Facile Synthesis of Mo$_2$C Nanoparticles from Waste Polyvinyl Chloride

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ABSTRACT: The resource utilization of waste plastic can not only control environmental pollution but can also ease up the problems of lack of energy resources. In this study, molybdenum carbide (Mo$_2$C) nanoparticles have been synthesized by utilizing waste polyvinyl chloride as a carbon source in a stainless-steel autoclave at 600 °C. X-ray diffraction pattern indicates that the product is orthorhombic phase Mo$_2$C. Electron microscopy photographs show that the obtained Mo$_2$C product consisted of crystalline nanoparticles with an average size of 50 nm. The possible formation mechanisms of Mo$_2$C have been also briefly discussed on the basis of the structures of the products synthesized with different reaction times. The effects of reaction temperature on the crystallinity and microstructure of the obtained products have been investigated. The results show that higher reaction temperature promotes the formation of Mo$_2$C with high crystallinity.

1. INTRODUCTION

Molybdenum carbide is an important ceramic material because of its unique properties, such as high melting point (2770 K), extreme hardness, and high chemical stability.1–4 Moreover, molybdenum carbide exhibits excellent catalytic properties on ammonia synthesis, H$_2$ production, and alcohol synthesis.5

Up to now, several methods have been developed to synthesize molybdenum carbides, such as direct pyrolysis of molybdenum hexacarbonyl,6 molten salt method,7 electrochemical method,8 solution route,9 carbothermal reduction of molybdenum oxide with carbon at high temperature,10,11 chemical vapor deposition (CVD),12–14 solid-state metathesis,15 thermal reduction of molybdenum chloride and carbon (graphite or carbon nanotube) with metallic sodium,16 and co-reduction of carbon tetrabromide and molybdenum pentachloride with metallic sodium in benzene.17 Mo$_2$C nanoparticle-decorated graphitic carbon sheets have been synthesized via a solid-state reaction of (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O and sodium alginate under Ar at 900 °C.18 Recently, Geng and co-workers have synthesized Mo$_2$C/graphene heterostructures by molten copper-catalyzed CVD.19

Polyvinyl chloride (PVC) materials have been widely used in the daily life because of their excellent properties such as transparency, chemical stability, and low density.20 However, the waste PVC in the environment generates a toxic compound dioxin which is very harmful to humans and animals.21 Developing an effective method of waste PVC disposal can help to reduce the dioxin emissions, which is good for environment protection. Up to now, many treatment methods for waste plastic have been reported.22–35 Zhang and his co-workers have synthesized carbon-based materials by utilizing waste plastic as a carbon source.28–33 We have developed a method to synthesize silicon carbide and transition-metal carbides from waste plastic.34–36 In this study, we have reported a facile method for synthesizing Mo$_2$C nanoparticles through the reactions between metallic sodium, molybdenum sulfide, and waste PVC at relatively low temperature. This work is aimed not only to develop a simple method to synthesize molybdenum carbide but also to explore an effective method of waste PVC disposal.

2. RESULTS AND DISCUSSION

The crystal structures of the obtained products are investigated by X-ray diffraction (XRD). A typical XRD pattern of the obtained product via our designed route is shown in Figure 1. All the peaks in the Figure 1 can be indexed to orthorhombic
phase molybdenum carbide (Mo$_2$C). The calculated lattice parameters $a = 4.7311$ Å, $b = 6.0258$ Å, and $c = 5.2105$ Å are almost consistent with the reported data (JCPDS no. 79-0744, $a = 4.7350$ Å, $b = 6.0250$ Å, and $c = 5.2100$ Å). No other diffraction peaks of byproducts such as MoS$_2$ and metallic Mo are found in the XRD pattern, which indicates that the conversion of waste PVC to molybdenum carbide has been completed via our designed route.

The field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the obtained Mo$_2$C product are shown in Figure 2a,b, respectively. It can be seen that the Mo$_2$C nanoparticles are agglomerated in the obtained product. The average size of Mo$_2$C nanoparticles is about 50 nm. A high-resolution TEM (HRTEM) image of the obtained Mo$_2$C product is presented in Figure 2c. The neighbor lattice interplanar spacing is about 0.24 nm, which is very close to the distance between two (200) planes in orthorhombic phase Mo$_2$C. A typical energy-dispersive X-ray (EDX) spectrum is shown in Figure 2d, which displays that the obtained product consists of Mo and C.

Magnetization on the obtained Mo$_2$C product is investigated with a superconducting quantum interference device (SQUID) at 10 Oe. Zero field cooling (ZFC) and field cooling (FC) temperature dependencies of magnetization $M$ for the obtained Mo$_2$C product are present in Figure 3. From Figure 3, the diamagnetism has been observed under the ZFC and FC conditions. The onset of the strong Meissner effect at about 9.80 K has been observed, which indicates the existence of superconductivity in the Mo$_2$C product. The observation is almost consistent with the results of the previous reported work.$^{37}$

