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Synthesis of transition metal carbide nanoparticles through melamine and metal oxides

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Abstract

By a facile reaction route, we synthesized five technologically important transition metal carbide nanoparticles including cubic NbC, TaC, VC, hexagonal WC and MoC at relatively low temperatures. Here, in this rapid reaction process, we choose an organic reagent melamine and transition metal oxides as reaction precursors. The experimental results indicate that melamine is a highly efficient carburization reagent, and the metal oxides are completely converted into the corresponding carbides at relatively low temperatures. It is found that NbC, TaC, VC and WC are composed of fine nanoparticles having average size of 7, 13, 5 and 18 nm with a fairly narrow size distribution, respectively. The potential reaction mechanism between melamine and transition metal oxides and some new characteristics involved in this route are presented and discussed.

Keywords: Transition metal carbides; Nanoparticles; Electron microscopy; X-ray methods; Carbides

1. Introduction

In the past decade, much effort has been devoted to the synthesis of carbides due to their fundamental and technological importance. Transition metal carbides are especially of interest because they have many superior properties such as high melting points, good thermal and catalytic behaviors, and excellent electronic characteristics.[1–3] NbC and TaC, for example, are excellent additives in the manufacturing of hard materials, and display excellent superconductivity.[4,5] VC is also an important dopant. It can markedly change the electrical conductivity of SiC single crystal.[6,7] WC is extremely refractory and possesses excellent catalytic properties similar to those of noble metal platinum.[8,9] Traditionally, transition metal carbides have been made by powder metallurgical techniques at elevated temperatures for extended time periods.[10] For example, industrial production of NbC and TaC is usually carried out by mixing oxide and carbon at temperatures over 1500 °C, and WC is commercially manufactured by reaction of elemental starting material at 2800 °C. These methods are high-energy processes, energy intensive and result in products with large micrometer size. The metal carbides with micrometer size are brittle and difficult to convert into fully dense solids with excellent fracture resistance for high stress and temperature applications.[4,11] As catalysts, these carbides also have lower performance due to their large particle size and low surface area. Therefore, it is desired to search for some new routes to prepare fine metal carbide nanoparticles to meet the demand of industrial applications.

Recently, a series of methods have been reported to obtain transition metal carbide nanoparticles. Gas–solid reactions,[12,13] gas-phase reactions,[14] electrochemical and sonochemical methods,[15,16] rapid metathesis reactions[17–21] and polymer derived ceramics approach[22–24] have been intensively investigated. However, the route to metal carbide nanoparticles through organic compounds and oxides has been rarely investigated. In this paper, we design a highly efficient and facile reaction route assisted by carbothermal reduction to prepare transition metal carbide nanoparticles. Here, we choose an organic reagent melamine ($C_3N_3(NH_2)_3$) as a precursor with another one being

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corresponding transition metal oxides. Melamine is an important starting material for several industrial applications, for example, the syntheses of melamine–formaldehyde resins and of fireproof materials.[25] Melamine is also widely used for architecture of supramolecular structures.[26] In our previous work,[27] we use melamine as nitridation reagent to prepare eight metal nitrides successfully. However, it is interesting to note that, at higher temperatures, melamine also is an efficient carburization reagent and some transition metal oxides are completely converted into the corresponding carbides. In particular, fine NbC, TaC, VC and WC nanoparticles with a narrow size distribution can be easily obtained by this facile reaction route.

2. Experimental procedure

All starting materials are of analytical pure grade and are purchased from commercial sources. In the typical synthesis, firstly, 8 mmol melamine ($C_3N_3(NH_2)_3$) and 2 mmol Nb_2O_5 were mixed together and then pressed to a pellet (here we use the excess of $C_3N_3(NH_2)_3$ to ensure the complete conversion of Nb_2O_5 to NbC). The pellet was put into a silica ampoule (out diameter, 15 mm; inner diameter, 12 mm). Secondly, the ampoule with the pellet was evacuated to 1×10^{-6} Pa and sealed at length of 10 cm. In succession, the ampoule was heated to 1100 °C at the rate of 5 °C min^{-1}. Then the whole system was kept at 1100 °C for half an hour. At last, the ampoule was cooled naturally to room temperature and black powder was found after cooling. The typical smell of ammonia was detected after opening the ampoule up. This phenomenon can be found in the syntheses of the following carbides. By similar methods, TaC, VC, WC and MoC can be also synthesized by the reaction of melamine and transition metal oxide Ta_2O_5, V_2O_5, WO_3 and MoO_3, respectively, at the moderate temperatures. The experimental conditions and the corresponding products are listed in Table. 1.

