

Nanostructured β -Mo₂C Prepared by Carbothermal Hydrogen Reduction on Ultrahigh Surface Area Carbon Material

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Nanostructured β -Mo₂C on an ultrahigh surface area carbon material ($>3000\text{ m}^2/\text{g}$), a kind of novel carbon material with uniform pore distribution, was prepared by the carbothermal hydrogen reduction method. The Mo precursor and Mo₂C have been characterized by X-ray diffraction, nitrogen adsorption, high-resolution transmission electron microscope, and temperature-programmed reduction mass spectroscopy. The data show that nanostructured β -Mo₂C can be formed on the ultrahigh surface area carbon materials by carbothermal hydrogen reduction at $\sim 700\text{ }^\circ\text{C}$. The particle sizes of β -Mo₂C increase with the increase of reaction temperatures. The carbothermal hydrogen reduction includes two successive steps: reduction of the MoO₃ precursor by hydrogen and reaction between partially reduced molybdenum oxides and surface carbon atoms of carbon materials under the hydrogen atmosphere.

Introduction

The transition-metal carbides have received considerable attention as advanced materials, especially as catalytic materials, because of their unique physical and chemical properties.^{1,2} Many methods including gas-phase reactions of volatile metal compounds, reaction of gaseous reagents with solid-state metal compounds, pyrolysis of metal complexes, and solution reactions have been developed for the preparation of high surface area carbides.^{2,3} These carbide materials show exceptionally high activity in hydrogen-involved reactions.^{4–10} It is also found that the catalytic properties of carbide materials strongly depend on their surface structure and composition, which are closely associated with the preparation methods. Among these preparation methods, the representative one is the temperature-programmed reaction between oxide precursors and a flowing mixture of hydrogen and the carbon-containing gases, such as CH₄,^{11–13} C₂H₆,^{14,15} C₄H₁₀,¹⁶ and CO.¹⁷ However, some problems also exist in this method of

preparation: the carburization and passivation processes must be carefully controlled, and the resultant carbide surface is usually contaminated by polymeric carbon from the pyrolysis of the carbon-containing gases. The carbon blocks the pores, covers the active sites, and is difficult to remove.

Recently, Ledoux and co-workers developed a novel synthesis route to preparing high surface area carbides which can avoid the formation of carbon residues on the surface.^{18–21} It involves the reaction of solid carbon with vaporized metal oxides at very high temperatures, even above 1000 °C. Activated carbon was used as the carbon source, and the final carbides appear to remain the characteristic of porous structure of the activated carbon. Moene and co-workers described a catalytic carbothermal method for converting carbon materials to high surface area SiC.^{22,23} Mordini et al. modified the carbothermal method and prepared activated-carbon-supported Mo₂C samples under moderate tempera-

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Table 1. Surface Area, Porosity, and Average Pore Size of HSAC, Mo/HSAC, and the Samples with Carbothermal Hydrogen Reduction

| sample | BET surface area (m ² /g) | pore volume (cm ³ /g) | average pore size (Å) |
|-------------|--------------------------------------|----------------------------------|-----------------------|
| HSAC | 3234 | 1.78 | 22.0 |
| Mo/HSAC-RT | 2446 | 1.31 | 21.4 |
| Mo/HSAC-600 | 2505 | 1.38 | 21.9 |
| Mo/HSAC-700 | 2341 | 1.35 | 23.7 |
| Mo/HSAC-800 | 2180 | 1.30 | 23.8 |

tures.²⁴ However, this method is still in an early stage of development. A broad range of supports and metal compounds need to be tested and studied in detail because metal compounds can be highly dispersed on carbon materials and the carburized materials are potential catalysts in hydrogenation reactions. In the present work, we have tried to prepare nanostructured Mo₂C using an ultrahigh surface area carbon material (>3000 m²/g), a kind of novel carbon material with uniform pore sizes,²⁵ as a carbon source and template by carbothermal hydrogen reduction.

Experimental Section

Ultrahigh surface area carbon material is made by a direct chemical activation route in which petroleum coke is reacted with excess KOH at 900 °C to produce the carbon materials containing potassium salts. These salts are removed by successive water washings. The surface area of the carbon materials measured by the Brunauer–Emmett–Teller (BET) method is about 3234 m²/g, and the pore volume is about 1.78 m³/g (Table 1).

