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Post-synthesis pore expansion of mesoporous silica SBA-15 in the organic template removal via solvothermal treatment

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Abstract The synthesis of mesoporous material SBA-15 has been extensively reported in the past decades, which possesses a pore diameter of 6–8 nm on average. Here, a simple post-synthesis procedure has been developed to synthesize SBA-15 with further expanded pore diameter to above 10 nm simply by a solvothermal treatment replacing traditional hydrothermal step for mesopore template removal, which results in efficient pore expansion and the significantly promoted condensation of silica framework as well. This facile approach is believed applicable for pore expansions of other kinds of mesoporous silica materials.

Keywords Solvothermal treatment · Template removal · Pore size expanding · Framework condensation · SBA-15

1 Introduction

Following the discovery of ordered mesoporous materials, more and more researchers have focused on the optimization of pore properties, which would provide great opportunities in the field of catalysis, separation and drug delivery [1–3]. In 1998, Zhao et al. [4] reported an important kind of mesoporous materials SBA-15 using Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) as the mesopore template under acid conditions for the first time. This kind of mesoporous silica is featured with much larger pore size of 6–8 nm on average than that of M41S family (2–3 nm). By changing the aging temperature or acid concentration of synthesis process, the physicochemical properties of SBA-15 could also be well tuned [5, 6].

Nevertheless, the mesopore size of 6–8 nm was still not large enough, which greatly hindered their applications, especially in the biomedicine for the encapsulation of biomacromolecules, such as proteins or DNA with high molecular weight. For synthesizing mesoporous silica with relatively large mesopores, many efforts had been made, and pore expansion is one of the most frequently used approaches. For example, choosing other kind of surfactants with larger sizes [4, 7] or introducing a swelling agent into the template [8, 9] has been the common practices on the enlargement of template micelles, which could result in the pore size expanding. Unfortunately, the correspondingly resultant mesostructure ordering, as well as the thermal stability, would be affected significantly. In addition, hydrothermal and alcothermal treatment have also been used to synthesize large-pore mesoporous materials [10, 11].

On the other hand, there have two general methods for organic template removal: calcination and solvent extraction [7, 12–14]. Besides, special approaches for template removal were also developed, such as microwave digestion, UV/ozone treatment, supercritical fluid extraction and liquid-phase calcination [15–18]. However, these methods suffer from the drawbacks of complexity and/or the need of necessary special equipment.

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In spite of all the above-mentioned efforts in removing the organic template, the pore diameter usually suffers from significant shrinkage by calcination or mostly remains unchanged during extraction. In this paper, we present the simultaneous pore expansion and complete template removal by solvothermal treatment of SBA-15 in a mixed solution for the first time. Importantly, it is different from the pore expansion by using large or enlarged micelles in most literatures that mesopores are effectively expanded beyond 10 nm in the post-synthesis template removal process, which benefits the further framework condensation, mesostructure stability enhancement and the retaining of surface Si–OH groups.

2 Experimental

2.1 Direct synthesis of pore-expanded SBA-15 with template removal

The preparation process of pore-expanded SBA-15 was similar to that of the conventional SBA-15 [4, 19], and the difference was that the hydrothermal treating step was replaced with a solvothermal treating process and that no calcination step was involved. The process was described as following. In a typical synthesis, 4.0 g triblock copolymer Pluronic P123 was dissolved in a mixture of 30 g water and 120 g of 2 mol/L HCl in a Teflon-lined autoclave, and the mixture was stirred at 35 °C overnight. Then, 8.50 g tetraethyl orthosilicate (TEOS) was added into the solution under vigorous stirring. After 5 min of stirring, the mixture was kept under static conditions at 35 °C for 20 h and the precursor for SBA-15 was obtained. The precursor for SBA-15 was filtered, then washed with water and dried for further solvothermal treating, which was named as SBA-15-pre-as. In the meantime, the organic solvent was prepared by mixing 0.22 g sodium sulfate, 12 mL deionized water, 25 mL glycol, 7 mL *n*-butyl alcohol and 0.83 g polyethylene glycol (PEG, molecular weight 6,000) in a 50-mL Teflon-lined autoclave. Finally, 0.4 g SBA-15-pre-as was immersed into the mixed solution and stirred well. After 24 h of heating at different temperatures, the samples were collected by filtration, then washed with water and ethanol, respectively, and dried. The samples were named as SBA-15-st-T, respectively, where T represents the related temperature.

For comparison, the SBA-15-pre-as was directly calcined at 550 °C in flowing air for 6 h at a heating rate of 1.5 °C/min, and the obtained material was named as SBA-15-pre-cal. Moreover, samples prepared via conventional synthetic process of hydrothermal treatment (100 °C for 24 h) and calcination (550 °C for 6 h) were named as SBA-15.

2.2 Characterization

Fourier translation infrared spectroscopy (FT-IR) was conducted on a Nicolet 5700 Thermo FT-IR spectrometer (USA) using the KBr wafer technique. Thermogravimetric analysis (TGA) curves were obtained on a thermogravimetry–differential thermal analysis (TG–DTA) instrument (Netzcsh STA 409 PC, Germany) at a heating rate of 10 °C/min under nitrogen atmosphere from room temperature to 550 °C. Powder X-ray diffraction (XRD) data were collected on Bruker D8 Focus diffractometer (Germany) equipped with Cu Kα radiation ($\lambda = 1.5405$ Å). XRD patterns were collected in the 2θ ranges between 0.6° and 6° with a speed of 0.6°/min. N_2 adsorption–desorption isotherms were measured at 77 K by using Quantachrome NOVA 4200e (USA). The Brunauer–Emmett–Teller (BET) method was utilized in the calculation of specific surface areas. The pore size distributions were derived from the adsorption branch of the isotherm by means of the Barrett–Joyner–Halenda (BJH) method. Field-emission scanning electron microscopy (FE-SEM) images were obtained by using a JEOL JSM-6700F field SEM (Japan). Transmission electron microscopy (TEM) observations were carried out on a JEOL-2100F electron microscope (Japan). Solid-state ^{29}Si nuclear magnetic resonance (NMR) spectra were performed on a Bruker Avance III 300 spectrometer (Germany), and each spectrum was recorded after 128 acquisitions with 120-s repetition time as a compromise between nuclear relaxation and kinetics of silica polymerization.

3 Results and discussion

3.1 Effects of solvothermal treatment on the mesostructure of SBA-15-st-T

Figure 1 shows the XRD patterns of the samples prepared under different conditions. As can be seen, all the samples, except for SBA-15-pre-cal, present three distinctive diffraction peaks in the small-angle region, which can be indexed as (100), (110) and (200), respectively, being attributed to the two-dimensional hexagonal (*p6mm*) mesostructure. This indicates that SBA-15-st-T samples possess similar mesostructures with the conventional SBA-15. Notably, it can be found that the (100) diffraction peaks of SBA-15-st-T samples shifted toward lower diffraction angles, suggesting that the larger cell parameters and mesopores of SBA-15-st-T are obtained. Besides, little difference has been found between the SBA-15-st-T samples,