_2C and WC. These clean powders are denoted as fresh samples.

The S_g and n_{CO} of WC are reported in Table I, together with those of other carbide samples. WC specific surface areas were less than 30 m^2 g^{-1}, irrespective of the precursor, carburizing mixture, or heating schedule.

The crystal structures of the carbides correspond to those reported in the literature for WC and β-W_2C.[19] WC

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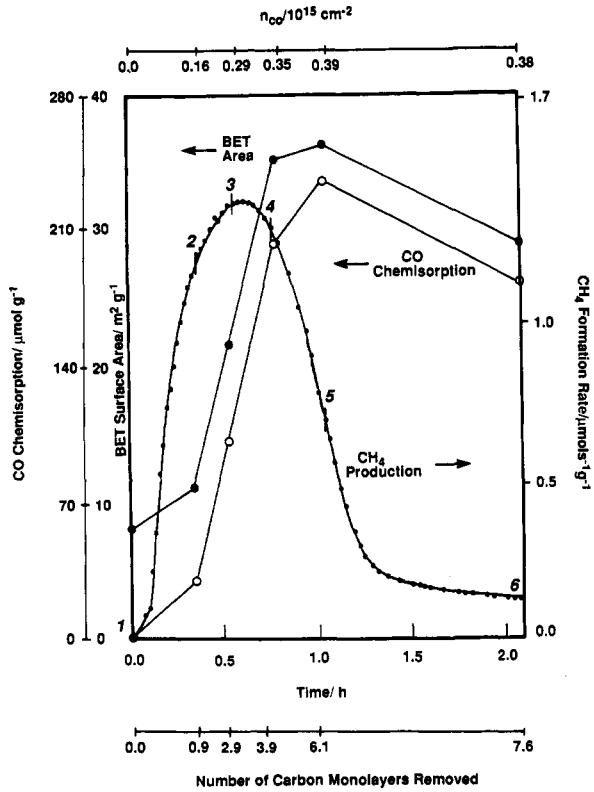

Figure 2. Carbon removal from WC by reaction with H_2 at 973 K (·). Effect of reaction time on the CO chemisorption uptake (○) and S_g (●). The number of carbon monolayers removed and n_{CO} are also given.

has a hexagonal structure with lattice parameters a = 290 ± 1 pm and c = 248 ± 1 pm and 6-nm crystallite size (Figure 1). β-W_2C has a FCC structure with a lattice parameter equal to 418 ± 1 pm and a 4-nm crystallite size (Figure 1).

Surface Composition. Because the carbide synthesis involves phase transformations and exposures to various gases at elevated temperatures, it is conceivable that the ultimate surface composition may be different from the simple bulk stoichiometry of the underlying tungsten carbide. Specifically, the possibilities include the following: (1) contamination by "coke" –polymeric carbon species on the surface but not associated with the carbide structure itself; (2) depletion of carbon at the surface, so that the solid structure and stoichiometry at the surface are different from those of the bulk carbide; (3) residual oxygen on the surface, left over from incomplete reduction of the tungsten oxide starting material.[19] Chemisorption and TPR measurements have been used to explore each of these possibilities, and the results are discussed below.

Removal of Surface Polymeric Carbon. Most of the preparation conditions on carbides (Table I) result in samples with excess polymeric carbon on the surface, which completely blocks chemisorption. It has been reported that a treatment in H_2 can remove this excess carbon,[11,13] but broad applications of this process has not been established. This process will be studied in more detail below.

Hydrogenation of surface carbon was studied by treating fresh samples with H_2 for different amounts of time; the rate of formation of CH_4 versus time, the BET area, and the CO chemisorption uptakes were measured. Six different reaction times ranging from 0 (zero) to 2.1 h were studied, each run using a different sample. The number density for CO chemisorption (n_{CO}) and the equivalent number of carbon monolayers removed during treatment by using a reference WC surface area of 36 m^2 g^{-1} and a W reference surface atom density of 1.0 × 10^{15} cm^{-2} are shown in Figure 2.

The removal of polymeric carbon from the surface by H_2 was previously discussed[20] and results of our work are shown in Figure 2. At the beginning of the treatment, the surface is completely covered by polymeric carbon, does not chemisorb CO irreversibly, and the S_g is low. As polymeric carbon is removed as CH_4, the tungsten carbide pore structure and surface are exposed. At this point, surface H coverage increases, more carbon reacts, and carbide surface is generated in autocatalytic fashion. Consequently, CO uptakes and S_g increase with time and when the rate reaches its maximum, the CO uptake and S_g are also near their maximum. After point 5 (Figure 2), the CO uptake and S_g start to decrease due to destruction of WC and formation of W: XRD showed a W phase for sample 6, but all the others showed only a bulk WC phase. The number density for CO (n_{CO}) reaches a constant value after point 4; yet, carbon is still being removed. Thus, no substantial amount of polymeric carbon was on the surface past point 4.

