Influence of template on synthesis and characterization of novel mesoporous silica nanosphere

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A new method is reported for the synthesis of mesoporous silica nanosphere using ultrasonic method. Characterization reveals that the material is mesoporous with a small particle size. The template method gives spherical samples; uniform particle size is obtained when $n$-octylamine is used. Three stage weight loss occurs in cetyltrimethylammonium bromide samples, while the other templates show two stage weight loss. Amorphous and mesoporous silica samples have identical infrared spectra. The as-synthesized sample shows type II nitrogen adsorption curve, while the calcined samples show type IV adsorption curves.

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The development of nano mesoporous materials has opened up a new area of application in the field of capsule agents for drug delivery, catalysis, coatings, composite materials and protecting sensitive agents such as enzymes and proteins. There are several procedures reported for its synthesis using templates like latex, silica or gold colloidal particles to vesicles. The occluded template is subsequently removed by hydrofluoric acid itching or by burning in a furnace. In principle, these have been synthesized by the layer-by-layer adsorption method. Recently, ultrasound has been reported to be effective in generating a vesicular hierarchical structure and in rapid synthesis of mesoporous silica vesicles. It has also been proposed that the ultrasound-generated high temperature near the liquid-air interface accelerates the polymerization of the inorganic moieties attached to the micelles resulting in a shorter preparation time.

Synthesis of silica mesoporous molecular sieves is of interest to catalysis researchers as it has a large surface area and a wide variety of morphology. Since problems associated with its synthesis is due to the higher particle size, efforts have been made to reduce the particle size. Herein we report the synthesis of a nanocrystalline mesoporous molecular sieve by applying ultrasonic on different templates.

Experimental

The surfactants, sodium dodecyl sulfate (99%, Aldrich, USA), cetyltrimethylammonium bromide (99%, Aldrich, USA), tetrapropylammonium bromide (99%, Aldrich, USA), $n$-octylamine (99%, Aldrich, USA), and tetraethylorthosilicate (98%, Acros organics, USA) were used as such without further purification. Sodium dodecyl sulfate (9 ml, 1 wt %) solution was sonicated (JAC ultrasonic –1505 KODO, South Korea, Sonic: high, Set temp.: 25°C) for 8 min. The amine (0.15 g ) was mixed to the above solution and further sonicated for another 20 min. and then 1.5 ml of tetraethyl orthosilicate was added. The resulting mixture was sonicated for another 5 min. The final gel was charged into a Teflon lined stainless steel autoclave heated in an oven at 200°C for 24 h.

X-ray diffraction analysis was carried out using Mac Science Co. Ltd., MO3XHF22 instrument in the 1-10° range. The particle size and shape were analyzed with a Topcon, SM-300 scanning electron microscope. The copper disc was pasted with carbon tape and the sample was dispersed over the tape. The disc was coated with gold in the ionization chamber. Simultaneous thermogravimetry/differential thermal analysis of the crystalline phases was performed on an automatic derivatograph (Setaram TG-DTA 92). All the samples synthesized in this study were analyzed by Fourier transform infrared spectroscopy (Nicolet 60SX). Nitrogen adsorption studies were carried out using Micromeritics Tristar surface area and Porosity analyzer.

Results and discussion

Figure 1 shows the small angle X-ray diffraction pattern of mesoporous silica nanosphere obtained with cetyltrimethylammonium bromide. The sample from $n$-octylamine is similar; however the tetrapropylammonium bromide sample did not show any peak in this region. The low angle peak indicates the mesoporosity of the samples. On calcination the peak position did not vary, although a small reduction in intensity occurs.

The scanning electron micrograph of cetyltrimethylammonium bromide templated sample shows (Fig. 2) the particles are in spherical shape with 200 to 500 nm particle size. Other template samples also show spherical morphology and only $n$-octylamine
template samples are having uniform size (figure is not given).

The thermogravimetry/differential thermal analysis of cetyltrimethylammonium bromide sample shows three stage exothermic losses (38 %), while the other templates show only two stages (Table 1). Also, weight loss is proportional to the template molecular weight.

Fourier transform infrared spectroscopic analysis of cetyltrimethylammonium bromide sample shows peaks around 1700 and 3430 cm⁻¹ corresponding to the carboxyl and hydroxyl groups respectively. The carboxyl peak appears due to the atmospheric carbon dioxide. The adsorption peak belonging to the Si-O stretching vibration of Si-OH bond appears at 960 cm⁻¹ (ref. 20). The weak peaks at 2855 and 2920 cm⁻¹ belong to the stretching vibrations of C-H bonds, which show that a few organic groups are adsorbed on the spheres. The strong peaks near 1100, 802 and 467 cm⁻¹ correspond to the Si-O-Si bond indicating that the condensation of silicon source. The spectra of all the studied samples are similar, indicating the similarity of mesoporous and amorphous silica spectra.

Nitrogen adsorption curves of as-synthesized cetyltrimethylammonium bromide sample shows it is of type II. However, the calcined shows type IV adsorption curves. This may be due to blocking of pores by templates in as-synthesized samples. The surface areas of as-synthesized samples are small, which however on calcination increases (Table 2). The sample synthesized from cetyltrimethylammonium bromide has higher surface properties.
Normally, tetraethylorthosilicate is not miscible with water, when we add surfactant which connects the organic and aqueous layer. The sample synthesized without surfactant and with template did not produce any solid product. The particle growth passes through three stages: nucleation, primary particle growth and secondary particle growth. In nucleation the isolated silicon monomer condenses to form small units, which further reacts to form small particles around the template in primary growth. These small particles later grow into big particle in the secondary growth phase. Normally, nucleation step take more time due to involvement of weak electrostatic forces. Here it is simplified due to application of ultrasonic wave. However the secondary particle growth takes more time due to involvement of gravitational force. The proposed synthesis has the following advantages: it uses a common surfactant and templates; it is not necessary to add co solvents, pH adjustment and stirring; silica spheres are stable even up to 550°C, and, nanosize mesoporous molecular sieve is obtained through a simple method.

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References