Hydrothermal Restructuring of the Cell and Window Sizes of Silica Foams

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Mesostructured molecular sieve silicas with uniform and well-defined pores have been recognized as promising materials for use in molecular separations,[1] metal ion trapping,[2] controlled drug release,[3] low dielectric films,[4] among other applications. Many strategies are being explored for controlling the size,[5] shape,[6] and connectivity of the pore systems in these materials[7] and optimizing the performance properties. Most notably, Stucky and co-workers recently achieved the assembly of mesostructured cellular foams of silica (denoted MCF silicas) with cell dimensions in the range of 24−44 nm and pore volumes of 1.0−2.4 cm^3/g, depending on the composition of the microemulsion template and the reaction conditions. These remarkable materials were obtained under strongly acidic hydrolysis conditions from tetraethyl orthosilicate (TEOS) as the silica precursor and an aqueous microemulsion of a triblock copolymer (e.g., Pluronic P123, $EO_{20}PO_{70}EO_{20}$) and 1,3,5-trimethylbenzene (TMB) as the porogen.[8] Analogous foam structures could also be formed using surfactant-coated polystyrene microspheres in place of the microemulsion.[5] In this approach based on functionalized microspheres as the porogen, open cell foams with window sizes of 7−19 nm and cell sizes of 32−86 nm were obtained under strongly acidic hydrolysis conditions, whereas under base-catalyzed conditions closed cell foams with window sizes (<5 nm) much smaller than the cell size (25−57 nm) were obtained. The ability to control the window to cell size of mesostructured silica foams could be advantageous for various materials applications. However, a synthesis strategy based on the one-time use of surfactant-functionalized polystyrene microspheres and cost-intensive TEOS presents certain processing disadvantages.

It has been shown more recently that mesostructured silica foams, denoted MSU-F silica foams, can be prepared from low-cost triblock surfactant microemulsions and water-soluble silicate precursors under near-neutral pH conditions.[9] In the present report, we demonstrate that the cell and window diameters of these foams can be easily controlled through the use of a simple postsynthesis restructuring procedure. The hydrothermal restructuring process is convenient and efficient and allows the cell and window sizes of the foams to be mediated over the ranges 16−35 and 5−23 nm, respectively.

In a typical synthesis of MSU-F silicas 1.2 g of P123 (0.206 mmol) was stirred with 10 mL of 1.0 M acetic acid (10 mmol) and 10 mL of water for 2 h. 1,3,5-Trimethylbenzene (TMB, 1.0 g, 8.33 mmol) was added to the surfactant solution and the mixture was allowed to age under ambient conditions for an additional hour. This resulted in the formation of an oil-in-water emulsion of the P123 surfactant and TMB. To this microemulsion was added 2.7 g of sodium silicate solution (Aldrich) containing 27 wt % SiO_2 (12.1 mmol) and 14 wt % NaOH (9.45 mmol) in 30 mL of water. The reaction mixture was placed in a mechanical shaker bath at ambient temperature for 24 h to obtain the initial foam product. The reaction mixture was then heated under static reaction conditions at 100 °C for different time intervals to expand the cell and window size of the foam framework. The samples were filtered, dried, and calcined at 600 °C for 4 h to ensure complete removal of the surfactant.

Figure 1 provides the nitrogen isotherms for calcined MSU-F silica foams that have been assembled at room temperature and then subjected to postassembly hydrothermal treatment at 100 °C. The corresponding cell size distributions are illustrated in Figure 2. Table 1 reports the BET surface areas, pore volumes, and the cell and window sizes of the reaction products, as determined by applying the BdB−FHH[10] model to the adsorption and desorption isotherms, respectively.

The foam assembled under ambient reaction conditions without postsynthesis hydrothermal treatment exhibited a broad hysteresis in the nitrogen adsorption−desorption isotherms (Figure 1, curve a). This behavior is typical of a "closed cell" foam, wherein cells of diameter 16.3 nm are connected by comparatively narrow 5.6-nm windows. In addition to exhibiting an average cell to window size ratio of 2.91, this initial silica foam is characterized by a BET surface area of 743 $m^2\ g^{-1}$ and a mesopore volume of 1.02 $cm^3\ g^{-1}$.