The WC crystallite size determined by XRD line broadening was the same (6 nm) for the samples with the lowest (sample 1) and the highest (sample 5) S_g in Figure 2. This result suggests that the carbon removal treatment increases S_g and CO uptake by removal of excess polymeric carbon from the surface and from pore mouths but does not interfere with the initial WC matrix. A 6-nm crystallite size corresponds to a surface area of 64 m^2 g^{-1}, calculated by using the expression $D = 6/\rho S_g$, where ρ is the density of the solid. The highest S_g in Figure 2 was 36 m^2 g^{-1}, suggesting that each WC particle consists of many crystallites bound together with little accessible porosity or internal S_g.

The amount of excess carbon, given in Figure 2 as number of carbon monolayers, seems very high but it must be pointed out that due to the preparation conditions some free carbon is expected to form that will be hydrogenated during the H_2 treatment. The sharp change in slope in the CH_4 production curve at 1.3 h might be associated with the depletion of free carbon.

Surface Stoichiometry in Carbidic Carbon. H_2 treatments can remove excess polymeric carbon but also significant amounts of surface carbidic carbon.[21,22] Therefore, we must ensure that the surface of the carbide is still in equilibrium with the bulk after our H_2 treatments.

The presence of carbon-deficient sites was studied after H_2 treatments; samples were prepared in the usual way, including treatment in H_2, and then treated using procedures intended to replenish the surface with carbidic carbon. In the first treatment, WC was heated in He to permit diffusion of bulk carbidic carbon to the surface. The second treatment consisted of passing a mixture of CH_4 in H_2 of suitable composition to recarburize the surface through an equilibrium between the surface and the gas mixture. The region labeled as WC in Figure 3 shows the range of CH_4 concentration that will not deplete the bulk from carbon or form polymeric carbon. Both treatments were carried out for 0.5 h at 1000 or 1100 K with flushing with He for 0.2 h before cooling to room

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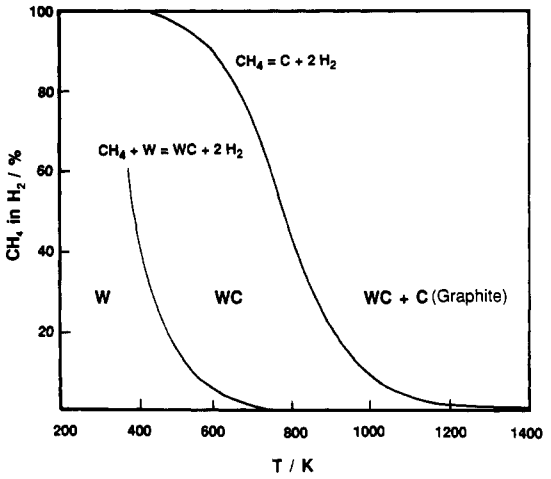

Figure 3. Thermodynamics of carburization of tungsten with a CH_4–H_2 mixture at 1 atm. Data taken from: Barin, I.; Knacke, O. *Thermochemical Properties of Inorganic Substances*; Springer-Verlag: Heidelberg, 1973.

Table II. Treatment of WC Samples in He or CH_4–H_2 at 1000 K for 0.5 h, except Where Indicated[a]

treatment	S_g/m^2 g^{-1}	no. density/10^{15} cm^{-2} n_H	n_O	fraction of O removed
fresh	30	0.37	1.4	0.11
He at 1000 K	32	0.34	1.3	0.11
He at 1100 K	25	0.28	1.2	0.12
CH_4 in H_2/%				
1	34	0.32	1.4	0.11
4	29	0.34	1.4	0.11
13	29	0.28	1.2	0.12
17	28	0.24	0.9	0.15
19	27	0.20	1.0	0.13
19 (3 h)	29	0.10	0.52	0.13
27	23	0.04	0.28	0.02
43	23	0.00	0.14	0.00
H_2 at 973 K (2 h)	26	0.36	1.6	0.11

[a] Number density calculated from S_g for irreversible room temperature chemisorption of H_2 (n_H) or O_2 (n_O) and fraction of chemisorbed oxygen that can be reacted by H_2 at room temperature.

temperature in order to avoid any changes in the surface stoichiometry while cooling in a reactive atmosphere.

