

Mesocellular Siliceous Foams with Uniformly Sized Cells and Windows

Patrick Schmidt-Winkel,^{†,‡} Wayne W. Lukens, Jr.,[†]
Dongyuan Zhao,[†] Peidong Yang,[†] Bradley F. Chmelka,^{§,‡} and
Galen D. Stucky^{*,†,‡}

Department of Chemistry, Materials Research Laboratory
and Department of Chemical Engineering
University of California, Santa Barbara, California 93106

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Molecular sieves with uniform large pores are desirable for chemical reactions and for use in separations involving large molecules.¹ Periodic cubic and hexagonal mesoporous silica phases with uniform large pores have been synthesized by using nonionic triblock and star diblock copolymers as templates.² Control over the pore size is achieved by adjusting the hydrophobic volumes of the self-assembled aggregates.^{2,3} In this paper, we describe how adding a sufficiently large amount of an organic cosolvent induces a phase transformation from the highly ordered *p6mm* mesostructure of SBA-15-type mesoporous silicas to remarkable mesostructured cellular foams (mesocellular foams, MCFs) composed of uniformly sized, large spherical cells that are interconnected by uniform windows to create a continuous 3-D pore system. The interconnected nature of the large uniform pores makes these new mesostructured silicas promising candidates for supports for catalysts and in separations involving large molecules, and they may be of interest in low-dielectric applications.

The MCFs have been synthesized in aqueous acid by using dilute Pluronic P123 solutions in the presence of 1,3,5-trimethylbenzene (TMB) as organic cosolvent.⁴ X-ray diffraction (XRD) experiments⁵ reveal well-resolved peaks at small angles, as shown in Figure 1 for a sample with a cell diameter of 33 nm. Careful analyses of the scattering data for MCFs show that the higher order peaks cannot be indexed to any plane or space group (e.g., *p6mm*) or to a lamellar diffraction pattern. In fact, after subtraction of the background,⁶ the X-ray data are in good agreement with simulated scattering⁷ due to monodisperse spheres (cells) of diameter *D* (see Table 1), while attempts to fit the X-ray data to

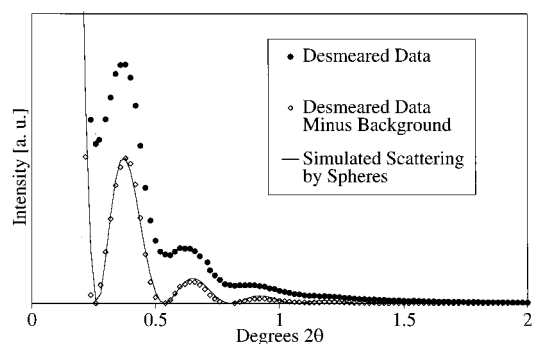


Figure 1. Small-angle X-ray scattering from a MCF with a cell diameter of 33 nm.^{5–7}

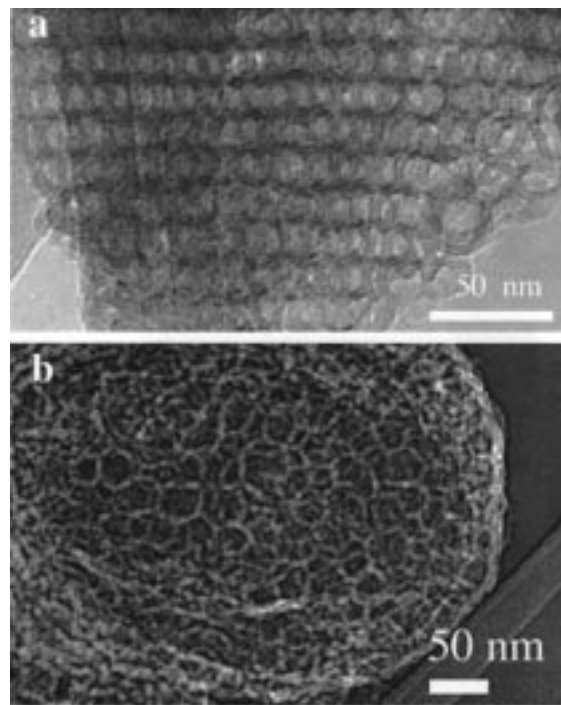


Figure 2. Transmission electron micrographs of MCFs with cell diameters of 22 (a) and 32 nm (b).⁸

scattering from polydisperse spheres have yielded only poor results. Transmission electron micrographs⁸ of the MCFs are shown in Figure 2: a MCF with a cell diameter of 22 nm displays local and long-range order (Figure 2a); another sample, possessing 32-nm-sized cells, shows less long-range order (Figure 2b).

