286 Chemistry Letters Vol.36, No.2 (2007)

A Novel Preparation of Tungsten Carbide Particles with High Specific Surface Area by Carburizing Tungsten Sulfides

Yoshinori Hara,* Noriko Minami, Hajime Matsumoto, and Hiroaki Itagaki
Mitsubishi Chemical Group Science and Technology Research Center, INC.,
1000 Kamoshida-cho, Aoba-ku, Yokohama 227-8502

(Received October 31, 2006; CL-061281; E-mail: 2309180@cc.m-kagaku.co.jp)

High surface area tungsten carbide (WC) was prepared by the carburization of tungsten sulfide (WS_2) with a mixture gas of H_2/CH_4. In particular, the surface area of WC derived from $W(CO)_6/S$ as starting material showed around $80\,m^2/g$, which is the highest value among reported. Transmission electron microscopy (TEM) results revealed that WS_2 decomposed into small WC crystals with a plate-like structure retaining the entire morphology of the original WS_2 when WS_2 was transformed into WC. That may be one of reasons why WC obtained in this way gives a high surface area.

The transition-metal carbides,[1] especially those of molybdenum and tungsten, have been paid considerable attention as promising substitutes for a Pt catalyst since Levy and Boudart first showed catalytic properties similar to those of platinum metals in the neopentane isomerization reaction in 1973.[2] Ever since, they have been investigated for applications in heterogenous catalysis[3] and electrocatalysis.[4] On the other hand, they have originally used in the field of metallurgy as bulk materials because of their unique properties.[5] For instance, WC has been extensively used in cutting tools and many other high wear applications owing to its hardness and antiattrition.[6] WC is generally prepared by direct carbonization method which is a two-step process wherein the tungsten oxide is firstly reduced to tungsten in a hydrogen atmosphere followed by the reaction with carbon at 1400–1600 °C to produce WC.[7] Although various synthetic methods such as ball milling[8] and solid-state metathesis[9] have been proposed for WC powder so far, they require high temperature of around 1000 °C. So the specific surface area of WC was not enough for the usage as a functional material. That is to say, it is desired to prepare WC with small particle size and high surface area which is suitable for catalyst application. It is generally recognized that the particle size or the surface area of the catalyst is a crucial factor in terms of the activity due to the presence of a large number of surface active sites.[10] In the present work, we describe a novel preparation method of WC particles with high specific surface area by carburizing WS_2 with a mixture gas of CH_4/H_2. In our preliminary experiments, we first found capable to carburize WS_2 at high temperature. Similarly, the analogous reaction of tungsten nitride has been reported, but it proceeds at much more mild condition.[11] In addition, the WS_2 nanoparicles have been known to form a variety of morphologies such as a nanotube and fullerene-like structure called inorganic fullerene (IF) in analogy to the carbon paradigm by the synthetic conditions.[12] We had taken interest in how the morphological change went when WS_2 was transformed into WC. Therefore, two different WS_2 were synthesized in the following ways (eqs 1 and 2) according to the literature.

$$W(CO)_6 + S \text{ in Xylene} \rightarrow WS_2(A) \tag{1}$$

$$WO_3 + H_2S \rightarrow WS_2(B) \tag{2}$$

WS_2(A) can be obtained at the lowest temperature of 140 °C by reacting $W(CO)_6$ with elemental sulfur in the liquid phase.[13] WS_2(B) was synthesized using WO_3 nanopowder (purchased from Aldrich) under the atmosphere of H_2S at 820 °C by Tenne's method.[14] The XRD pattern of each WS_2 sample was identified with the listing in the ICDD database. Figure 1 shows the XRD chart of the WS_2 particles synthesized by these methods.

