

SILICEOUS MESOSTRUCTURED CELLULAR FOAMS WITH UNIFORMLY SIZED AND SHAPED PORES

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ABSTRACT

Mesostructured siliceous cellular foams (mesocellular foams, MCFs) with homogeneous ultra-large mesopores are described. MCFs consist of uniform spherical cells 21-36 nm in diameter and possess surface areas up to 900 m²/g. Uniform windows, 7-18 nm in diameter, interconnect the cells to form a continuous 3-D pore system, which makes the MCFs attractive candidates for supports for catalysis and in separation and immobilization involving large molecules. They may be of interest in low-dielectric applications. The size of the cells can be controlled by the concentration of the added organic cosolvent. Adding small amounts of NH₄F selectively enlarges the windows. We propose that the MCFs are templated by oil-in-water microemulsion droplets. The large-pore MCF materials resemble aerogels, with the benefit of a facilitated synthesis procedure in combination with well-defined pores and wall structure.

INTRODUCTION

Large-pore molecular sieves with uniform pores are desirable materials offering a variety of possible applications such as hosts for chemical reactions, use in separation, immobilization or encapsulation involving large molecules [1], as low-dielectric materials [2], etc. Mesoporous materials with pore sizes from 20 to 500 Å are attractive in this respect, and thus interest in this area continues unabated. Most procedures for preparing ordered mesoporous materials use supramolecular templates that are formed by self-aggregating properties of various kinds of surfactants [3]. Colloidal templating routes that employ metastable emulsions [4] or polymer latex spheres [5] as templates have enabled the preparation of ordered macroporous and large-pore mesoporous materials. Block copolymer-based supramolecular templates have also been used for this purpose [6]. By changing the reaction temperature or by adding organic cosolvents to adjust the hydrophobic volumes of the supramolecular templates, the pore sizes of mesoporous materials have been controlled [6a,b, 7]. Here we describe mesostructured cellular foams (MCFs) that are proposed to be templated by microemulsions [8]. MCFs are composed of uniformly sized spherical cells, which are interconnected by uniform windows to give 3-D continuous pore systems. This new class of large-pore mesoporous materials is promising as supports for catalysts, for separation and immobilization involving large molecular moieties, and for low-dielectric applications.

EXPERIMENT

The MCFs were prepared in aqueous hydrochloric acid by using dilute solutions of the nonionic surfactant Pluronic[®] P123 (poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide), EO₂₀-PO₇₀-EO₂₀, M_w=5800) in the presence of 1,3,5-trimethylbenzene (TMB) as organic cosolvent. In a typical preparation, 2.0 g of P123 (0.4 mmol) were dissolved in 75 mL of 1.6 M HCl (120 mmol HCl) at room temperature while stirring. After complete dissolution of the polymer, 23 mg of NH₄F (0.6 mmol) - if desired - and 2.0 g of 1,3,5-

trimethylbenzene (TMB, 17 mmol) were added. Then, 4.4 g of tetraethoxysilane (TEOS, 21 mmol) were added as source of silica after 45-60 min at 35-40 °C. After 20 h of stirring at 35-40 °C, the cloudy reaction mixture was transferred into a polypropylene bottle and aged at 100 °C for 24 h under static conditions. The filtered white precipitate was dried in air and calcined at 500 °C for 8 h in air to give a MCF material.

RESULTS

Careful analyses of small-angle X-ray measurements of the MCFs revealed that the well-resolved peaks correspond to scattering from homogeneously sized spherical particles, as shown in Figure 1. The X-ray data were recorded in transmission mode and desmeared as described by Singh et al. [9]. In order to reduce the data to coherent scattering and minimize the contribution of diffuse scattering, a background described by a power law curve of the form $y=a+b(x-c)^d$ was subtracted and weighted to lie on the desmeared data for angles $2\theta > 2^\circ$ and on the local minima for angles $2\theta \leq 2^\circ$ [10]. The higher-order peaks in the X-ray patterns could not be indexed to any space group. We carried out scattering simulations to fit the X-ray data. The simulation parameters included intensity, sphere diameter, and zero-angle correction [11]. The X-ray data were in