The ultrahigh surface area carbon material was impregnated in a rotary evaporator at room temperature with an aqueous solution of ammonium heptamolybdate. The molybdenum content is 10 wt %. After evaporating and drying in air at 120 °C overnight, the materials were transferred to a quartz reactor inside a tubular resistance furnace controlled by a temperature programmer. The amount of the sample was about 4 g/batch. Pure hydrogen was passed through the sample at a flow rate of 200 cm³/min. The temperature was increased at a linear rate of 1 °C/min to the final temperature, which was held for 1 h. The samples were quenched to room temperature at flowing argon and then passivated by a 1% O₂/N₂ mixture.

X-ray diffraction analysis of the samples was carried out using a Rigaku D/Max-RB diffractometer with a Cu K α monochromatized radiation source, operated at 40 KV and 100 mA. Temperature-programmed reduction (TPR) of the sample was carried out in a stream of 95% argon and 5% hydrogen with a flowing rate of 30 cm³/min. The catalyst bed was heated linearly at 20 °C/min from room temperature to 950 °C. Mass spectroscopy was used as the detector. Transmission electron microscopy (TEM) studies were carried out on a JEOL 2000 electron microscope. High-resolution transmission electron microscopy (HRTEM) and electron diffraction were performed on a JEM-4000EX electron microscope with an acceleration voltage of 200 KV. Nitrogen adsorption and desorption isotherms at 77 K were measured using Micrometrics 2010. Surface areas were calculated from the linear part of the BET plot.

Results and Discussion

Surface area and porosity of the ultrahigh surface area carbon and the samples after carbothermal hydro-

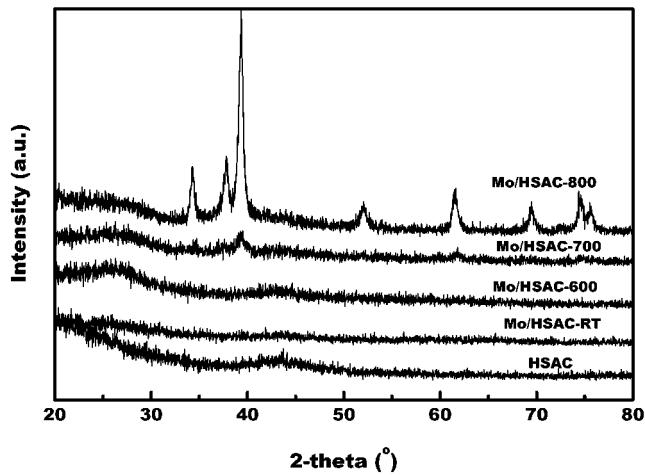


Figure 1. XRD patterns of HSAC, Mo/HSAC precursor, and the samples with carbothermal hydrogen reduction.

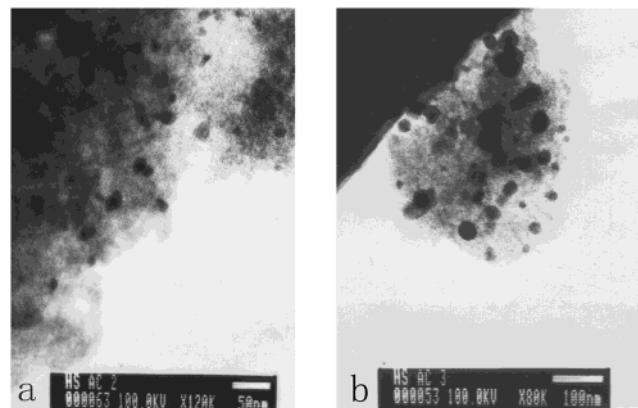


Figure 2. TEMs of samples with carbothermal hydrogen reduction: (a) obtained at 700 °C; (b) obtained at 800 °C.

gen reduction are compiled in Table 1. After the impregnation of carbon material, its surface area decreases from 3234 to 2446 m²/g, its porosity from 1.78 to 1.30 m³/g, and its average pore size from 22.0 to 21.4 Å. It can be assumed that a molybdenum precursor fills and blocks a fraction of the pores of carbon materials. The surface area and porosity of the samples show a decrease, to some extent, with the increase of the temperatures of carbothermal hydrogen reduction, while the average pore size shows an increasing trend. The changes of the surface area, porosity, and average pore size may be attributed to the reaction of carbon materials with hydrogen and molybdenum precursor and the changes of molybdenum species.

