



Salt-assisted synthesis of mesostructured cellular foams consisting of small primary particles with enhanced hydrothermal stability



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ABSTRACT

Mesoporous silica materials have attracted considerable attention as adsorbents, catalyst supports, and drug delivery carriers due to their large surface area, high pore volume, and controllable pore size. To increase the adsorption or mass transport properties, large pore sized mesoporous silica is highly desired. Here, we demonstrate a new green synthetic route for obtaining salt-assisted mesostructured cellular foams (S-MCFs) using a triblock copolymer as a single structure-directing agent by addition of inorganic salt without using a hydrophobic pore expander. The S-MCF was composed of ~27 nm cellular pores and 10 nm windows and had distinct pore walls and a cellular structure. S-MCFs showed an enhanced hydrothermal stability compared to other mesocellular silica. In addition, the primary particle size of the S-MCF was 100–300 nm, which is much smaller than that of previously reported mesostructured cellular foams (MCFs) and mesocellular silica foam (MSU-F). The adsorption study using a model protein revealed that small primary particle size in S-MCF is beneficial for mass transfer in a short period of time. Therefore, S-MCF may serve as a potential platform for higher mass transport or adsorption of large molecules with good stability.

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1. Introduction

Mesoporous silica molecular sieves have attracted considerable attention as adsorbents, catalyst supports, and drug delivery carriers due to their large surface area, high pore volume, and controllable pore size [1–6]. There are many parameters, such as concentration of reagents, temperature, and stirring rate, related to the control of morphology, pore size, and ordering of pore structures in the resulting mesoporous silica. One important parameter is the addition of inorganic salts during the synthesis of mesoporous silica. It has been reported that inorganic salts have a strong influence on the outcome of the soft-template based synthesis of mesoporous silica materials. Ryoo et al. showed that the hydrothermal stability of MCM-41 silica materials was improved by addition of various inorganic salts, presumably due to attenuation of the electrostatic interaction between the cationic surfactant and anionic silicates by the salts [7–9]. Zhao et al. reported that the addition of inorganic salts participates in lowering the local curvature energy, and this allows the formation

of mesoporous silica with different morphologies [10–13]. Yu et al. showed a remarkable extension of synthesis conditions using inorganic salts, demonstrating low temperature synthesis of ordered mesoporous silica [14]. Other reports presented the roles of inorganic salts on the growth of single-crystal-like mesoporous silica or control of mesostructural regularity [15–17].

Large pore sized mesoporous silica is highly desired to increase the adsorption of large biomolecules and mass transport in catalysis and enzyme reactions. Mesostructured cellular foams (MCF), one example of large pore sized mesoporous silica, consist of a 3-dimensional pore structure of large cells interconnected by narrower windows [18,19]. Due to their large pore size and three-dimensionally interconnected structure, these mesocellular silica have better mass transport properties compared to other mesoporous silica, allowing enhanced performance as a support for immobilized enzymes and as adsorbents [20–22]. In general, to synthesize MCF-type silica, a hydrophobic pore expander such as 1,3,5-trimethylbenzene (TMB) is incorporated into the hydrophobic cores of the micelles prior to the silica sol–gel reaction. Stucky and coworkers first reported the synthesis of MCF with pore sizes ranging from 20 to 30 nm under strongly acidic conditions using a triblock copolymer (P123) and tetraethylorthosilicate (TEOS) as an organic template and silica precursor, respectively, in the presence

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of TMB as a pore expander [18]. Pinnavaia and coworkers reported a similar structured mesocellular silica foam (MSU-F) with 22 nm cells using cheap sodium silicate as a silica precursor in the presence of TMB [19]. Recently, Kim and Hyeon et al. reported on the synthesis of a biomodal mesocellular mesoporous silica, which is denoted hierarchical mesocellular mesoporous silica (HMMS), composed of a mixed structure of cellular pores and one-dimensional pores using P123 as a single structure-directing agent and sodium silicate as a silica precursor [23,24].

Here, we demonstrate the synthesis of salt-assisted mesocellular silica foams (S-MCF) using P123 as soft templates by addition of inorganic salt without using a hydrophobic pore expander. The inorganic salt was added to the synthetic solution of HMMS, resulting in MCF-type large pore sized silica materials. S-MCF had distinct pore walls and cellular structures composed of ~27 nm cellular pores and 9–13 nm sized windows depending on the amount of the salts. The primary particle size of S-MCF was 100–300 nm, which is much smaller than that of MCF and MSU-F, demonstrating that S-MCF is likely to have potential for higher mass transport or adsorption of large molecules.