The reaction of adsorbed oxygen with H_2 at room temperature was used to test for the presence of nonequilibrated WC surfaces. Adsorbed oxygen cannot be removed from the surface of W by H_2 at room temperature; however, it can be removed from WC surfaces,[4] a reduction property that results from the passivation of W by surface carbon. Thus, if WC surfaces are carbon deficient after H_2 treatment, the carbon replenishing treatments will increase the fraction of initially adsorbed oxygen that can be removed by H_2 at room temperature.

The He treatment at 1000 or 1100 K did not change the fraction of oxygen that could be reacted by H_2 at room temperature (Table II). The sample treated at the higher temperature, however, was sintered.

Treatments in mixtures of CH_4 in H_2 decreased the uptake of H_2 and O_2 as well as specific surface areas, especially as the CH_4 concentration in the mixture increased (Table II), suggesting extensive deposition of polymeric carbon. Before carbon was deposited on the surface, it should replenish nonequilibrated carbon-deficient sites. Although n_H decreases by a factor of 4 when samples are treated in 19% CH_4 in H_2, the fraction of oxygen that reacts with H_2 at room temperature changed only slightly (Table II). In the last two samples (27 and 43% CH_4 in H_2), the fraction of oxygen reacted by H_2 at room temperature actually decreased, apparently because most of the surface was covered by polymeric carbon. Thus, we conclude that the surface is equilibrated with bulk WC and that in polycrystalline WC samples there is only a fraction of adsorbed oxygen that can be reacted with H_2 at room temperature.

Table III. Fresh Samples of Tungsten Carbide and Nitride: Physisorption and Chemisorption

	β-W_2C	WC	β-W_2N
N_2 BET surface area/m^2 g^{-1}	100	30	100
no. density for irreversibly chemisorbed species at room temp[a]/10^{15} cm^{-2}			
CO	0.24	0.39	
H	0.21	0.37	0.24
O	1.03	1.39	
N	0.22	0.34	0.20

[a] 1 monolayer $\approx 1.0 \times 10^{15}$ cm^{-2}.

Additional evidence that the H_2 treatment does not deplete the surface from carbidic carbon was obtained by treating a sample of WC in H_2 for 2 h, instead of 0.8 h at 973 K, to remove polymeric carbon (sample 6 in Figure 2). This treatment produced a mixture of WC and W, but the same fraction of oxygen was reacted by H_2 at room temperature (Table II). This suggests that bulk carbon can replenish surface carbide carbon removed as CH_4 during the H_2 treatment. Stefan[23] reported that treatment of WC(0001) at 1100–1350 K led to the removal of carbon and oxygen as CO. However, the surface carbon signal as detected by AES was unchanged; thus, carbon diffusion from the bulk to the surface replenished the carbon removed during the treatment.

Another way of looking at the presence of carbon-deficient sites is to run a TPR in H_2/He on samples exposed to O_2 and observe the temperature at which adsorbed oxygen will be removed. These data are presented in Figure 4 for three of the samples in Table II after their exposure to air. The temperature at which oxygen is desorbed, either as CO or as H_2O, hardly changes with the sample treatment. Again, the results indicate that the surface of WC is in equilibrium with the bulk after the H_2 treatment.

The TPR results will be discussed at length in another section but for now it is necessary only to note that on the sample treated in 19% CH_4 in H_2 (Figure 4c) the CH_4 peak is at a lower temperature and the amount of CH_4 is also higher than on WC (Figure 4a). This observation is in agreement with the lower chemisorption uptakes reported in Table II, which confirm that this sample had indeed additional deposits of polymeric carbon on its surface. Before this carbon is deposited, it should replenish carbon deficient sites on the surface and so the fraction of oxygen removed on the TPR should have changed. The TPR also shows that oxygen binds with different energies on the surface and that indeed only a fraction of it can be removed by H_2 at room temperature.

In conclusion, the procedure of removing polymeric carbon by reaction with H_2 keeps the surface in equilibrium with bulk WC.

Chemisorption and Residual Surface Oxygen. Physisorption and chemisorption data for tungsten carbides after a treatment in H_2 at 973 K are shown in Table III. Surface number density data for N (n_N) calculated from the NH_3 TPD are also included. The surface number density for irreversibly chemisorbed CO (n_{CO}), H (n_H), and

