A Novel Carbothermal Method for the Preparation of Nano-sized WC on High Surface Area Carbon

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Nano-sized WC was successfully synthesized on high surface area carbon by a novel carbothermal method wherein carbonization of mixture of hydroxypropyl cellulose (HPC) and K_2WO_4 at 800 °C resulted in the simultaneous formation of carbon and WC nano-particles. Different with the common carbothermal method, porous carbon was obtained by pyrolysis of hydroxypropyl cellulose and the reducing gas of H_2 was not necessary.

Since the tungsten carbide WC was found to display Pt-like behavior in several catalytic reactions,[1] interest in WC as an inexpensive alternative to the noble metals has grown steadily for application in heterogeneous catalysis and electrocatalysis. Today, WC is usually prepared by a two-step process wherein the tungsten oxide is firstly reduced to tungsten in a hydrogen atmosphere, then the obtained tungsten metal reacts with carbon at 1400–1600 °C to produce carbides. The prepared WC by this method gives a very low surface area. With the goal of application of carbides including WC in ceramic science, catalysis, and adsorption, preparation of transition-metal carbides with small particle size and high surface area is under intensive investigation. Generally, solution-state reactions[2,3] and gas–solid reactions[4–12] are employed to prepare high surface area transition-metal carbides. Temperature-programmed reaction of carbon-containing gaseous reagent (methane, ethane, butane, etc.) with solid state metal compound is one representative method.[4,5] Moreover, carbothermal method was explored to prepare transition-metal carbides or activated-carbon supported carbides, whereby solid carbon was used as carbon source to react with vaporized or supported metal oxides in flowing H_2. By this method, vanadium carbides,[6] molybdenum carbides,[7–10] and tungsten carbides with high specific surface area[11,12] were obtained. And their catalytic activities were examined in hydrotreating processes, such as hydrodenitrogenation, hydrogenation reactions, hydrocarbon-reforming reactions. For tungsten carbides prepared by the carbothermal method, the main components of tungsten compound are W_2C together with tungsten oxides. Whereas, carbon-supported WC has been not successfully prepared at relatively low temperature because of the difficulty of forming WC. In the present work, we described a novel carbothermal method to prepare high surface area carbon-supported WC at 800 °C. Hydroxypropyl cellulose and K_2WO_4 were used as carbon and WC precursors, respectively. Porous carbon and nano particles of WC were simultaneously produced to construct a composite of WC and carbon (WC–C) during the carbonization process.

Firstly, 4.0 g of potassium tungstate K_2WO_4 was dissolved in 30 mL of H_2O followed by adding 150 mL of ethanol. Then, 5.0 g of hydroxypropyl cellulose was slowly added under stirring. A white gel was obtained after 1–2 h. Subsequently, a rotary evaporator was used to remove the solvents at 60 °C. After drying at 100 °C overnight, the obtained mixture of hydroxypropyl cellulose and K_2WO_4 was put into a ceramic boat and moved into a tubular resistance furnace controlled by a temperature programme. Carbonization of hydroxypropyl cellulose with K_2WO_4 was performed in a N_2 flow (200 mL/min) by heating to 800 °C at a heating rate of 5 °C/min and soaking time of 1–5 h. The obtained black solids were added into a 0.5 M KOH solution to remove the unreacted K_2WO_4. After washing several times with distilled water, filtration and drying, WC–C composites were finally obtained.

XRD patterns of the products were shown in Figure 1. The existence of tungsten metal and W_2C was confirmed in WC–C prepared by 1 h carbonization (Figure 1a). When the carbonization time was increased from 1 to 5 h, the peaks of W and W_2C gradually disappeared while the peaks of WC appeared. This suggested that W and W_2C reacted with carbon to form WC at 800 °C. In Figure 1c, the diffraction peaks of only WC could be resolved, indicating that the formation of WC is complete. Matching with the literature values (JCPDS 25-1047), the diffraction peaks were attributed to hexagonal WC. The surface area and porosity of WC–C composites were investigated using nitrogen adsorption and desorption isotherms (shown in Figure 2). The pore distribution was obtained by analyzing desorption isotherms using DH (Dolimore–Heal) method. With an increase of carbonization time, the BET specific surface areas of WC–C increased. Mesoporosity of WC–C was suggested by the type IV isotherms and the calculated pore size distribution. For WC–C obtained from 5 h carbonization, the morphology was studied by field-emission-type scanning electron microscopy (FESEM) (Figure 3). Image in Figure 3b′ was acquired with

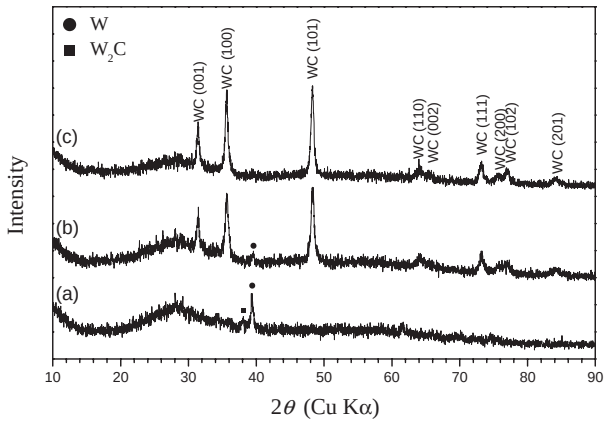

Figure 1. X-ray powder diffraction patterns of WC–C composites prepared at 800 °C for 1 h (a), 3 h (b), and 5 h (c).