Nitrogen sorption measurements^{9a} strongly support the proposed MCF pore structure. The isotherms show large hystereses, which in conjunction with BdB pore size analyses^{9b–d} and X-ray experiments suggests that the MCFs possess ink-bottle-type pores in which large cells are connected by narrower windows.¹⁰ The

(6) The subtracted background is described by a power law curve, $y = a + b(x - c)^d$, and was weighted to lie on desmeared data for $2\theta > 2^\circ$ and on local minima of the desmeared data for $2\theta < 2^\circ$. See: Mateu, L.; Tardieu, A.; Luzzati, V.; Aggerbeck, L.; Scanu, A. M. *J. Mol. Biol.* **1972**, *70*, 105.

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(8) Transmission electron microscopy was performed on a JEOL 2000 microscope (200 kV) using copper grids.

(9) (a) Nitrogen sorption was carried out on a Micromeritics ASAP 2000 system at 77 K with samples outgassed at 180–200 °C under high vacuum for at least 4 h. (b) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1967**, *9*, 8. (c) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1968**, *10*, 153. (d) Broekhoff, J. C. P.; de Boer, J. H. *J. Catal.* **1968**, *10*, 368.

* To whom correspondence should be addressed. Telephone: (805) 893-4872. Fax: (805) 893-4120. E-mail: stucky@chem.ucsb.edu.

[†] Department of Chemistry.

[‡] Materials Research Laboratory.

[§] Department of Chemical Engineering.

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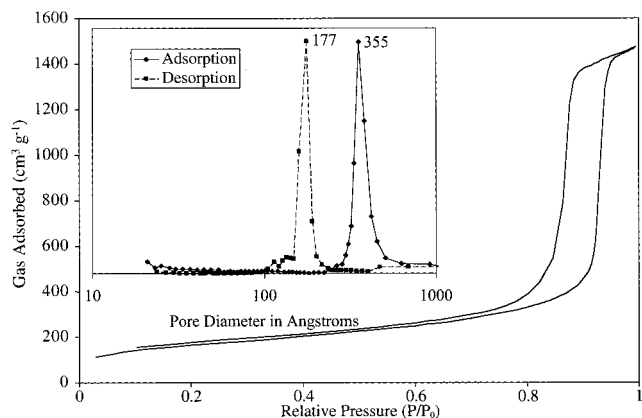
(4) In a typical preparation, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer (EO₂₀PO₇₀EO₂₀, Pluronic P123, $M_w = 5800$, BASF/Aldrich, 2.0 g, 0.4 mmol) was dissolved in 75 mL of aqueous HCl (1.6 M, 120 mmol) at room temperature. NH₄F (23 mg, 0.6 mmol)—if desired—and 1,3,5-trimethylbenzene (TMB, 2.0 g, 17 mmol) were added. After at least 45 min at 35–40 °C, tetraethoxysilane (4.4 g, 21 mmol) was added. After 20 h at 35–40 °C, the cloudy mixture was kept at 95–100 (samples P- -) or 120 °C (samples Z- -) for 24 h. The filtered precipitate was dried in air (4.9 g of white, as-made silica). Typical yields: 94–100% based on Si. As-made silicas were calcined at 500 °C for 8 h in air to yield MCFs.

(5) X-ray powder diffraction (XRD) patterns were recorded on a Scintag PADX diffractometer using Cu K α radiation detected by a Si(Li) solid-state detector cooled by a Peltier cell. The data were desmeared by the direct method: Singh, M. A.; Ghosh, S. S.; Shannon, R. F. *J. Appl. Crystallogr.* **1993**, *26*, 787.

Table 1. Physical Data for Siliceous Mesocellular Foams

sample	TMB/P123 (wt ratio)	sphere diam D^a (nm)	cell diam ^b (nm)	window diam ^b (nm)	surface area ^c ($\text{m}^2 \text{g}^{-1}$)	pore vol ^b ($\text{cm}^3 \text{g}^{-1}$)	porosity ^b (%)
No Fluoride Added							
P1	0.3	27	24 (8.0)	7.2 (1.3)	585	1.0	69
Z1	0.5	28	22 (6.2)	6.9 (1.3)	746	1.2	73
P2	0.75	35	31 (5.7)	9.8 (1.8)	900	2.2	83
P3	1.5	(d)	36 (5.0)	11 (1.1)	655	1.7	79
With Fluoride ^e							
P4F	0.75	31	30 (5.6)	16 (1.8)	543	1.9	81
P5F	1	32	34 (7.3)	18 (2.4)	532	2.2	83
P6F	1.5	33	36 (6.3)	18 (2.0)	625	2.4	85

