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Journal of Solid State Chemistry 179 (2006) 29–32

JOURNAL OF SOLID STATE CHEMISTRY

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A facile preparation of nanocrystalline Mo_2C from graphite or carbon nanotubes

Zeheng Yang[a,b], Peijun Cai[a], Liang Shi[a], Yunle Gu[a], Luyang Chen[a], Yitai Qian[a,*]

[a]*Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China*
[b]*School of Chemical Engineering, Hefei University of Technology, Hefei, Anhui 230009, China*

Received 13 July 2005; received in revised form 20 September 2005; accepted 24 September 2005
Available online 2 November 2005

Abstract

Nanocrystalline Mo_2C powders were successfully synthesized at 500 °C by reacting molybdenum chloride ($MoCl_5$) with C (graphite or carbon nanotube) in metallic sodium medium. X-ray powder diffractometer (XRD), transmission electron microscope (TEM), X-ray photoelectron spectroscope (XPS) and surface area analyzer (BET method) were used to characterize the samples. Experiments reveal that the carbon source used for the carbide synthesis has a great effect on the particle size and the surface area of the samples. When micro-sized graphite was used as C source the obtained nanocrystalline Mo_2C powder consists of particles of 30∼100 nm, with a surface area of $2.311\,m^2/g$. When carbon nanotubes were used as C source, the as-synthesized Mo_2C sample is composed of particles of 20∼50 nm, with a surface area of $23.458\,m^2/g$, which is an order of magnitude larger than that of the carbide prepared from the graphite.

Keywords: Molybdenum carbide; Nanoparticle; Chemical synthesis; Transmission electron microscopy; Surface area

1. Introduction

Molybdenum carbides are well known for their hardness, thermal stability and surface reactivity. They have also been found to show catalytic behavior similar to the noble metals [1]. Due to their ability to withstand high temperatures and resistance to poisoning [2,3], molybdenum carbides may be an inexpensive alternative to the noble metals as catalysts.

Previously, molybdenum carbides were prepared by various high temperature reactions, such as pyrolysis of metal precursors [4], carbothermal reduction of molybdenum oxides [5], metal hydride reduction of $MoCl_5$ [6], and arc melting of metallic molybdenum or its oxides [7]. These syntheses route to molybdenum carbides need high temperature (for instance, 800 °C) and the obtained products exist in micro-sized particles or in molybdenum carbide particles encapsuled with carbon. It is known that the catalytic activity increases with the increase of surface-to-volume. Recently, the synthesis of nanocrystalline molybdenum carbides has attracted much interest. Nanostructured Mo_2C has been prepared by several methods [8–11]. Suslick et al. used sonochemical method to decompose the volatile organometallic precursor $Mo(CO)_6$ under Ar flow to prepare nanostructured Mo_2C. Liang et al. prepared nanostructured Mo_2C by carbothermal hydrogen reduction at 700–800 °C. Bokhonove et al. prepared encapsulated Mo_2C nanoparticles by annealing mechanically activated mixtures of amorphous carbon with molybdenum at a temperature of 860 °C. Qian et al. synthesized nanocrystalline Mo_2C via sodium co-reduction of $MoCl_5$ and CBr_4 at 350 °C in benzene solvent.

Herein, we reported a simple chemical route to the synthesis of nanocrystalline Mo_2C at 500 °C by reacting molybdenum chloride ($MoCl_5$) with C (graphite or carbon nanotubes) in metallic Na medium. The reaction was carried out in an autoclave and can be described as follows:

$$2MoCl_5 + C + 10Na = Mo_2C + 10NaCl.$$

Compared with the previous methods to nanocrystalline Mo_2C, this simple route has the advantage of lower reaction temperature, no volatile reagent or toxic solvent

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[*] Corresponding author. Fax: +86 551 3607 402.
E-mail address: zehengy@mail.ustc.edu.cn (Y. Qian).

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doi:10.1016/j.jssc.2005.09.037

and no complicated apparatus. So it is practical for industry consideration.