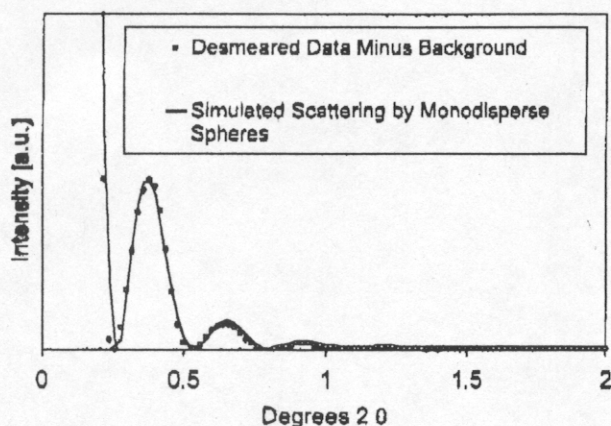


Figure 1. Representative Small-Angle X-ray Scattering from a MCF.

good agreement with simulated scattering from monodisperse spheres.

The MCFs were subjected to nitrogen sorption measurements [12]. The type IV isotherms show steep, pronounced hystereses at large relative pressures p/p_0 , which is indicative of large pores with narrow size distributions (see Figures 2, 3). Both Broekhoff-de Boer (BdB) pore size analyses [13] and X-ray experiments mentioned above are in agreement with ink-bottle-type pores in which large cells (bottles) are connected by narrower windows (bottle necks) [14a]. In such pore systems, analyses of the adsorption branches provide information about the cells, whereas the desorption branches contain information regarding the windows [13, 14a]. Figure 2 shows a typical isotherm of a MCF, prepared with a weight ratio of TMB/P123=0.4, and the corresponding BdB pore size distributions.

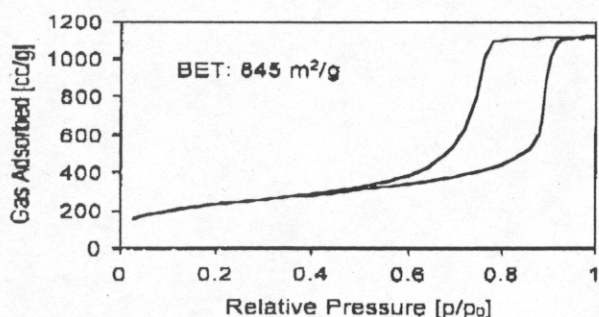


Figure 2a. Nitrogen sorption isotherm of a representative MCF prepared with TMB/P123=0.4 (w/w).

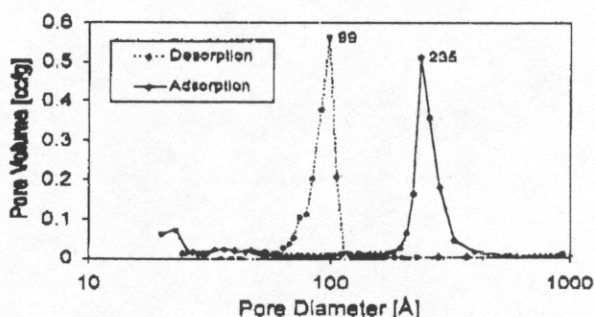


Figure 2b. Corresponding BdB-Analysis [13]. Cell Size: 235 Å. Window Size: 99 Å.

During our studies we found that adding small amounts of NH_4F ($\text{NH}_4\text{F}/\text{Si}$ molar ratio: 0.03) during the MCF syntheses selectively enlarges the windows. This became evident from nitrogen sorption measurements. Figure 3 shows a nitrogen sorption isotherm and the corresponding BdB pore size analyses of a typical MCF that was prepared in the presence of NH_4F (TMB/P123=1.5 (weight ratio)). Compared to Figure 2a, the desorption branch in Figure 3a is shifted much more to larger relative pressures p/p_0 than the adsorption branch, giving rise to a narrowed hysteresis; however, the shapes of the hystereses are similar (type H1 [14b]).