Hydrothermal treatment of the as-made foam for a period of 1 h produced a product (denoted MSU-F-P1) that exhibits N_2 adsorption−desorption isotherms that are very similar in shape to those of the as-made sample (cf., curves a and b in Figure 1). This indicates that little or no change in cell or window size occurs after a 1-h hydrothermal treatment, as verified by the data in Table 1 (compare samples MSU-F-P0 and MSU-F-P1). However, the surface area is increased substantially by ≈125

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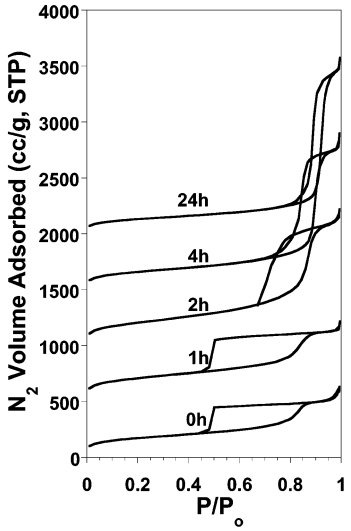

Figure 1. Nitrogen adsorption/desorption isotherms for calcined MSU-F silicas prepared through postsynthesis hydrothermal treatment of the as-made mesostructure for periods of 0−24 h at 100 °C.

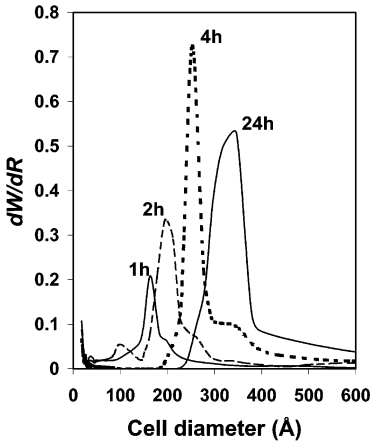

Figure 2. Cell size distributions for calcined MSU-F silicas prepared trough postsynthesis hydrothermal treatment of the as-made mesostructure for periods of 0−24 h at 100 °C. The cell sizes were determined by applying the BdB−FHH model to the adsorption isotherms shown in Figure 1.

Table 1. Textural Properties of MSU-F Silica Foams after Postsynthesis Hydrothermal Treatment for Different Time Periods[a]

sample	time (h)	cell size[b] (nm)	window size[b] (nm)	cell size/ window size	surface area (m^2/g)	pore volume (cm^3/g)
MSU-F-P0	0	16.3	5.6	2.91	608	1.02
MSU-F-P1	1	16.4	5.6	2.92	743	1.14
MSU-F-P2	2	19.5	9.1	2.14	745	1.91
MSU-F-P4	4	25.3	16.9	1.49	573	2.18
MSU-F-P8	8	28.1	20.5	1.37	492	2.33
MSU-F-P24	24	34.7	22.9	1.51	468	2.39

[a] Each sample was assembled at ambient temperature using a TMB/P123 mass ratio of 0.83 prior to hydrothermal treatment and subsequently calcined at 600 °C for 4 h to remove the surfactant and co-surfactant. [b] The cell and window sizes were determined using the modified BdB−FHH model.[10]

$m^2\ g^{-1}$, along with an increase in pore volume, after a 1-h postassembly hydrothermal treatment. This suggests that the foam framework is not fully formed under ambient conditions and that subsequent hydrothermal treatment facilitates framework ordering.