2. Experimental

The anhydrous $MoCl_5$ was of 99.5% purity from Alfa Aesar Company. Metallic Na and graphite were of 99% purity from Shanghai Chemical Company. The carbon nanotubes (CNTs) were prepared by the thermal catalytic decomposition of hydrocarbon [12]. All manipulations were carried out in a dry glove box with Ar flowing. In a typical procedure, an appropriate amount of anhydrous $MoCl_5$ (0.02 mol), C (0.01 mol), and excessive metal Na (0.2 mol) was put in a glass lined stainless autoclave of about 50 ml capacity. The autoclave was sealed and maintained at 500 °C for 12 h, then cooled to room temperature naturally. The product was washed with absolute ethanol, dilute hydrochloric acid and distilled water, respectively, to remove Na, NaCl and other impurities. After drying in vacuum at 60 °C for 4 h, the final gray powder product was obtained.

The samples were characterized by X-ray powder diffraction (XRD) patterns, which were recorded on a Japan Rigaku Dmax-γA X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) pattern were taken with a Hitachi H-800 transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VGESCALAB MK II X-ray photoelectron spectrometer, with non-monochromatized Mg$K\alpha$ X-ray as the excitation source. Surface areas of the samples were determined by BET measurements on nitrogen adsorption at 77 K with a Beckman Coulter Surface Area Analyzer SA 3100.

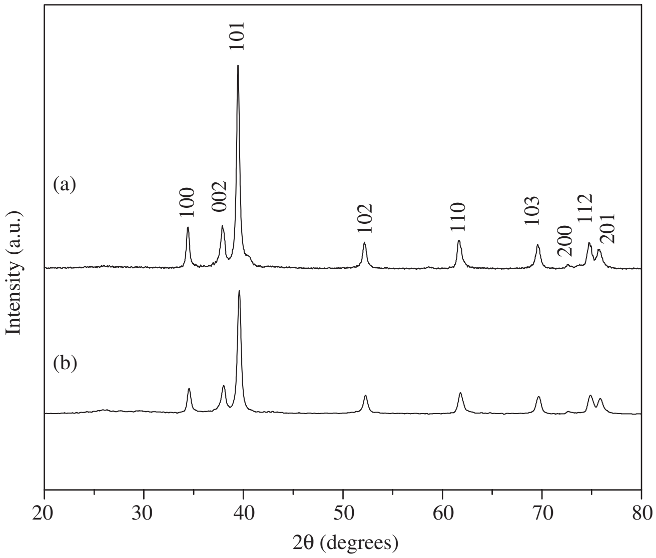

Fig. 1. XRD patterns of the prepared samples. (a) Sample A: prepared with graphite as C source at 500 °C, 12 h; (b) sample B: prepared with carbon nanotube as C source at 500 °C, 12 h.

3. Results and discussion

The phase purity of the sample was studied with the help of XRD. Fig. 1 shows the XRD patterns of the prepared samples. Fig. 1(a) is the XRD pattern of sample A prepared at 500 °C for 12 h, with graphite as C source. All the peaks can be indexed as hexagonal Mo_2C. After refinement, the lattice constants, $a = 3.01$ Å, $c = 4.74$ Å, are very close to the reported values for Mo_2C ($a = 3.00$ Å, $c = 4.73$ Å, ICDD card, No.01-1188). Fig. 1(b) is the XRD pattern of sample B prepared at 500 °C for 12 h, with carbon nanotubes as C source. Similarly, all the peaks can be indexed as hexagonal crystalline Mo_2C. It can be seen from the two XRD patterns that the diffraction peaks for sample B are broader than those for sample A. This