X-ray powder diffraction (XRD) analysis was conducted on a PaNalytical X'Pert Pro MPD X-ray diffractometer with 2θ ranging from 10° to 90°, using graphic monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). The morphology and chemical composition of the products were characterized using a Hitach (Tokyo, Japan) S-4200 field-emission scanning electron microscope (FE-SEM) equipped with energy-dispersive

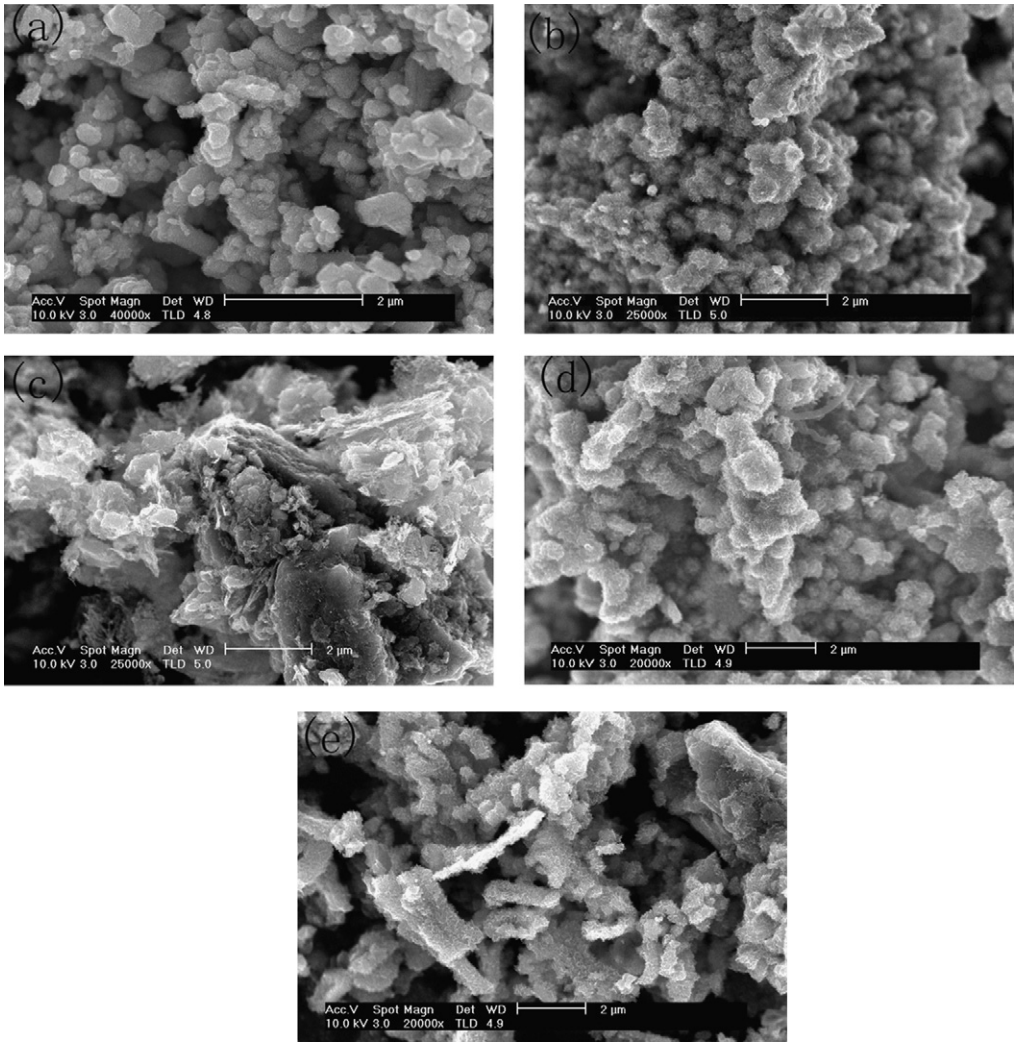

Fig. 1. SEM micrographs of the obtained transition metal carbides: (a) NbC; (b) TaC; (c) VC; (d) WC; (e) MoC.