The crystal sizes of WS_2(A) and WS_2(B) were estimated to be 3.4 and 11.6 nm, respectively, by the XRD line-broading analysis. WS_2(A) is less crystalline reflecting the synthetic condition. On the other hand, that of commercial available WS_2 (purchased from Mitsuwa Chemicals) is 36.1 nm. Then, WC was synthesized by methane carburizing WS_2 with a mixture gas of 80% H_2 and 20% CH_4 at the flow rate of 100 mL/min at 900 °C for 7 h according to eq 3.

$$WS_2 + CH_4/H_2 \rightarrow WC \tag{3}$$

The reactivity of WS_2 turned out to be significantly dependent on its synthetic pathway. For instance, commercial WS_2 hardly underwent carburization toward WC under the reaction condition described above. Whereas, it went to completion within 8 h even at 840 °C for WS_2(A). The order of reactivity seems to be $WS_2(A) > WS_2(B) \gg$ commercial WS_2. Its reactivity is supposed to be associated with the reaction temperature at which the WS_2 particles were synthesized. Each XRD pattern of WC(A) and WC(B), derived from WS_2(A) and WS_2(B), respec-

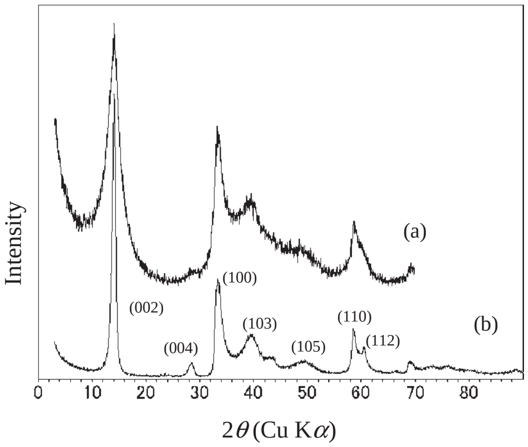

Figure 1. X-ray powder diffraction patterns of WS_2, (a) WS_2(A), and (b) WS_2(B).

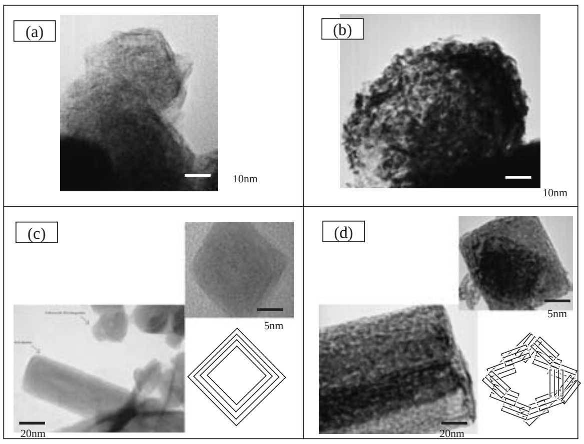

Figure 2. Typical TEM morphology of WC and WS_2, (a) WS_2(A), (b) WC(A), (c) WS_2(B), and WC(B).

tively, well matched that of the powder diffraction database, indicating a hexagonal phase. The crystal sizes of WC(A) and WC(B) were 3.3 and 4.9 nm, respectively. The BET surface areas of each sample were determined by N_2 adsorption at around 77 K using an AMS 1000 (Ohkura Riken) porosimeter. The surface areas of the precursors, WS_2(A) and WS_2(B) were 30 and 34 m^2/g, respectively. Surprisingly, the surface area of WC was found to greatly increase by the carburization of WS_2 in spite of treating at the high temperature. WC(A) gave the surface area of 83 m^2/g, and in the case of WC(B), it was 52 m^2/g. On the other hand, the surface area of WC obtained by the conventional method which was synthesized by direct carburization of WO_3 at 877 °C was only 5 m^2/g.[15] Thus, the surface area of WC(A) prepared from WS_2(A), to the best of our knowledge, exhibited the highest value among reported in the literature to date. Such extraordinary behaviors aroused our interests in elucidating the microstructural difference between WC and WS_2.