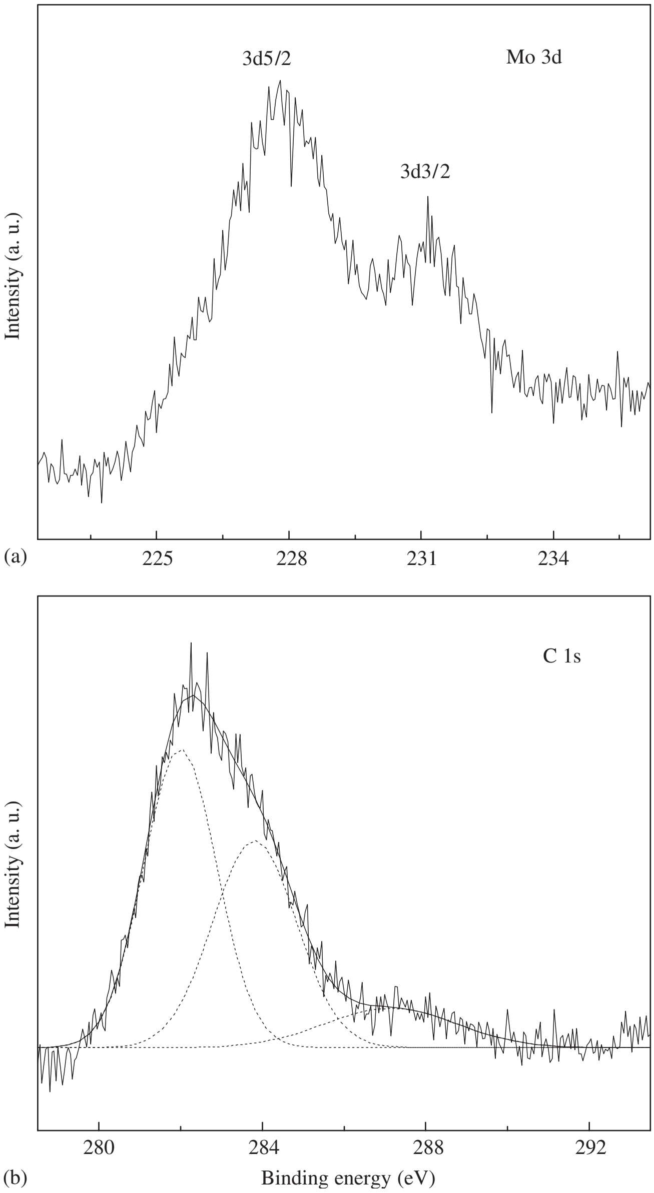

Fig. 2. XPS spectra of the Mo_2C sample (sample A). (a) Mo $3d$ region; (b) C $1s$ region.

indicates that the average crystallite size of sample B is smaller than that of sample A.

The composition information of the Mo_2C sample (sample A) was obtained from the XPS. The Mo 3*d* and C 1 s core-level regions were examined, as shown in Fig. 2. The binding energy of Mo 3*d* 5/2 is observed at 227.8 eV. The major signal of the C 1*s* is found at 281.9 eV. The binding energies for Mo 3*d* and C 1*s* are consistent with the reported value for Mo_2C [13]. Other two C 1*s* peaks at 284.4 eV and 287.2 eV are also found, which may be attributed to a small amount of residual carbon and absorbed CO_2 on the powder surface, respectively. The quantification of the peak intensities reveals that the atomic ratio of Mo to C is 2.02:1.0, which closely agrees with the stoichiometric composition of Mo_2C.

The yield of Mo_2C was approximately 83.6% due to the loss in the process of washing and filtering.

Fig. 3 shows TEM morphologies of the products and the carbon reagents. Fig. 3(a) is the TEM images of sample A prepared at 500 °C for 12 h, with graphite (micro-sized plate-like particles) as C source. It indicates that the obtained Mo_2C crystallites are particles with grain sizes ranging from 30 to 100 nm. The inset of Fig. 3(a) is the SAED pattern of the corresponding Mo_2C sample, which is consistent with the high crystallinity of the sample. Fig. 3(b) is the TEM images of sample B prepared at 500 °C for 12 h, with carbon nanotubes as C source. Under the reaction conditions, the one-dimensional structure of the carbon nanotubes was destroyed into many small sections and converted into Mo_2C particles with grain sizes ranging from 20 to 50 nm, which are similar to the diameters of the carbon nanotubes. Fig. 3(c) is the TEM images of the reagent carbon nanotubes. As it can be seen, the carbon nanotubes have outside diameters of 20–50 nm and length of several micrometers.

Surface areas of the samples were measured by BET method. For sample B, the BET surface area is 23.458 m^2/g, which is similar to the surface areas reported elsewhere for nanocrystalline hexagonal Mo_2C [14]. However, for sample A, its BET surface area is only 2.311 m^2/g, which is an order of magnitude lower than that of sample B. For the two samples, the magnitudes of the surface area are consistent with their grain sizes observed by TEM.

The above measurements show that the carbon source used for the carbide synthesis has a great effect on the particle size and the surface area of the samples. Owing to the templating role of their nanosize and well-dispersed distribution (see Fig. 3(c)), carbon nanotubes have advantage over the micro-sized graphite powders for preparing Mo_2C products with smaller particles and larger surface areas.