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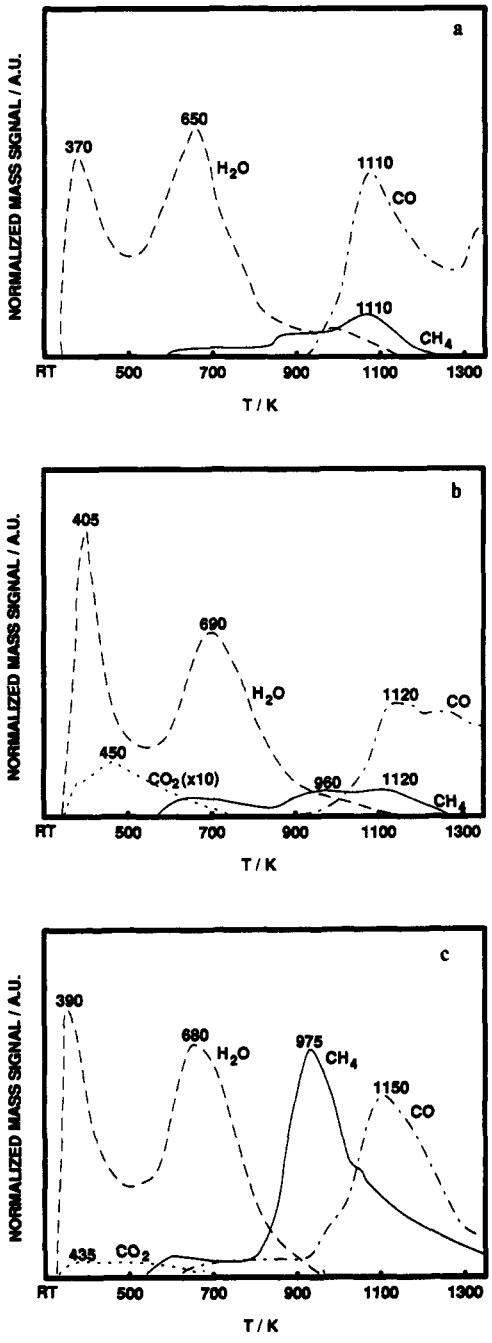

Figure 4. Temperature-programmed reduction in 33% H_2 in He of carbides exposed to air: (a) WC (CO_2, CO, H_2O, and CH_4 amounts were 15, 600, 1770, and 315 μmol g^{-1}, respectively); (b) WC treated in He at 1100 K (Table II) (CO_2, CO, H_2O, and CH_4 amounts were 10, 270, 650, and 75 μmol g^{-1}, respectively); (c) WC treated in 19% CH_4 in H_2 (Table II) (CO_2, CO, H_2O, and CH_4 amounts were 20, 360, 660, and 615 μmol g^{-1}, respectively).

N (n_N) were similar. Thus, we can measure the number of strong binding sites on a fresh sample by any of these techniques. The same agreement between the irreversible chemisorption of CO[11] and NH_3[24] is also true for Mo_2N. The fact that N and H number densities for β-W_2C and β-W_2N are very similar indicates that the H_2 treatment on β-W_2C after carburization of β-W_2N is very effective in removing excess polymeric carbon from the surface of β-W_2C.

Although the surface number density was similar for CO, H, and N, the maximum uptake for WC, as shown in

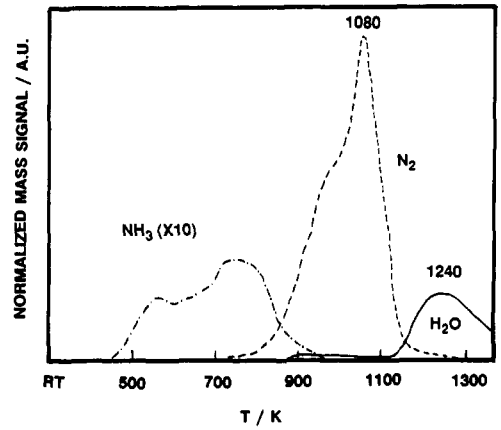

Figure 5. Temperature-programmed reduction in 33% H_2 in He of fresh β-W_2N. The amounts of NH_3, H_2O, and N_2 were 310, 690, and 3010 μmol g^{-1}, respectively.

Figure 2, is less than 1 monolayer. The CO uptake at room temperature on a model tungsten carbide surface W-(100)-(5×1)C is 1 monolayer,[25] and the density of polymeric carbon on the surface of our polycrystalline samples is too low to explain the low CO uptakes. The low values of n_{CO} on tungsten carbide powder (Table III) could arise from the presence of crystallographic surface planes of tungsten carbide that do not chemisorb CO irreversibly at room temperature. Indeed, Stefan[23] reported that on a single crystal of WC(0001), CO does not chemisorb irreversibly at room temperature.

The tungsten carbide overlayer W(100)-(5×1)C[26] chemisorbed about 1 monolayer of oxygen at room temperature; it could only be removed (as CO) by heating the crystal to 1400 K. Our samples also chemisorb approximately 1 monolayer of oxygen (Table III); the strong bond between carbide and oxygen is revealed by the evolution of CO above 1000 K in TPR experiments.