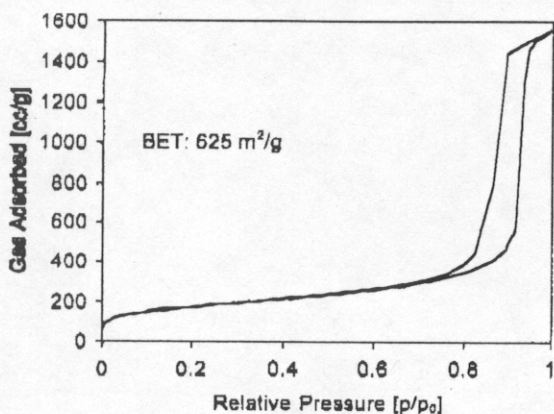


Figure 3a. N_2 sorption isotherm of a MCF prepared with NH_4F and TMB/P123=1.5 (w/w).

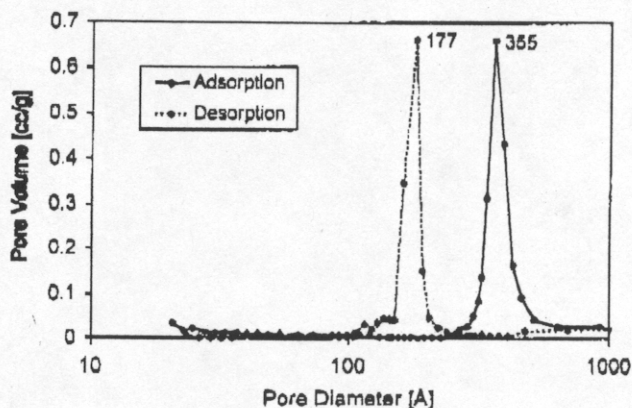


Figure 3b. Corresponding BdB-Analysis [13]. Cell Size: 355 Å, Window Size: 177 Å.

The BdB pore size analyses corroborate this observation (Figures 2b and 3b). The cell size increased by 50 % due to higher cosolvent concentration in Figure 3b. The window size, on the other hand, increased by 79 %. By comparing MCFs prepared with and without NH_4F , we found that only 11 % of this increase in window size can be attributed to higher cosolvent concentration, whereas 68 % is due to NH_4F addition, which does not appreciably affect the cell sizes.

Transmission electron microscopy [15] has shown that MCFs with smaller cells and windows display structures exhibiting long-range order (Figure 4a). The MCFs with larger cells and windows, especially the ones synthesized in the presence of NH_4F , display disordered strutlike matrix arrays (see Figure 4b) reminiscent of aerogels [16].

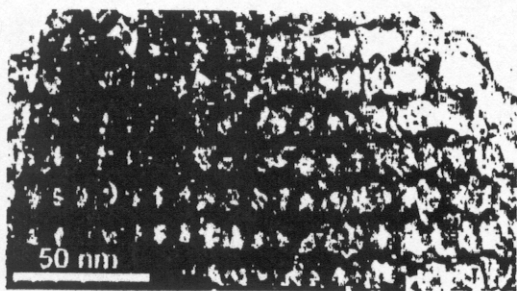


Figure 4a. TEM image of a MCF with Cell Diameter of 21 nm.

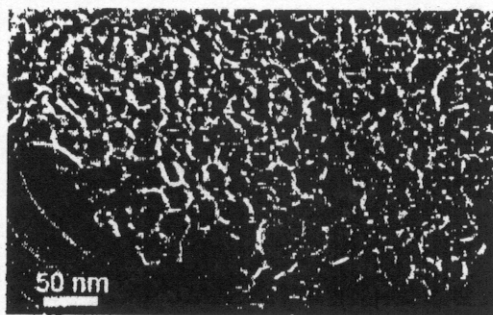


Figure 4b. TEM image of a MCF with Cell Diameter of 30 nm.