As to the reaction mechanism, we consider that the formation of Mo_2C might be based on the reaction of Mo and C. In the reaction process, with the temperature increasing, $MoCl_5$ was reduced by Na to produce Mo, which has been confirmed by the XRD analysis (omitted here, see Supporting Information). The newly formed Mo particles were so active that they could react directly with C (graphite or carbon nanotube) to form Mo_2C at the reaction temperature. The possible formation process of Mo_2C can be expressed by the following equations:

$$MoCl_5 + 5Na \rightarrow Mo + 5NaCl,$$

$$2Mo + C \rightarrow Mo_2C.$$

According to free energy calculations, the present synthetic route is thermodynamically spontaneous and highly exothermic. During the reaction process, a great amount of heat was generated and resulted in a high local temperature, which favored the crystallization of Mo_2C.

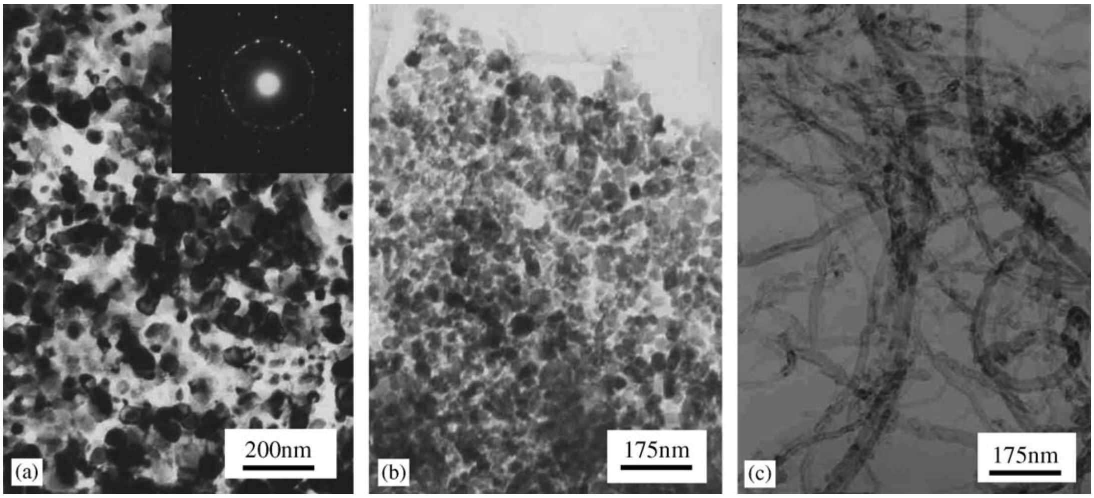

Fig. 3. TEM images of the samples. (a) TEM image of sample A: prepared with graphite as C source at 500 °C, 12 h, inset: the corresponding SAED pattern of the Mo_2C sample; (b) TEM image of sample B: prepared with carbon nanotubes as C source at 500 °C, 12 h; (c) TEM image of the carbon nanotubes used as C source.

Meanwhile, the vaporization of $MoCl_5$ (bp = 268 °C) during the reaction process could bring about high pressure in the autoclave. Based on the ideal gas law, the pressure in the autoclave could be as high as 2.9 MPa, which was also beneficial to the formation of crystalline Mo_2C. On the other hand, the excessive metallic Na (mp = 97.8 °C) existing in liquid in the autoclave helped the crystallization of the Mo_2C because it could provide better diffusion and mixing for the solid reactants Mo and C.

4. Conclusion

In summary, Mo_2C nanocrystals were successfully synthesized at 500 °C. Nanocrystalline Mo_2C powder with grain sizes from 30 to 100 nm was obtained when graphite was used as C source. While carbon nanotubes were used as C source, the as-synthesized Mo_2C sample consists of particles of 20–50 nm. This simple approach can be extended to the synthesis of other transition metal carbides and ZrC nanocrystals have also been prepared.

Acknowledgments

We would thank Prof. Z.L. Yu of the Institute of Chengdu Organic Chemistry of Chinese Academy of Sciences for providing the carbon nanotubes. This work was supported by the Key Project of National Fundamental Research and the National Natural Science Foundation of China.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2004.08.007.

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