The amount of oxygen in the samples after preparation was measured by TPR in 33% H_2-He. These experiments also established the bulk stoichiometry of tungsten carbides and nitrides by measuring the amounts of H_2O, CO, CO_2, CH_4, and N_2 evolved as they are transformed into low surface area tungsten powders. In this way, measurements of the amount of carbon, nitrogen, and oxygen in the samples were obtained.

This procedure worked well for freshly prepared β-W_2N. The sample was transformed into low surface area tungsten powder (2 m^2 g^{-1}) during TPR in H_2-He (Figure 5). The stoichiometry for the nitride was $WN_{1.1}O_{0.1}$. The excess nitrogen probably forms superficial WN (ca. 4 monolayers), undetected by X-ray diffraction. The amount of NH_3 evolved during TPR corresponds to a surface density of 0.20×10^{15} cm^{-2}, the same value found for the number density of chemisorbed hydrogen (Table III). The surface species that give rise to NH_3 during TPR block sites that chemisorb H; the uptake of H_2 was complete only after the nitride was heated in vacuum at 800 K for 0.5 h, conditions that lead to NH_3 desorption. For β-W_2N, the oxygen content measured by TPR in H_2-He (Figure 5) corresponds to 40% of a monolayer. This oxygen content is also an upper limit for the amount of oxygen on β-W_2C, since this material is prepared by direct carburization of β-W_2N. Note that oxygen is removed as H_2O only after the β-W_2N structure is destroyed, which does not permit an estimation of how strongly this oxygen is bound. We also do not know

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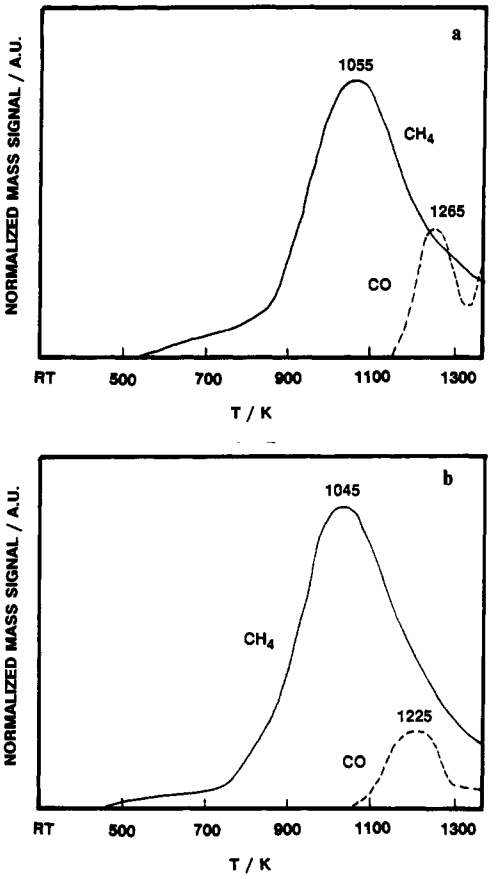

Figure 6. Temperature-programmed reduction in 33% H_2 in He of fresh carbides: (a) WC (CO and CH_4 amounts were 60 and 220 μmol g^{-1}, respectively); (b) β-W_2C (CO and CH_4 were 120 and 775 μmol g^{-1}, respectively).

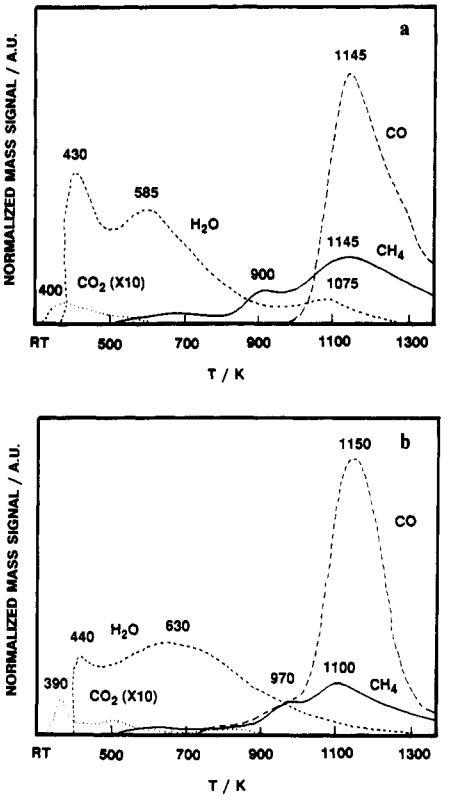

Figure 7. Temperature-programmed reduction in 33% H_2 in He of carbides after irreversible O_2 chemisorption at room temperature: (a) WC (CO_2, CO, H_2O, and CH_4 amounts were 2, 340, 390, and 205 μmol g^{-1}, respectively); (b) β-W_2C (CO_2, CO, H_2O, and CH_4 amounts were 8, 875, 725, and 300 μmol g^{-1}, respectively).

if the oxygen is at the surface or in the bulk.