The effect of reaction time on the formation of Mo$_2$C nanoparticles has been investigated. Figure 4a shows the XRD pattern of the product obtained from the reaction of molybdenum sulfide, metallic sodium, and waste PVC at 600 °C for 10 min. The diffraction peaks labeled as “●” in Figure 4a can be indexed as hexagonal phase MoS$_2$ (JCPDS card no. 87-2416), and the other three diffraction peaks labeled as “▼” can be indexed as cubic metallic molybdenum (JCPDS card no. 89-4896). From the XRD result, we found that the product (obtained from the reaction for 10 min) is the mixture of MoS$_2$ and metallic molybdenum, which proves that part of the raw material (MoS$_2$) has been reduced to metallic molybdenum by metallic sodium. The reaction of reducing MoS$_2$ can be expressed as eq 1

$$\text{MoS}_2 + 4\text{Na} \rightarrow 2\text{Na}_2\text{S} + \text{Mo}$$  

(eq 1)

According to the calculations of free energy, the reaction 1 at 600 °C is highly exothermic ($\Delta H_m = -454.3$ kJ/mol) and thermodynamically spontaneous ($\Delta G_m = -384.5$ kJ/mol). Meanwhile, waste PVC could be reduced by metallic sodium to activated carbon, which can be expressed as follows

$$2/3[\text{C}_2\text{H}_4\text{Cl}]_n + 2\text{Na} \rightarrow 2\text{NaCl} + 4\text{C} + 3\text{H}_2$$  

(eq 2)

The diffraction peaks of carbon cannot be detected in the XRD pattern (Figure 4a), probably because the carbon is amorphous. Because of the poor thermal stability of PVC, the waste PVC has been reduced to produce carbon in this process.

Figure 4b,c shows the XRD patterns of the products obtained from the reaction of molybdenum sulfide, metallic sodium, and waste PVC at 600 °C for 30 and 60 min. The three diffraction peaks labeled as “▼” in Figure 4b,c can be indexed as cubic metallic molybdenum (JCPDS card no. 89-4896), and the other diffraction peaks labeled as “★” can be indexed as orthorhombic phase Mo$_2$C (JCPDS card no. 79-0744). The results of XRD analysis show that MoS$_2$ has been...
completely reduced to metallic molybdenum by metallic sodium. Meanwhile, part of the newly formed molybdenum has reacted with the newly formed carbon (produced from Na thermal reduction of waste PVC) to produce Mo$_2$C, which can be expressed as

$$2\text{Mo} + \text{C} \rightarrow \text{Mo}_2\text{C} \tag{3}$$

Figure 4d shows the XRD pattern of the obtained product from the reaction of molybdenum sulfide, metallic sodium, and waste PVC at 600 °C for 5 h. All the diffraction peaks in Figure 4d can be indexed as orthorhombic phase Mo$_2$C (JCPDS card no. 79-0744), which reveals that the MoS$_2$ can completely convert into Mo$_2$C under the present experimental conditions for 5 h.

On the basis of the abovementioned experimental results, the chemical reaction of synthesizing Mo$_2$C nanoparticles can be represented as follows

$$34\text{Na} + 8\text{MoS}_2 + 2/n\text{[C}_2\text{H}_4\text{Cl}]_n \rightarrow 4\text{Mo}_2\text{C} + 16\text{Na}_2\text{S} + 2\text{NaCl} + 3\text{H}_2 \tag{4}$$

Because the $\Delta H_m$ values of Na$_2$S ($-364.8$ kJ/mol) and NaCl ($-411.2$ kJ/mol) are much negative, a large amount of heat generated in the process may promote the formation of Mo$_2$C. Besides, the excess metallic sodium could melt (melting point of sodium is 97.8 °C) at the reaction temperature, providing liquid medium for the formation of Mo$_2$C.

Moreover, the effect of the reaction temperature on the formation of Mo$_2$C nanoparticles has been investigated. The reaction temperature is a key factor in the formation of Mo$_2$C. When the temperature is 550 °C, the main product is Mo$_2$C with poor crystallinity (Figure 5a). When the temperature is below 500 °C, the product is amorphous (Figure 5b). Therefore, the optimum temperature for synthesis of Mo$_2$C is about 600 °C.

3. CONCLUSIONS

In this article, Mo$_2$C nanoparticles have been prepared by using waste PVC as a carbon source at 600 °C in an autoclave.
The effect of reaction temperature on the crystallinity of the obtained product has been studied. This synthetic method may be hopefully used to synthesize other transition-metal carbides at low temperature.

4. EXPERIMENTAL SECTION

4.1. Chemicals. Waste PVC used in the experiment was collected from waste PVC hose and cut into foils. Molybdenum sulfide and metallic sodium were purchased from Shanghai Chemical Reagents Company without further purification.

4.2. Preparation of Molybdenum Carbide. Typically, molybdenum sulfide (0.32 g), waste PVC (0.10 g), and metallic Na (1.80 g) were put into a stainless-steel autoclave of 20 mL capacity. After the autoclave was sealed and put into an electronic furnace, the electronic furnace was heated from room temperature to 600 °C with a heating rate of 10 °C/min and kept at 600 °C for 10 h, and then cooled to room temperature naturally. The product collected from the autoclave was washed with dilute HCl (1.0 mol/L), distilled water, and alcohol to remove the byproducts. Finally, the obtained product was dried under vacuum at 60 °C for 5 h.

4.3. Characterization. The obtained products were investigated by XRD (Philips XPert diffractometer with Cu Kα radiation λ = 1.54178 Å), FESEM (JEOL-JSM-6700F), and HRTEM (JEOL-2010, 200 kV). The magnetization measurement was investigated by using a SQUID magnetometer (MPMS, Quantum Design) in the temperature range of 3−25 K with an applied field of H = 10 Oe.

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Notes
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