The phases and dispersion of the molybdenum compound were also measured by XRD after the supported samples were reduced in hydrogen. Figure 1 shows XRD patterns of the samples with carbothermal hydrogen reduction at different temperatures, together with the ultrahigh surface area carbon and the supported Mo precursor. XRD pattern of the ultrahigh surface area carbon shows clearly that the carbon material is non-graphitizable. XRD pattern of the supported molybdenum precursor sample does not show any diffraction peaks of molybdenum precursors, indicating that the molybdenum species is well-dispersed on the carbon material and that the particle size is smaller than 4 nm. The result is consistent with that obtained using HRTEM by Mordini et al.²⁴

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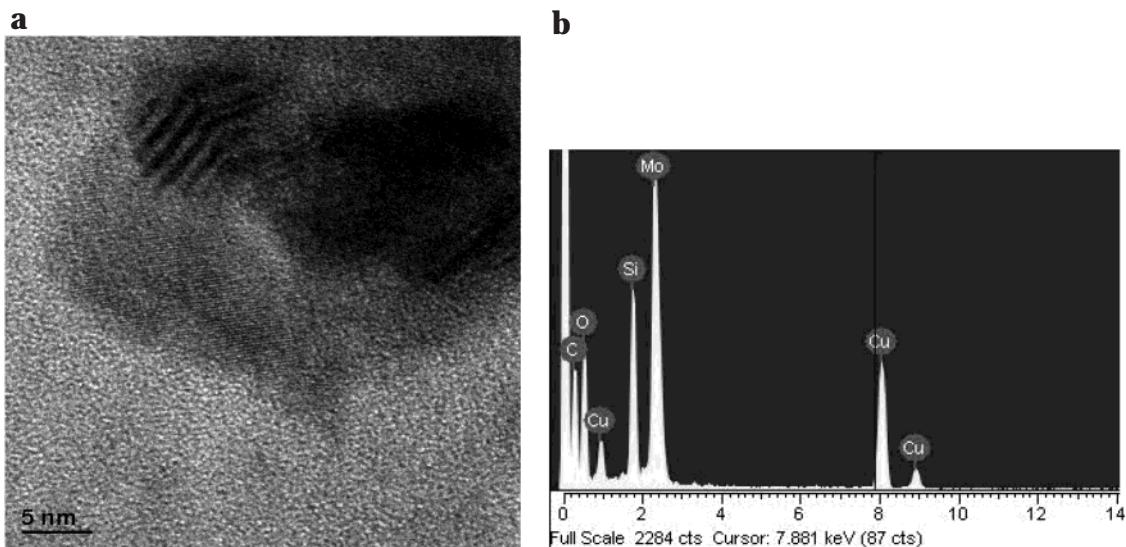


Figure 3. (a) HRTEM of sample with carbothermal hydrogen reduction at 700 °C; (b) EDX analysis of the sample in (a).

The XRD pattern of the sample with carbothermal hydrogen reduction at 600 °C does not show any diffraction peak due to a MoO_2 phase, indicating the highly dispersed MoO_2 . However, this result is different with that of a molybdenum precursor supported on activated carbon,²⁴ where the MoO_2 was detected by XRD. The good dispersion of the MoO_3 precursor and MoO_2 may be due to the ultrahigh surface area and pore volume of the carbon material used in this study. The XRD pattern of the sample with carbothermal hydrogen reduction at 700 °C shows a diffraction peak at 39.4°, which is due to $\beta\text{-Mo}_2\text{C}$ with a hexagonal closed packed structure. When the carbothermal hydrogen reduction temperature is further increased up to 800 °C, typical diffraction peaks due to $\beta\text{-Mo}_2\text{C}$ show clearly at 39.4°, 37.8°, 34.3°, 52.0°, 61.7°, 69.6°, 74.5°, and 75.7°. The average particle size of $\beta\text{-Mo}_2\text{C}$ may be estimated from the parameters of XRD according to the Scherrer formula. The average particle sizes of $\beta\text{-Mo}_2\text{C}$ at 700 and 800 °C are 6 and 17 nm, respectively. It is clear that the particle sizes of $\beta\text{-Mo}_2\text{C}$ increase with the increase of carbothermal hydrogen reduction temperature.

To estimate the particle sizes of $\beta\text{-Mo}_2\text{C}$, TEM and HRTEM were carried out. The TEMs of the samples with carbothermal hydrogen reduction at 700 and 800 °C were shown in Figure 2. It can be seen that the particle sizes of $\beta\text{-Mo}_2\text{C}$ at 700 °C are about 10 nm in diameter dispersed on the outer surface of carbon materials (Figure 2a), while the particle sizes of $\beta\text{-Mo}_2\text{C}$ at 800 °C are about 25 nm in diameter (Figure 2b) and larger than that at 700 °C. The particle sizes obtained by TEM are larger than the sizes obtained by XRD.