TPR data for fresh WC and β-W_2C are shown in Figure 6. The CH_4 TPR profile is very similar for both samples as is the total CH_4 production per initial surface area (7.3–7.8 μmol m^{-2}). Thus, the carbon reactivity is the same irrespective of the bulk-phase structure. The total amount of carbon removed corresponded to (0.44–0.47) × 10^{15} cm^{-2}, approximately half a monolayer. This low CH_4 production suggests that the final product after TPR is not W powder; therefore, a quantitative analysis of the total amount of carbon and oxygen was not feasible. In fact, as revealed by XRD, the carbides maintained their initial bulk phase, except for the appearance of a WC phase in β-W_2C. As a consequence, the total amount of oxygen on these samples based on the amount of CO detected will be a lower limit. For WC (Figure 6a) and β-W_2C (Figure 6b), if oxygen detected in the TPR resided exclusively at the surface, it would cover 12 and 7% of the surface, respectively. This high-temperature CO peak might be due to strongly bound surface oxygen or to bulk oxygen. The assignment of this high-temperature CO peak is further complicated by the fact that there is also a loss of S_g (20–70%) during the TPR and oxygen sites that bind oxygen strongly might disappear upon carbide sintering freeing oxygen to combine with carbon.

We have no direct evidence for the presence of surface oxygen, but the data described in this section provide a lower limit for the coverage of surface oxygen.

Surface Reactivity. The desorption of preadsorbed molecules on a surface is a useful way to probe surface reactivity. Two probes, O_2 and NH_3, were employed in our studies. O_2 is an especially useful probe because powdered carbides are usually exposed to air before catalytic tests, and the amount of oxygen left under reaction conditions is important.[7-9] NH_3 desorption is interesting because NH_3 appears to adsorb on the same sites as CO; these sites in turn appear to be the active sites for hydrocarbon reactions.[7-9]

The interaction of oxygen with the WC surface was described in an earlier section. We found that only a fraction of the oxygen chemisorbed on WC reacts with H_2 at room temperature. This fraction is even lower on β-W_2C surfaces (0.01) than on WC surfaces (0.1). Since these fractions are so small, a TPR in H_2/He will better reveal the interaction of oxygen with the carbides. TPR of samples exposed to air were shown previously in Figure 4, but those were exposed to air and contain adsorbed water, making the interpretation of TPR data more difficult. Therefore, the interaction of oxygen with tungsten carbides was also studied on samples that were not exposed to air before TPR (Figure 7). Oxygen was removed as CO_2, CO, and H_2O during TPR. First, oxygen is evolved as water in two peaks at 430–440 and 585–630 K. WC binds oxygen less strongly than β-W_2C and desorbs a larger amount of H_2O at lower temperatures. This result is consistent with the smaller fraction of chemisorbed oxygen that can be reacted with H_2 at room temperature in β-W_2C than in WC. CO desorbed at about 1150 K on both samples. CO and not H_2O is formed because the reaction C + H_2O = CO + H_2 becomes increasingly favorable at high temperatures. The ratio of the amount of H_2O to CO in the products is about 1 on both samples, which points out to a similar distribution of sites on both samples. The total amount of oxygen detected on these samples, after subtraction of the amount of CO already present on the fresh samples, is very similar to the amount of chemisorbed oxygen in Table III. Thus, oxygen can be completely removed from the carbide samples only above 1300 K.

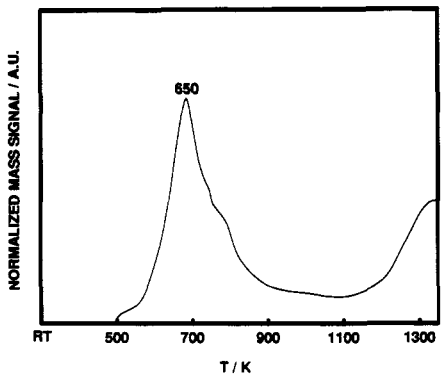

Figure 8. Temperature-programmed reduction in 33% H_2 in He of W after irreversible O_2 chemisorption at room temperature: The amount of H_2O was 134 μmol g^{-1}.

Comparison of the above TPR curves with the ones for the fresh samples (Figure 6) shows that CO desorbs at similar temperatures, which suggests that the oxygen on the fresh samples resides at the surface. However, the amount of CO evolved from fresh samples is 6 times lower than on samples exposed to O_2. The amount of CH_4 on the fresh and O_2 exposed samples is about the same for WC but lower on β-W_2C exposed to O_2. The cause for this difference is not known, but it might be added that the CH_4 production was not very reproducible on the samples exposed to O_2. On Mo_2C this extra oxygen decreases the amount of carbon on the sample;[21] this could also apply to tungsten carbides.