2. Experimental

2.1. Synthesis of S-MCF

S-MCF was synthesized using triblock copolymer Pluronic P123 (Aldrich) as a template, sodium silicate (Aldrich) as a silica precursor, and potassium chloride (KCl) as an inorganic additive. In a typical synthetic procedure, 5 g of P123 was dissolved in a mixture of 100 ml of water and 2.2 ml of acetic acid and 1, 3, 5, 10, 15, and 20 g of KCl until a homogenous solution was obtained. Then, the mixture solution was stirred at 60 °C for 1 h. The silica precursor solution, 8 ml of sodium silicate diluted with 100 ml of water, was added to the P123 solution under vigorous stirring; the temperature of resulting solution decreased from 60 °C to around 45 °C by the addition of silica precursor solution, and white precipitates were formed after a few minutes. During this process, the pH of the reaction mixture was 6.3–6.4. The solution was then heated to 60 °C and kept at that temperature for 20 h with stirring, followed by hydrothermal treatment at 100 °C for 24 h. The resulting white precipitate was collected by filtration, washed with excess water to remove the salt, and was dried overnight. As-synthesized S-MCF was calcined at 550 °C for 6 h to remove the P123 template. The resulting mesoporous silica materials were designated as S-MCF-*x*, where *x* represents the amount of KCl added in the synthesis. HMMS [23], MCF [18], and MSU-F [19] were prepared according to previous reports.

2.2. Characterization

Transmission electron microscope (TEM) images were obtained with a JEOL 2100 electron microscope operating at 200 kV. Prior to measurements, the material was supersonically dispersed in ethanol, and the suspended particulates were deposited onto a perforated carbon film supported on a copper grid. Nitrogen adsorption–desorption isotherms of mesoporous silica samples were measured on a Micromeritics ASAP 2000 apparatus at liquid nitrogen temperature (77 K). Pore size distribution was calculated from the adsorption branch of the isotherm using the Barret–Joyner–Hallenda (BJH) model. Scanning electron microscope (SEM) images were performed with a JEOL JSM-6700F. The samples were distributed on carbon tape attached on a sample mount. Before analysis, all samples were coated with a thin layer of Pt by sputter coating.

2.3. Hydrothermal stability test

For hydrothermal stability test, 0.3 g of MCF, HMMS and S-MCF-5 were each dispersed in 300 ml of distilled water. The mesoporous silica solutions were boiled for 2 days under reflux. Then, the precipitates were filtered and dried at 100 °C in air. The resulting white powders were analyzed with N₂ sorption and small-angle X-ray diffraction (XRD).

2.4. Bovine serum albumin (BSA) adsorption

For adsorption measurements, 5 mg of mesoporous silica (MCF, MSU-F, or S-MCF-5) were dispersed in PBS, and 3 or 5 mg of BSA dissolved in PBS were added followed by mixing with a vortex mixer. After that, the BSA/silica mixture solution was shaken at 150 rpm. At designated time points, the solution was centrifuged at 10,000 rpm for 1 min to precipitate the silica, and the supernatant was analyzed with UV–vis spectroscopy to measure the concentration of unadsorbed BSA. The adsorbed BSA was calculated by subtraction of unadsorbed BSA left in the supernatant from the initial BSA.

3. Results and discussion

3.1. Synthesis and characterization of S-MCF

The synthesis of S-MCF stems from a previous report on the synthesis of HMMS, a mesocellular silica foam with ordered mesoporous walls [23]. HMMS is prepared using an amphiphilic triblock copolymer, Pluronic P123, as a structure-directing agent. We evaluated the effect of inorganic salts on the synthetic procedure of HMMS. Interestingly, the addition of inorganic salts resulted in a dramatic change in pore structure in the resulting mesoporous silica. This synthetic method can be regarded as a green method to prepare mesostructured cellular foams due to its neutral synthetic conditions and lack of need for organic additives such as TMB.

First, to investigate the effect of added KCl in the synthesis of HMMS, 5 g of KCl was added to the P123 solution prior to addition of the sodium silicate solution. Fig. 1 shows the representative TEM images of HMMS (Fig. 1a) and S-MCF-5 (Fig. 1b and c), respectively. The TEM image of HMMS shows that HMMS is a bimodal mesoporous silica material composed of ~30 nm cellular pores and ~10 nm one-dimensional pores as reported [23]. However, the addition of KCl (5 g) resulted in a uniform, unimodal cellular pore of ~30 nm without the one-dimensional pores in S-MCF-5. The overall pore structure of S-MCF was very similar to the previously reported mesocellular-type mesoporous silica materials MCF [18] and MSU-F [19]. The pore structure was further characterized using small angle X-ray scattering (SAXS, Fig. 1d). HMMS showed broad peaks at $q \approx 0.2, 0.45, \text{ and } 0.9 \text{ nm}^{-1}$. Here, the first peak indicates the cellular pores around 31.4 nm, and the latter two peaks reflect the hexagonal (100) plane with a lattice parameter of 16.1 nm. In contrast, S-MCF-5 showed a prime peak at $q \approx 0.25 \text{ nm}^{-1}$ derived from uniform cellular pores around 30 nm. These observations indicate that the addition of KCl led to the loss of hexagonal ordering and the generation of disordered 30 nm-sized cellular pores.

Next, to clarify the relationship between the amount of KCl and the pore structure, the amount of KCl added to the P123 solution was varied, i.e., 1, 3, 5, 10, 15 or 20 g, which corresponds to weight ratios to P123 of 0.2, 0.6, 1, 2, 3, and 4, respectively. The pore structure change upon increasing KCl was characterized using TEM (Fig. 2). S-MCF-1 clearly shows the disappearance of one-dimensional pores in the TEM image (Fig. 2a). The uniform cellular pores of ~30 nm were well-maintained in S-MCF-3, -5, and

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