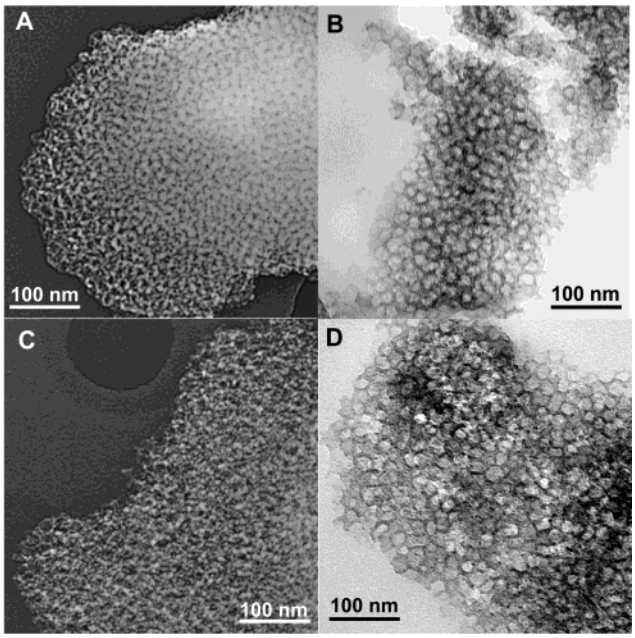

Figure 3. TEM images of calcined MSU-F silica foams. Images (A) and (B) are for whole particle and thin-sectioned samples, respectively, of the closed cell foam assembled at ambient temperature. Images (C) and (D) are whole particle and thin-sectioned samples, respectively, of the open cell structure obtained after 24 h of postassembly hydrothermal treatment at 100 °C.

Increasing the postsynthesis treatment time to 2 h shifts the step in the adsorption branch toward higher pressure and causes the hysteresis loop to become narrower (see curve c, Figure 1), signifying an increase in both the cell size and window size (cf., Table 1). At this point in the hydrothermal treatment the cell to window size ratio is 2.14, and the foam can still be classified as a "closed cell" structure. However, after 4 h of hydrothermal treatment the cells and windows grow even larger to values of 25.3 and 16.9 nm, respectively, and the cell to window ratio decreases to 1.49, which is consistent with an open cell foam structure. After 8 h of treatment still greater increases in cell and window sizes are realized, but after 24 h, the cell and window sizes approach near-equilibrium values of 34.7 and 22.9 nm, respectively, and a cell to window size ratio of 1.51. The surface areas decrease and the total pore volumes increase as the cell and window sizes become larger with increasing hydrothermal treatment, as expected. The observed behavior confirms that the cell size of MSU-F can be tailored through postassembly hydrothermal treatment and that closed cell foams can be readily transformed into open cell structures through this process.

Further evidence for mesostructured cellular foams of MSU-F silica is provided by the transmission electron micrographs in Figure 3. Images A and B for the closed cell product assembled at room temperature are typical of a mesostructured cellular foam structure. Images C and D for the product after being hydrothermally treated for 24 h are similar, except that the cell size is larger, in accordance with the nitrogen adsorption results.

Various hydrothermal treatment methods have been used previously to enlarge the pore sizes of mesostruc-

tured frameworks.[11−17] A postassembly hydrothermal treatment of hexagonal MCM-41 silicas, for example, is known to expand the pore size of the mesostructure.[11,12] Klinowski et al.[13] suggested that the swelling action of hexadecyldimethylamine (DMHA), generated in situ from the decomposition of the intercalated cetyltrimethylammonium ion surfactant, was responsible for pore size enlargement of MCM-41 at high temperatures. Also, Sayari and co-workers[14,15] have showed that DMHA forms during the hydrothermal restructuring of the MCM-41 framework in the mother liquor and acts as a cosurfactant in expanding the pore size.

The unique feature of the present work, however, is the exceptional degree to which the foam dimensions can be expanded *without* altering the composition of the porogen. The cell and window dimensions can be increased by as much as 18 nm. The pore expansion mechanism for MSU-F materials most likely involves a repartitioning of the intercalated P123 surfactant and TMB under hydrothermal conditions and the concomitant growth of the structure-directing microemulsion. It should be noted, however, that drastic decreases in surface area and pore volume occur for postsynthesis hydrothermal treatments longer than 48 h, indicating that the foam structure begins to disintegrate as the window size more nearly approximates the cell size.

In summary, the present work represents the first report of a postsynthesis restructuring process useful for expanding both the cell size and the window size of a foam structure. The observed framework expansion is unprecedented, with the cell and window dimensions being increased by as much as a factor of 2.1 and 4.1, respectively, while retaining the fundamental foam structure. Increases of ≈18 nm in cell and window sizes are possible over a hydrothermal treatment time of 24 h, indicating that the silica framework remains labile and responsive to the temperature dependence of the emulsion droplet size within the cells. This makes it especially convenient to transform a closed-cell foam into an open-cell structure.

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