Figure 2 shows the high-resolution TEM images of WC particles synthesized from WS_2(A) and WS_2(B) along with that of their WS_2 precursors. WS_2(A) was observed as a nest cluster and clearly had the lattice fringes (002) of 2H-WS_2. WC(A) seem to keep the same morphology in appearance as that of WS_2(A). However, as can be seen in Figure 2b, the surface of WC(A) grew grained and the microstructure was quite different from that of WS_2(A). It was observed that WC(A) consists of lot of nanoorder plate-like crystallites within a few nm in size. Such a phenomenon can be more evidently observed in the case of WS_2(B). As described above, WS_2(B) was synthesized under the condition which would form an IF-like structure such as the multilayer polyhedra (onions) and nanotubes. TEM image of WS_2(B) indicates the presence of hollow nanotubes with diameter of 5–20 nm and some onion-like structure of about 20 nm which reveals the presence of layers with a spacing of 0.6 nm, in accord with the literature.[14] We were concerned with how such a microstructure of hollow nanotubes and onion-like IFs change as WS_2(B) was converted to WC(B). As shown in Figure 2d, TEM image of WC(B) also seemingly shows nanotube and onion-like structure similar to that of WS_2(B). However, it seems that such nanoclusters are assembled from small crystalline WC particles consisting of nanoplates with ca. 5 × 5 nm in size at high resolution. And the crystalline WC has a layer structure with a lattice fringe (interlayer spacing) of 0.25 nm, corresponding to the (001) of WC. That is to say, the nanotube and onion-like IFs in WC(B) are though to be made up of agglomerates of many crystalline nanoplates. Thus, the TEM observation indicates that the crystalline WS_2 decomposes into small crystalline WC particles with a plate-like structure retaining the entire morphology of the original WS_2 when WS_2 is transformed into WC. That may be one of the reasons why WC obtained by the carburizing of WS_2 gives a higher surface area than those prepared from other routes.

In summary, we have successfully prepared high surface area WC particles by the novel method using WS2.

References

1 S. T. Oyama, *Catal. Today* **1992**, *15*, 179.
2 R. B. Levy, M. Boudart, *Science* **1973**, *181*, 547.
3 A.-F. Lamic, T. L. H. Pham, C. Potvin, J.-M. Manoli, G. Djéga-Mariadassou, *J. Mol. Catal. A: Chem.* **2005**, *237*, 109.
4 P. N. Ross, P. Stonehart, *J. Catal.* **1977**, *48*, 42.
5 S. H. Jhi, S. G. Louie, M. L. Cohen, J. Ihm, *Phys. Rev. Lett.* **2001**, *86*, 3348.
6 G. Jiang, H. Zhuang, W. Li, *Ceram. Int.* **2004**, *30*, 185.
7 L. Leclercq, M. Provost, H. Pastor, J. Grimblot, A. M. Hardy, L. Gengembre, G. Leclercq, *J. Catal.* **1989**, *117*, 371.
8 G. M. Wang, S. J. Campell, A. Calka, W. Akaczmarek, *J. Mater. Sci.* **1997**, *32*, 1461.
9 A. M. Nartowski, I. P. Parkin, M. Mackenzie, A. J. Craven, *J. Mater. Chem.* **2001**, *11*, 3116.
10 N. Toshima, T. Yonezawa, *New J. Chem.* **1998**, 1179.
11 J. B. Claridge, A. P. E. York, A. J. Brungs, M. L. H. Green, *Chem. Mater.* **2000**, *12*, 132.
12 R. Tenne, *Adv. Mater.* **1995**, *7*, 965.
13 L. Vradman, M. V. Landau, M. Herzkowitz, V. Erersky, M. Talianker, S. Nikitenko, Y. Koltypin, A. Gedanken, *J. Catal.* **2003**, *211*, 163.
14 Y. Feldman, V. Lyakhovitskaya, R. Tenne, *J. Am. Chem. Soc.* **1998**, *120*, 4176.
15 S. Decker, A. Lofberg, J. M. Bastin, A. Frennet, *Catal. Lett.* **1997**, *44*, 229.

Published on the web (Advance View) January 18, 2007; doi:10.1246/cl.2007.286