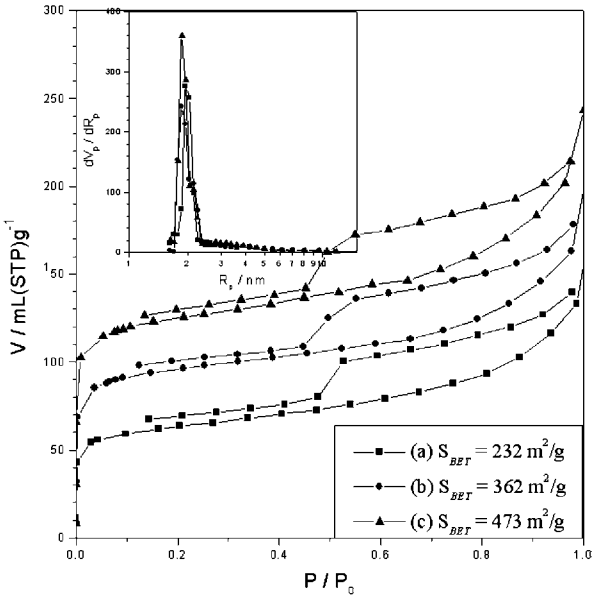

Figure 2. Nitrogen adsorption/desorption isotherms and pore size distribution (in the inset) of WC–C composites prepared at 800 °C for 1 h (a), 3 h (b), and 5 h (c).

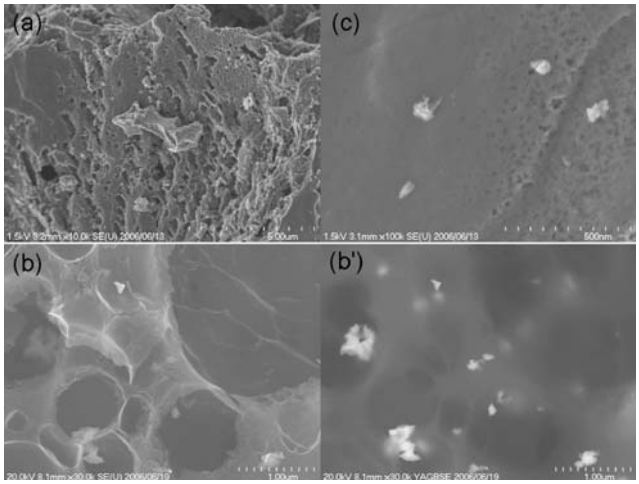

Figure 3. FESEM images of WC–C composite prepared at 800 °C for 5 h. (a), (b), and (c) Bar 5 μm, 1 μm, and 500 nm, respectively; (b′) YAGBSE image of (b).

the YAGBSE detector for backscattered electrons to distinguish WC particles on surfaces of carbon. The observations (Figures 3c and 3b′) revealed that besides a few larger grains (200–500 nm), most of WC particles have a size ranged from 30 to 200 nm. Furthermore, large amount of macropores were observed in the figure.

The results of XRD showed that K_2WO_4 was reduced to tungsten metal at 800 °C in the absence of H_2. This indicated that strongly reducing agents were produced during the carbonization of hydroxypropyl cellulose. The pyrolysis of cellulose has been well studied.[13] When heated at moderate temperatures (300–450 °C) under an inert atmosphere, cellulose undergoes various dehydration, fragmentation, elimination, and condensation reactions to give gaseous products ($CO + H_2O + CO_2$), tar, and char. Above 500 °C, CO and H_2 are mainly released. Reasonably, it was deduced that CO or H_2 was responsible for the reduction of K_2WO_4 to W metal. The W metal was subsequently carburized to form WC. Because high temperature is required for the formation of WC by reacting W with C in solid state, WC is possibly produced by the following reaction: $W + 2CO \rightarrow WC + CO_2$. At last, we concluded that in the process of carbonization, K_2WO_4 was firstly reduced to tungsten metal then the obtained W reacted with CO to produce WC. About the porosity of WC–C composites, the formation of mesopores in WC–C may be due to the existence of potassium. It was reported that carbonization of the potassium loaded cellulose resulted in the formation of carbons with mesoporosity.[14] Furthermore, FESEM images confirmed the presence of macropores which may be due to the removal of unreacted K_2WO_4 during the washing process. When EtOH was added into the aqueous solution of K_2WO_4, parts of K_2WO_4 precipitated from the solvent because of its low solubility in EtOH–H_2O solution. The large grains of K_2WO_4 were dispersed inside the dried hydroxypropyl cellulose after solvent removal. Carbonization caused only small amount of K_2WO_4 (ca. 4%) to be changed to WC. Washing of WC–C composites consequently resulted in the formation of macropores in the carbon. Hydroxypropyl cellulose is used in this work because it is soluble in H_2O–EtOH solution and large amount of H_2 and CO due to pyrolysis can be produced to reduce K_2WO_4.

We have successfully prepared high surface area WC–C composites. From FESEM images, it is verified that the produced WC particles are in nano size. Different with the common carbothermal method that activated carbon is used, high surface area carbon is obtained by pyrolysis of hydroxypropyl cellulose. Furthermore, the more striking results are that the reducing gas of H_2 is not necessary during the carbonization process and WC can be produced even at 800 °C. To our best knowledge, this is the lowest reaction temperature for the production of WC by the carbothermal method.

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