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THE TOPOTACTIC TRANSFORMATION OF TUNGSTEN OXIDE TO A CUBIC TUNGSTEN CARBIDE

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Abstract—The solid transformation of tungsten trioxide to a cubic tungsten carbide via nitride has been studied. Product carbide particles possessed specific surface area of *ca.* 90 m^2g^{-1} and average diameter of *ca.* 4 nm. Transmission electron microscope (TEM) exhibited that these particles formed porous aggregates with a spotty electron diffraction pattern. This provides an evidence that the topotactic solid transformation has been involved.

INTRODUCTION

Tungsten carbide exhibits platinum-like catalytic behavior for some surface and catalytic reactions [1,2]. Due to this interesting property of tungsten carbide, considerable efforts have been directed towards the development of procedures to prepare tungsten carbide with high specific surface area and high purity [3]. A new method developed by Boudart and coworkers involves temperature-programmed reactions (TPR) of a metal oxide with ammonia forming a metal nitride followed by temperature-programmed carburization of the nitride with CH_4-H_2 mixture to form uncommon metastable cubic carbide [4,5]. When the starting material was MoO_3 with specific surface area (S_g) less than 1 m^2g^{-1}, cubic Mo_2N and αMoC_{1-x} powders with S_g of *ca.* 200 m^2g^{-1} were synthesized [5]. The transformations of oxide-to-nitride and nitride-to-carbide were shown to be topotactic as {100} planes of Mo_2N were parallel to {010} planes of MoO_3, and the face-centered cubic (fcc) structure of Mo_2N remained unaltered when αMoC_{1-x} was formed.

Although a high S_g tungsten carbide could be produced by the same procedure [4], it was not determined if the topotactic transformation was involved in the synthesis as well. It is of interest because the preparation temperature of tungsten carbide is at least 100 K higher than that of molybdenum counterpart. For this purpose, the present study employs transmission electron microscopy(TEM) coupled with selected area electron diffraction (SAD), which has been proved to be an ideal tool to identify topotaxy in the case of the molybdenum oxide-to-nitride transformation [6]. The results of catalytic reactions on this tungsten carbide βW_2C will be published elsewhere [7].

EXPERIMENTAL

1. Sample preparation

The procedure to prepare βW_2C powders is summarized schematically in Fig. 1. About 100 mg of high purity WO_3 (99.998%, Johnson-Matthey) was loaded onto a fritted disc fixed in a quartz cell. A stream of NH_3 (Matheson, anhydrous) at atmospheric pressure was flown througth the cell at a rate of 100 μmol s^{-1}. Then the temperature of the sample was varied by a controller/programmer coupled to an electric furnace containing the cell. Following rapid heating to 870 K, the sample was further heated up to 1050 K by TPR with a linear heating rate of 30 K h^{-1}. This first step of preparation yields fcc W_2N powder with S_g of 91 m^2 g^{-1}. In the second step, W_2N powder cooled to 870 K were carburized by the same TPR used for nitride preparation with a gas mixture of 80% CH_4 (deoxygenated by passage through an MnO trap) and H_2 (Liquid Carbonic) purified by Pd-diffusion, flowing at 80 μmol s^{-1}. The surface of tungsten carbide thus obtained is completely covered by polymeric carbon, and does not chemisorb CO or H_2. In the final step of preparation, this polymeric carbon is selectively removed by H_2 treatment at 1000 K. The CH_4 produced from the hydrogenolysis of polymeric carbon was continuously monitored by a gas chromatograph. When the maximum CH_4 concentration was observed, the sample was immediately quenched to room temperature (RT) by removing the furnace.

2. Gas adsorption and X-ray diffraction

To measure the gas adsorption, the preparation cell

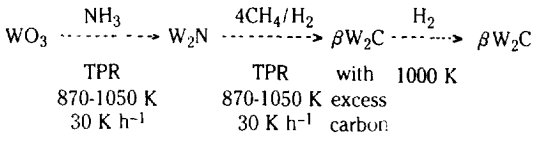


Fig. 1. Preparation of βW_2C from WO_3 by temperature-programmed reaction (TPR).

was isolated and transferred to a volumetric adsorption system equipped with a Texas Instruments differential pressure guage. To measure the amount of CO adsorption, the cell was evacuated to 10^{-4} Pa at 670 K, and various amounts of CO were dosed sequentially at RT to obtain a first adsorption isotherm. The cell was then evacuated again to 10^{-4} Pa at RT for 0.5 h to remove the weakly adsorbed CO. Then a second adsorption isotherm was taken to measure the amount of weakly adsorbed CO. The linear portion of the isotherms was extrapolated to zero pressure and the difference between the two extrapolated values was taken as the amount of strongly chemisorbed CO. To determine H_2 chemisorption a similar procedure was employed, but only the first isotherm was taken. A physical isotherm of N_2 was obtained and analyzed by means of the BET method to determine S_g. The bulk structure of the tungsten carbide was checked by powder x-ray diffraction. The widths of (111) and (200) diffraction peaks at half-maximum were used to estimate the average crystal size. Both peaks yielded similar values of D_c. Since the sample is pyrophobic when suddenly exposed to air, it was passivated at RT with flowing 1% O_2 in He before removal from the preparation cell for the x-ray diffraction measurement.

