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Preparation of monodispersed microporous SiO_2 microspheres with high specific surface area using dodecylamine as a hydrolysis catalyst

Jiaguo Yu*, Li Zhao, Bei Cheng

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Luoshi road 122#, Wuhan 430070, PR China

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Abstract

A novel and simple method for the synthesis of monodispersed microporous SiO_2 microspheres with high specific surface area was developed by hydrolysis of tetraethoxysilane (TEOS) in a water–ethanol mixed solution and using dodecylamine (DDA) as hydrolysis catalyst and template. The as-prepared products were characterized with differential thermal analysis–thermogravimetry, scanning electron microscopy, high-resolution transmission electron microscopy, small angle X-ray diffraction and nitrogen adsorption. The effects of experimental conditions including hydrolysis temperatures, calcination temperature and concentrations of TEOS and DDA on the morphology and pore parameters of the as-prepared SiO_2 microspheres were investigated and discussed. The results showed that hydrolysis temperature and concentrations of TEOS and DDA are important parameters for the control of size and morphology of particles. The specific surface area and specific pore volume of the as-prepared SiO_2 microspheres increased with increasing DDA concentration and calcination temperature. DDA may act not only as a good hydrolysis catalyst but also as a template for the formation of monodispersed SiO_2 microspheres with high specific surface area. This research may provide new insight into the synthesis of monodispersed microporous SiO_2 microspheres.

Keywords: SiO_2 microspheres; Microporous; Monodispersed; TEOS; Dodecylamine

1. Introduction

The preparation and characterization of oxide particles with a specific size and morphology are of primary importance for the development of advanced functional materials [1–4]. Micrometer spheres of ceramic materials are of particular interest for fundamental research in order to explain physical properties or surface interactions quantitatively [5]. Especially, monodispersed SiO_2 microspheres have received much attention owing to its wide application potential, not only in the field of physical chemistry but also in such industries involving catalysts, chromatography, ceramics, pigment, photographic emulsion, etc. [6–9]. Therefore, a great deal of effort has been devoted in recent years to obtain porous SiO_2 spheres with defined size and pore structure [10–15].

Micrometer-sized SiO_2 microspheres have been synthesized by many experimental methods such as spray gelling, coacervation process, sol–gel and hydrolyzing silicon esters in an emulsion system [16,17]. However, the tailoring of the pore size, pore volume and surface texture of the silica spheres prepared by these methods remain questionable. So the synthesis of porous SiO_2 microspheres in the presence of organic templates and/or additives has been intensively investigated in recent years. For example, Vacassy et al. [18] used 3-aminopropyltriethoxy-silane and glycerol as templates to prepare microporous SiO_2 spheres. Qi [19] used double-hydrophilic block copolymers (PEO-b-PMMA) as template under strong acidic conditions to form microporous SiO_2 spheres. Ma et al. [20] used a triblock copolymer $EO_{20}PO_{70}EO_{20}$ as template in combination with a co-surfactant CTAB to prepare SiO_2 microspheres via a two-step synthesis process. Yano and Fukushima [21] discovered that microporous SiO_2 spheres were prepared using CTAB as template under basic

*Corresponding author. Fax: +86 27 8788 2395.
E-mail address: jiaguoyu@yahoo.com (J. Yu).

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condition. Although a variety of porous SiO_2 spherical particles have been synthesized so far, almost all the SiO_2 spheres have been obtained by using a triphasic system of a quaternary ammonium surfactant with an additional auxiliary organic solvent and co-surfactant.

1-alkylamines as templates for the preparation of porous materials were first reported by Pinnavaia and co-workers [22–24] in 1994. Recently, some researchers used 1-alkylamines as templates to synthesize microporous or mesoporous silica materials [25–27]. However, the effects of experimental conditions on the morphology and pore parameters of the prepared SiO_2 microspheres using dodecylamine (DDA) as hydrolysis catalyst and template have not been clear. In this work, monodispersed microporous SiO_2 microspheres have been successfully prepared by the hydrolysis and condensation of tetraethoxysilane (TEOS) in a water–ethanol mixed solution and using DDA as hydrolysis catalyst and template. Accordingly, the effects of experimental conditions including concentrations of TEOS and DDA, temperatures of hydrolysis and calcination on the resulting particle size, morphology and pore parameters were investigated and discussed.