^a Determined from small-angle X-ray scattering.⁵⁻⁷ ^b Determined from nitrogen sorption.⁹ In parentheses: full-width-at-half-maximum values, obtained from pore size distribution peaks.¹¹ ^c Determined by the BET method.²⁰ ^d Scattering peaks not resolved in the X-ray experiments. ^e F/Si molar ratio: 0.03.⁴

**Figure 3.** Nitrogen sorption isotherm and corresponding pore size distributions (inset) of a representative MCF.⁹

sizes of the cells and windows have been determined from the adsorption and desorption branches of the nitrogen sorption isotherms, respectively.⁹ A representative isotherm and the corresponding pore size distributions are shown in Figure 3. The cell sizes obtained from nitrogen sorption are similar to the values of D obtained from X-ray scattering experiments.⁵⁻⁷ From the data in Table 1, it is apparent that the cell sizes increase with the amount of added TMB. In fact, a linear relationship exists between the cell diameter and the cube root of the amount of added TMB, which supports both the spherical cell model and the proposed templating mechanism (see below). Adding ammonium fluoride (F/Si molar ratio, 0.03) enlarges the windows between the cells but does not appreciably affect the cell sizes.

Adding TMB to the aqueous Pluronic P123 solution (TMB/P123 \geq 0.2 (w/w)) leads to MCFs with uniformly sized spherical cells that are interconnected by windows of uniform size.¹¹ The phase transition from the SBA-15 phase to the MCF phase depends on synthesis parameters such as mixing conditions and temperature. We propose that adding TMB to the Pluronic P123 solution produces uniform droplets of TMB/P123 in water and leads to a microemulsion.¹² Subsequently added tetraethoxysilane (TEOS) may hydrolyze at the surface of the TMB/P123 droplets and then polymerize to give a composite material with intercon-

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(11) Full-width-at-half-maximum (fwhm) values (Table 1) depend on the number of data points, equilibration time, etc., so they represent upper limits. We expect the actual size distributions to be smaller, which is in agreement with X-ray simulation experiments (see text).

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nected spherical cells whose size is controlled by the size of the TMB/P123 droplets. Windows between cells would form at regions where adjacent droplets come into contact and thus arise from droplet-packing effects.¹³ We are currently investigating the more detailed aspects of the phase transition and mechanism of formation of these novel materials.

For a homologous series of MCFs with varying cell sizes, the area of a cell occupied by a single window should be similar if each cell has the same number of neighbors. For MCFs synthesized without fluoride, windows formed by assembly of 12 close-packed neighboring droplets could occupy up to 30% of a cell's surface; these MCFs resemble arrays of large spheres that are interconnected by smaller windows. In MCFs synthesized with fluoride, the windows occupy a larger fraction of the surface of the cell (up to 80%). Therefore, the latter MCFs resemble a lattice of struts rather than an array of spheres (see Supporting Information).

Because of their strutlike structure (see Figure 2b), the MCFs synthesized with fluoride resemble aerogels.¹⁴ However, two major differences exist between our MCFs and aerogels: (i) the pore sizes in MCFs are well-defined. While aerogels may have a characteristic pore size, their size distribution is quite large.¹⁴ (ii) MCFs are easy to synthesize; unlike aerogels, they do not require prolonged gel times, solvent exchange, or supercritical drying. Aqueous emulsions were previously employed in syntheses of mesoporous fibers,¹⁵ hollow spheres,¹⁵ and discrete spherical mesoporous particles.¹⁶ The MCF synthesis, however, is more reminiscent of a nonaqueous emulsion templating route to prepare macroporous oxides with much larger cells.¹⁷ To produce materials with a narrow pore size distribution, that route requires the emulsion droplets to be fractionated. Using thermodynamically more stable microemulsions,¹² rather than metastable emulsions,¹⁷ appears to circumvent the necessity of fractionating the template. Other routes to large-pore silicas use either colloidal polystyrene microspheres¹⁸ or ionic block copolymers¹⁹ as templates. Compared to those routes, the MCF synthesis described here is simpler, more efficient, and less time-consuming.

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Supporting Information Available: One schematic illustration, depicting the structures of the mesocellular foams (1 page, print/PDF). See any current masthead page for ordering and Web access instructions.

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