3. Transmission electron microscopy

For transmission electron microscopy (TEM), the passivated sample were dispersed ultrasonically in ethanol and then deposited on a TEM grid that had been coated with a holey carbon film. A Hitachi 500H microscope was operated at 100 kV.

RESULTS AND DISCUSSION

Table 1 shows characterization data for βW_2C. After preparation, the specific surface area S_g determined by the N_2 BET method was 90 m^2g^{-1}. This corresponds to particle size D_p of *ca.* 4 nm. The amount of chemisorbed CO and H_2 was found by extrapolating isotherms to zero pressure. In the case of CO chemisorption, only the fraction that could not be evaculated at RT was regarded as being irreversibly chemisorbed at this temperature. The number density n_{CO} or n_{H_2} was calculated as the amount of CO or H_2 chemisorbed per unit BET area.

Table 1. Characterization data of βW_2C powder

Specific surface area, S_g/ m^2g^{-1}	90
Chemisorption at RT/μmol g^{-1}	
CO	351
H_2	224
Number density/ 10^{14} cm^{-2}	
n_{CO}	2.35
n_{H_2}	1.50
Particle size/ nm	
D_p by BET[a]	4
D_c by X-ray[b]	4

a: $D_p = 6/\rho S_g$, ρ = density of the solid.

b: $D_c = \lambda/(\beta \cos\theta)$, λ= wavelength of CuK_α X-ray radiation, θ = Bragg angle, β = halfwidth of diffraction peak corrected for K_α radiation and instrumental broadening.

The X-ray diffraction peaks indicated a FCC crystal structure with a cubic lattice parameter of 418 pm. An average crystal size D_c of 4 nm was estimated from the application of Scherrer's equation to the width of the x-ray diffraction peak at half-maximum, corrected for instrumental broadening. Agreement with D_p from BET area is good.

In order for βW_2C to be an efficient catalyst, it should not only have a large surface area but should also have a surface free of any contamination. The most common surface contaminants in metal carbides are oxygen and polymeric carbon. Kojima et al. [8] found that evacuation above 1270 K activated TaC, TiC, and WC for the hydrogenation of ethylene due to the removal of oxygen or oxide. The polymeric carbon is more difficult to avoid because it originates from the preparation itself. It was shown that the presence of polymeric carbon on WC suppressed the chemisorption of H_2 [2]. According to thermodynamics shown in Fig. 2 graphite formation by CH_4 decomposition is favored for CH_4-H_2 mixture with more than *ca.* 5% CH_4 at 1050 K, the highest temperature of the preparation. Below 5% of CH_4 concentration, tungsten carbide is still stable relative to the metal. However, it was found that βW_2C formed under this condition contained a metallic W phase probably due to the slow diffusion of carbon atoms into the bulk. A βW_2C sample with a metal impurity always possesses a lower S_g than that of a pure sample.

The 80% CH_4 in H_2 was chosen as the carburization mixture knowing that the surface of βW_2C would be completely covered by polymeric carbon. As expected, it did not chemisorb CO or H_2 at RT right after carburization. The H_2 treatment at 1000 K provides a

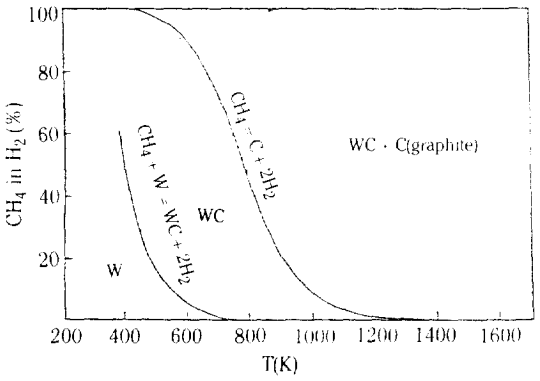
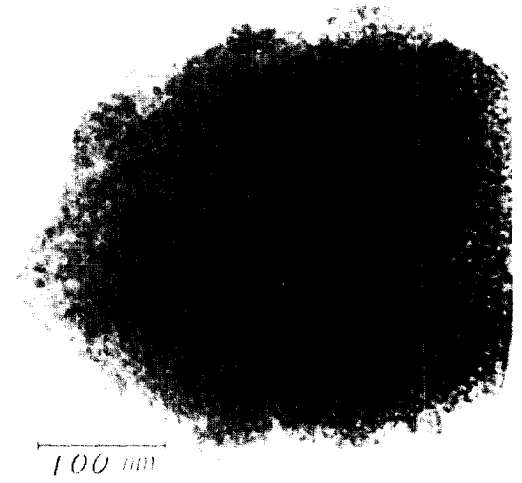


Fig. 2. Thermodynamics of carburization with a CH_4-H_2 mixture at atmospheric pressure.
Thermodynamic data were obtained from Barin, I. and Knacke, O.: "Thermochemical Properties of Inorganic Substances", Springer-Verlag, Heidelberg, 1973.

method to remove polymeric carbon from the surface of this sample. The treatment should be interrupted immediately after observing maximum CH_4 concentration. Further treatment beyond this maximum results in decrease in S_g and CO chemisorption since it starts to destroy underlying carbide structure.