WC samples exposed to air (Figure 4) show TPR peaks at about the same position as the samples that had chemisorbed oxygen. The only difference between those set of samples is the much higher amount of oxygen on the samples exposed to air. To calculate the amount of oxygen, the amount of adsorbed H_2O was first determined by running a TPD in He for the WC sample. The amount of H_2O desorbed was 380 μmol g^{-1}[1]. The total amount of oxygen (4.0×10^{15} cm^{-2}) for the WC sample corresponds to 3 times the uptake of chemisorbed oxygen on a fresh sample, while the total amount of oxygen on the other two samples exposed to air were not much different from the one on a fresh sample (Table II). Thus, there is additional oxidation when the carbides are exposed to air, the same being reported before for molybdenum carbides.[21,22]

The TPR of adsorbed oxygen on carbides reveal strongly bound oxygen, which we now know is not due to a nonequilibrated surface. We would like to know what happens in the TPR when the oxygen is bound to W, with no carbidic carbon. To address this issue, we have run a TPR of W powder with adsorbed oxygen. This sample was prepared by reduction of WO_3 with H_2 for 24 h at 1000 K and then O_2 was adsorbed on the sample at room temperature. The TPR (Figure 8) reveals that oxygen is desorbed as H_2O in two peaks, with most of the H_2O coming out in a peak centered at 650 K. The major difference by comparison with the carbide samples exposed to O_2 is the absence of the H_2O desorption peak at 430–440 K. Thus, carbon introduces some sites that bind oxygen much less strongly than W, but there still remains some sites on tungsten carbides that bind oxygen as strongly as tungsten.

Surface oxygen remains on the surface of samples exposed to O_2 even after hydrogen treatment at high temperatures (T = 700 K). Therefore, in any previous study where carbide samples were exposed to air or were prepared with an oxygen containing molecule, e.g., CO, catalytic properties reflect those of O-modified surfaces. If chemisorbed oxygen influences the rate and selectivity of such reactions, samples exposed to oxygen will show a

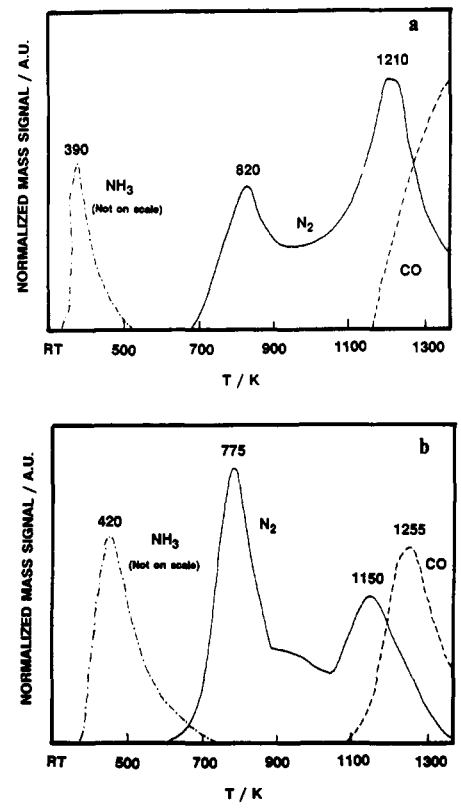

Figure 9. Temperature-programmed desorption in He of adsorbed NH_3 on fresh carbides: (a) WC (NH_3, N_2, and CO amounts were 5, 85, and 40 μmol g^{-1}, respectively); (b) β-W_2C (NH_3, N_2, and CO amounts were 13, 169, and 57 μmol g^{-1}, respectively).

behavior different than fresh carbides. Indeed, we report elsewhere that strongly bound oxygen plays a crucial role in modifying the selectivity of catalytic hydrocarbon reactions.[7,8]

The reducibility of surface oxygen described above appears to contradict earlier reports[14,17] that oxygen on carbides exposed to air is removed by H_2 at much lower temperatures (773 K). These differences arise because extensive surface coverage by polymeric carbon on these samples causes preferential titration of surface sites that also bind oxygen strongly and thus makes these sites unavailable for oxygen species. In fact, the catalytic activity on these materials are about 10^3 lower than on our samples.[7,8]