Table I. Summary of Physical Data for MCF materials.

a) TMB: 1,3,5-trimethylbenzene, P123: Pluronic[®] surfactant; b) From small-angle X-ray scattering; c) From N₂ sorption and Broekhoff-de Boer analysis; d) BET method. e) X-ray peaks poorly resolved; f) NH₄F/Si molar ratio: 0.03.

MCF Sample	TMB/P123 ^{a)} [w/w]	Sphere Diameter ^{b)} [nm]	Cell Diameter ^{c)} [nm]	Window Diameter ^{e)} [nm]	Surface Area ^{d)} [m ² /g]	Pore Volume ^{c)} [cm ³ /g]	Porosity ^{e)}
Without NH ₄ F							
1	0.3	27	24	7.2	585	1.0	0.69
2	0.75	33	31	9.8	900	2.2	0.83
3	1.5	e)	36	11	655	1.7	0.79
With NH ₄ F ^{d)}							
4F	0.75	31	30	16	543	1.9	0.81
5F	1	32	34	18	532	2.2	0.83
6F	1.5	33	36	18	625	2.4	0.85

The cell sizes obtained from X-ray scattering, nitrogen sorption analyses and TEM are in agreement. The size of the cells increases linearly with the cube root of the amount of added TMB, which is consistent with the spherical cell model ($V_{\text{sphere}}=4/3\pi r^3$) and the suggested templating mechanism. We propose that the addition of TMB to the Pluronic[®] P123 surfactant solution may lead to oil-in-water microemulsions with uniform surfactant-coated TMB droplets in water. Subsequently added hydrophobic TEOS may first migrate into the hydrophobic TMB/P123 droplets and swell them, hydrolyze at the surface of the TMB/P123 droplets and then condense to give a composite material in which both the size and shape of the cells are controlled by the TMB/P123 droplets. The windows interconnecting the cells may arise from droplet-packing effects and form at regions where adjacent droplets come into contact. A related mechanism has been described for surface-templated inverse opal structures [17]. The details of the mechanism of formation of the MCFs are currently under investigation in our laboratories.

For a homologous series of MCFs with varying cell sizes, the ratio $r_{\text{win}}^2/4r_{\text{cell}}^2$, corresponding to the area of a cell occupied by a single window, should be similar if each cell has the same number of neighbors. The maximum number of neighboring cells is assumed to be twelve, corresponding to close-packed structures. For MCFs synthesized without NH₄F, $r_{\text{win}}^2/4r_{\text{cell}}^2 \approx 2.5\%$. Windows formed by assembly of twelve close-packed neighboring droplets could hence occupy up to $12 \times 2.5\% = 30\%$ of a cell's surface, so these MCFs resemble arrays of large spheres that are interconnected by smaller windows. For MCFs synthesized with NH₄F, $r_{\text{win}}^2/4r_{\text{cell}}^2 \approx 6.7\%$, suggesting that the windows occupy up to $12 \times 6.7\% \approx 80\%$ of the surface of the cell. Therefore, the latter MCFs resemble a lattice of struts rather than an array of spheres.

Due to the strutlike structure, the large-pore MCFs resemble aerogels. However, two major differences exist between our MCFs and aerogels. First, the pores in our MCFs are well-defined. While aerogels may have a characteristic pore size, the width of their size distribution is quite large [16]. Secondly, MCFs are readily accessible; unlike aerogels, they do not require prolonged gel times, solvent exchange, or supercritical drying steps.

The MCF synthesis is reminiscent of the emulsion templating route described by Imhof and Pine to prepare macroporous oxides with much larger pores measuring 50 nm to 5 μm in diameter [4]. In order to produce materials with a narrow pore size distribution, that synthesis

method requires the emulsion droplets to be fractionated. The use of thermodynamically stable microemulsions [18], rather than kinetically stabilized emulsions [19], appears to circumvent the necessity of fractionating the colloidal template. Other synthesis procedures use polymer latex spheres [5] or ionic block copolymers [6c] for the preparation of large-pore silicas. In comparison to those templating routes, the MCF synthesis is simpler, more efficient, and less time-consuming.