The HRTEM picture of Figure 3a shows that the molybdenum carbide contained a high density of planar defects and dislocations after synthesis and passivation at room temperature. The EDX analysis performed on this phase indicated the presence of Mo, C, and O (Figure 3b). The existence of O is due to the formation of passivated layer, which avoided violent oxidation of the sample when it was exposed in air.

To understand the carbothermal hydrogen reduction process, the reactant and principal products were monitored with mass spectroscopy in real time. The

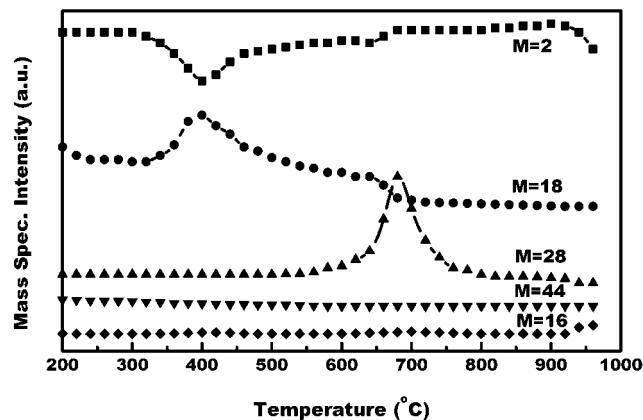
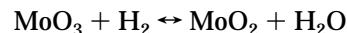


Figure 4. TPR-MS profiles of MoO_3 /HSAC precursor.

sample was first dried at 150 °C in the stream of nitrogen for 2 h and then cooled to room temperature in order to avoid the desorption peak of water at about 100 °C. Figure 4 shows the synthesis traces of masses (M) 2, 16, 18, 28, and 44 with the increase of temperature. The signals at $M = 2$ and 16 represent hydrogen and methane, while the signals at $M = 18, 28$, and 44 represent water, carbon monoxide, and carbon dioxide, respectively. The temperature-programmed reduction mass spectroscopy (TPR-MS) traces show that the carbothermal hydrogen reduction reaction proceeds in three stages in the range of temperature studied. First, there was a considerable amount of hydrogen consumption and water formation at about 400 °C. From it, one can conclude that MoO_3 was reduced into molybdenum oxide with a low chemical valence. However, actual H_2 consumption is more than the value for the following reaction:

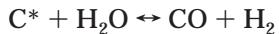


Second, a CO mass spectrometer signal appears when the temperature is above 530 °C, further increases with the increasing temperature, and reaches the maximum at 680 °C. Meanwhile, a decrease in the hydrogen mass spectrometer signal accompanied by simultaneous water evolution was observed. CO formation is mainly due to

a carbothermal reaction between reactive carbon atoms or groups on carbon material²⁶ and Mo compounds in the presence of hydrogen.



C^* is the surface carbon atom or groups of carbon material. In addition, CO can be also formed from carbon material and water produced by the reduction of the oxides and from the decomposition of the C—O groups.

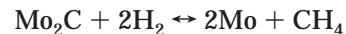


In this stage, β -Mo₂C was formed by the reaction between MoO₂ and CH_x species from reactive carbon atoms or groups on carbon material and hydrogen, and in this process β -Mo₂C particle sizes become larger and larger with the increase of temperature.

Finally, a methane signal appeared when the temperature increases up to 900 °C. Simultaneously, a peak for hydrogen consumption is also observed. So, it can be assumed that hydrogen reacted with carbon material

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or carbide was hydrogenated according to the following reactions:



Conclusion

An ultrahigh surface area carbon material with the narrow distribution of pore sizes was used as carbon source and support during the process. The uniform β -Mo₂C particles with about 10 nm were obtained after carbothermal hydrogen reduction at 700 °C. And, the particle sizes of β -Mo₂C increase with the increase of reaction temperature. The carbothermal hydrogen reduction includes two successive steps: reduction of a molybdeum precursor by hydrogen and reaction between partially reduced molybdenum oxides and carbon materials under the hydrogen atmosphere. The method of carbothermal hydrogen reduction is a useful and simple way to synthesize nanostructured carbides under mild conditions.

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