The TPR results described above probe the oxygen chemisorption sites. We suggest that oxygen chemisorption sites differ from CO chemisorption sites because their number densities are so different (Table III). CO chemisorption sites are of interest in carbides because they appear to reflect the number of active sites for hydrocarbon reactions.[7-9] The number densities for H and NH_3 are similar to those for CO suggesting that they chemisorb on similar sites. Ammonia was then used to probe the sites on the surface of tungsten carbides that chemisorb CO. The temperature-programmed desorption of preadsorbed NH_3 from WC and β-W_2C samples shows a low-temperature peak of physisorbed NH_3 and two N_2 evolution peaks at 800 and 1200 K (Figure 9). The other interesting factor is that n_N, calculated from the NH_3 TPD, is the same as n_{CO}, which implies that NH_3 is adsorbed associatively at room temperature. As the temperature increases, NH_3 dissociates and ultimately desorbs as N_2 at higher temperatures. Similarly, adsorption of NH_3 on Mo_2N[24] is associative at room temperature and NH_3 dissociates to atomic N upon heating. Thus, the active sites (sites that

adsorb CO and NH_3 irreversibly) of WC and β-W_2C adsorb NH_3 quite strongly and other molecules might also adsorb on them strongly.

Chemisorption of most O and NH_3 is very strong on fresh carbide samples. This is an interesting result, especially because our data suggest that the surface is equilibrated with bulk stoichiometric carbide. The addition of carbon to tungsten should decrease the binding energy of adsorbed molecules. In fact, CO chemisorbs at room temperature associatively on WC(100)-(5×1)C but dissociatively on tungsten.[27,28] Carbon clearly changes the properties of our carbide samples because the removal of some chemisorbed oxygen with H_2 occurs at room temperature, a process that occurs only at much higher temperatures on W metal sites (cf. Figures 7a and 8). The reactivity of less strongly bound species may account for the unique rate and selectivity of tungsten carbide in many catalytic hydrocarbon reactions.[7,8]

Summary

A new procedure to prepare WC with high specific surface area was developed. The surface of WC does not have appreciable amounts of polymeric carbon and seems equilibrated with bulk stoichiometric carbide. Following chemisorption of H_2 and CO, and NH_3 TPD, the surface number density was the same for H, CO, and N. Thus the active sites on the surface of a fresh sample can be counted by irreversible chemisorption of CO. The amount of oxygen on the surface of a fresh sample is less than 10% of a monolayer of oxygen. Most of the carbide surface still binds oxygen and NH_3 strongly. After oxygen is adsorbed on WC at room temperature, only 10% of the surface oxygen can be removed by H_2 at room temperature. The TPR in H_2-He of tungsten carbides exposed to O_2 showed that 50% of the oxygen could be desorbed only at 1150 K, so that it is difficult to rid a tungsten carbide surface of oxygen once it is exposed to O_2.

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Registry No. W_2C, 12070-13-2; WC, 12070-12-1; O_2, 7782-44-7; NH_3, 7664-41-7; CO, 630-08-0; H, 1333-74-0.

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Electrochemical and Photoelectrochemical Processes on Thin Films of Perylenetetracarboxylic Dianhydride

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Thin films of perylene derivative perylenetetracarboxylic dianhydride (PTCDA) have been examined as electrodes and photoelectrodes on both metal and metal oxide substrates. These thin films gave only anodic photocurrents (reverse bias condition) in contact with various aqueous electrolytes and facile dark currents negative of ca. -0.1 V vs. Ag/AgCl (forward bias condition). The origin of this photoeffect appears to be due to differential rates of charge injection at the PTCDA/solution interface and/or an asymmetric distribution of traps at that same interface. Electron microscopy of the PTCDA films indicated that they were deposited as elongated crystallites, with spaces between individual crystallites that strongly affected their dark and photoelectrochemical behavior, especially on Au substrates. Electrochemical polymerization with α-naphthol was carried out to passivate sites that were electrochemically active in the dark, a treatment that greatly enhanced the overall photoelectrochemical activity of the PTCDA thin films. Cathodic polarization of the PTCDA thin films caused surface bound electrochemically active redox couples to be produced at the film's surface, and this polarization step further enhanced the photoelectrochemical activity. These experiments suggest that the PTCDA photoelectrochemical activity is strongly dependent upon near-surface composition and morphology and that, because of the highly porous nature of these thin films, the photoactive interfaces extend throughout most of the bulk of the PTCDA film.

Introduction

Cyclic conjugated molecules such as perylenes (Pe) and phthalocyanines (Pc), primarily in thin-film form, continue to be of interest as molecular electronic materials. Their electronic properties (dark and photoconductivity) can be adjusted over a wide range through additions of electron acceptors or donors.[1-4] In addition to the influence of other molecular additives, chemical reactions at interfaces with metals and inorganic semiconductors have been implicated as controlling the electronic properties of certain Pc's and Pe's.[5-7] The importance of these reactions are

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