It is believed that an appreciable amount of polymeric carbon still remains on the surface of βW_2C even after treatment with H_2, because the removal of surface carbon was interrupted when the maximum CH_4 formation was observed. However, a large fraction of the surface is clean as indicated by CO and H_2 chemisorption. Assuming that the surface consists of equal portions of the low index planes, we can expect the density of metal atoms on a clean βW_2C surface to be 1.1×10^{15} cm^{-2}. With adsorption stoichiometry of 1:1 for CO molecule and H atom, W atoms chemisorbing CO molecules or H atoms correspond to *ca.* 23% and 27%, respectively. Benziger et al. [9] showed that a considerable amount of CO could be removed below RT by flash desorption. Thus CO uptake reported here may represent a lower bound estimation of the number of clean W atoms. The remaining portion of surface W atoms which was not titrated by CO or H_2 is believed to be covered by the polymeric carbon.

Below 2800 K, the stable tungsten carbide phases include simple hexagonal αWC and hexagonal close-packed W_2C [10]. The FCC carbide of interest here (βW_2C) is metastable and has been obtained at low temperature only by rapid quenching of W-C mixture from temperatures above 2800 K [11]. The preparation method employed here thus allow us to obtain this un-



(a)

(b)

Fig. 3. A Small aggregate of βW_2C under a transmission electron microscope.
(a) Bright-field image.
(b) Corresponding selected area diffraction pattern. The spots show the {100} orientation.

usual phase at much lower temperatures. As has been demonstrated elsewhere for the case of FCC molybdenum carbide [4,5], the solid transformations involved in our preparation appear to be *topotactic* because of the relationship of crystal structure between the parent and the product throughout the bulk of the solid [12,13]. Thus, the cubic lattice of βW_2C is simply inherited from cubic W_2N which, in turn, has developed its cubic lattice from the *oriented* (insead of *random*) nucleation of its phase relative to the parent WO_3 crystal. The large surface area of W_2N (91 m^2g^{-1}) is also a consequence of a topotaxy of WO_3-to-W_2N transformation [5]. During the formation of βW_2C, it appears that nitrogen atoms are replaced with carbon atoms without disturbing the W lattice, thus preserving a high S_g or a small particle size of W_2N.

An ideal tool to identify topotaxy during a reaction of powdered solids is TEM with selected area electron diffraction (SAD). Figure 3 shows a bright field image and corresponding SAD pattern of a small representative βW_2C aggregate. Dominant feature of the pattern (Fig. 3b) is spots although diffuse ring pattern is barely seen. The square pattern of spots that belongs to the [100] zone axis shows that the {100} planes of βW_2C are predominantly oriented parallel to the flat aggregate as would be the case with a single crystal. Although a crystal of WO_3 is broken into many 4 nm crystallites of βW_2C during the WO_3-to-βW_2C transformation, these crystallites form an aggregate in which the position of a W atom in a crystallite relative to other W atoms, even in other crystallites, is not altered as far as the crystallites remained in the same aggregates. In other words, individual βW_2C crystallites comprising the aggregate maintain the same crystalographic relationship as in the starting WO_3, thus confirming the topotactic relationship to WO_3. The diffuse rings may arise from slight misorientation between the crystallites.

The image (Fig. 3a) shows a random mosaic of small domains along the edges of the aggregate. This type of image contrast is caused by density variation in the specimen and is commonly encountered in porous solids. Thus the material, originally non-porous, developed voids. Since large oxygen atoms are replaced by small carbon atoms maintaining relative positions of W atoms, a great reduction in specific volume per 1g of W must occur. This difference in specific volume must be balanced by developing pores. The sponge aggregate seen by TEM can be viewed as a highly porous defect single crystal of βW_2N. All these TEM observations are very similar to those made previously for MoO_3-to-Mo_2N transformation [4], and shows that the reactions involved in the preparation of βW_2C from WO_3 belong to the class of topotactic solid transformation. Also as in the case of the MoO_3-to-αMoC_{1-x} transformation, the reason for the topotaxy in WO_3-to-βW_2C transformation is believe to be the mild preparation conditions limiting the movement of W atoms during the transformation [5].

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