2. Experimental and characterization

2.1. Experimental procedure

TEOS, DDA and ethanol were purchased from Shanghai Chemical Reagent Factory and were analytical reagent grade. Distilled water was used as the water source in all cases.

In a typical procedure, DDA was dissolved in a mixed solution of ethanol (0.16 L) and distilled water (0.1 L). Then TEOS was added dropwise to the above solution at different temperatures under magnetic stirring. After the addition of TEOS, the clear solution gradually turned opaque owing to the formation of a white precipitate. After continuous stirring for 4 h, the white precipitate was filtrated. The products were repeatedly washed with water and ethanol for four times, then dried in a vacuum oven at 80 °C for 4 h, finally calcined at 200, 400 and 600 °C for 4 h in a muffle furnace to remove the templates, respectively. In the experiments, the concentration of TEOS was varied from 0.11 to 0.25 mol L^{-1}, the concentration of DDA was varied from 0.016 to 0.030 mol L^{-1}, the temperature of the solution was varied from 5 to 35 °C, and the calcination temperatures were kept at 80, 200, 400 and 600 °C for 4 h, respectively.

2.2. Characterization

The as-prepared SiO_2 microspheres were characterized by scanning electron microscopy (SEM) (type JSM-5610LV) with an accelerating voltage of 20 kV. Differential thermal analysis (DTA) and thermogravimetric (TG) were performed with a Netzsch STA 449C thermal analyzer in an air flow of 100 mL min^{-1} at a heating rate of 10 °C min^{-1} from room temperature to 600 °C. The high-resolution transmission electron microscopy (HRTEM) was carried out with a Philips TECNAL-10 at 100 kV. The small angle X-ray diffraction (XRD) pattern was obtained on an HZG41B-PC X-ray diffractometer using Cu $K\alpha$ radiation with a 2θ range of 1–5°. The Brunauer–Emmett–Teller (BET) specific surface area (S_{BET}) and pore parameters of the SiO_2 products were analyzed by nitrogen adsorption–desorption isotherm measurements on an AUTOSORB-1 (Quantachrome Instruments, USA) nitrogen adsorption apparatus. For the samples obtained at 80 °C, the samples were degassed at 70 °C prior to actual measurements. However, for the samples calcined at high temperatures (from 200 to 600 °C), the degassing temperature was 180 °C. The BET specific surface area was determined by the multipoint BET method using the adsorption data in the relative pressure (p/p_0) range of 0.05–0.25. The desorption branch of the nitrogen isotherm was used to determine the micropore size distribution using the Horvath–Kawazoe (HK) method [28]. The porosity was calculated according to the following equations (the skeleton specific volume of SiO_2 is taken as 0.37 $cm^3 g^{-1}$) [29]:

$$P = V_p/(V_p + 0.37), \quad (1)$$

$$V_p = 1.547 \times 10^{-3} V_d, \quad (2)$$

where V_p is the volume of the liquidated nitrogen corresponding to the total pore volume, which was calculated from the saturation adsorption volume at STP, V_d.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows DTA/TG curves of the SiO_2 microspheres obtained at 15 °C under the standard synthesis conditions

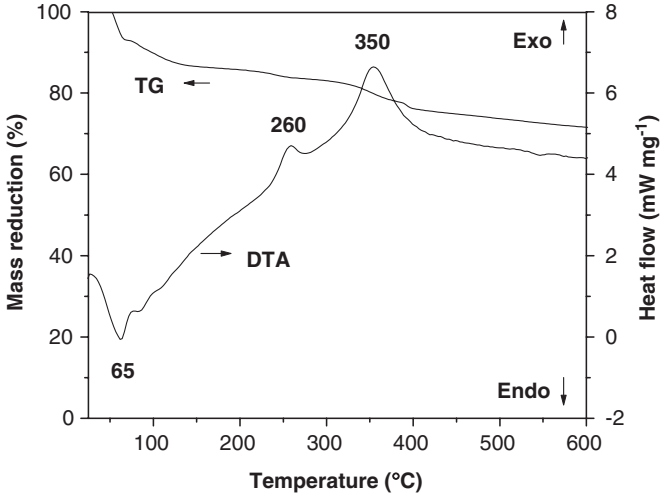

Fig. 1. DTA/TG curves of SiO_2 microspheres obtained at 15 °C and dried at 80 °C for 4 h. [DDA] = 0.024 mol L^{-1} and [TEOS] = 0.18 mol L^{-1}.