CONCLUSIONS

We have described mesostructured cellular foams as a new class of 3-D continuous large-pore mesoporous materials that are synthesized by microemulsion templating. The novel MCF materials are composed of uniformly sized, spherical cells whose size can be controlled by the amount of added organic cosolvent. Uniform windows interconnect the cells. The window size can be selectively enlarged by adding small amounts of NH_4F . We believe that both the MCFs and the microemulsion templating reported in this paper represent valuable additions to the existing class of and routes to mesoporous materials with well-defined pores larger than 10 nm in diameter. The large-pore MCFs may find considerable interest in areas where widely used aerogels have been applied; MCFs have the additional advantage of well-defined pores and simple preparation. The possibility to enlarge selectively the windows simply by adding NH_4F to the MCF syntheses appears promising for applications such as supports for catalysts, where mass transport has often been limited by narrow pore openings.

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REFERENCES

1. a) R.H. Perry and D. Green, *Perry's Chemical Engineers' Handbook*, (McGraw-Hill, New York, 1984). b) M.T.W. Hearn, *HPLC of Proteins, Peptides, and Polynucleotides*, (VCH, New York, 1991). c) M.E. Davis, *Chem. Ind.* **4**, 137 (1992).
2. D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmelka, G.D. Stucky, *Adv. Mater.* **10**, 1380 (1998).
3. For recent reviews, see: a) J.Y. Ying, C.P. Mehnert, M.S. Wong, *Angew. Chem. Int. Ed.* **38**, 56 (1999). b) U. Ciesla and F. Schütt, *Microporous Mesoporous Mater.* **27**, 131 (1999).
4. A. Imhof and D.J. Pine, *Nature* **389**, 948 (1997); *Adv. Mater.* **10**, 697 (1998).
5. a) O.D. Velev, T.A. Jede, R.F. Lobo, A.M. Lenhoff, *Nature* **389**, 447 (1997); *Chem. Mater.* **10**, 3597 (1998). b) M. Antonietti, B. Berton, C. Göltner, H.-P. Hentze, *Adv. Mater.* **10**, 154 (1998). c) B.T. Holland, C.F. Blanford, A. Stein, *Science* **281**, 538 (1998). d) P. Yang, T. Deng,

- D. Zhao, P. Feng, D. Pine, B.F. Chmelka, G.M. Whitesides, G.D. Stucky, *Science* **282**, 2244 (1998). e) B.T. Holland, C.F. Blanford, T. Do, A. Stein, *Chem. Mater.* **11**, 795 (1999).
6. a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science* **279**, 548 (1998). b) D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* **120**, 6024 (1998). c) E. Krämer, S. Förster, C. Göltner, M. Antonietti, *Langmuir* **14**, 2027 (1998).
7. a) J.S. Beck, J.C. Vartuli, J.W. Roth, M.F. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* **114**, 10834 (1992). b) Q. Huo, R. Leon, P.M. Petroff, G.D. Stucky, *Science* **268**, 1324 (1995).
8. P. Schmidt-Winkel, W.W. Lukens Jr., D. Zhao, P. Yang, B.F. Chmelka, G.D. Stucky, *J. Am. Chem. Soc.* **121**, 254 (1999).
9. M.A. Singh, S.S. Ghosh, R.F. Shannon, *J. Appl. Crystallogr.* **26**, 787 (1993).
10. L. Mateu, A. Tardieu, V. Luzzati, L. Aggerbeck, A.M. Scanu, *J. Mol. Biol.* **70**, 105 (1972).
11. L.A. Feigin and D.I. Svergun, *Structure Analysis by Small-Angle X-Ray and Neutron Scattering*, (Plenum Press, New York, 1987), pp. 59-105.
12. Nitrogen sorption measurements were performed at 77 K on a Micromeritics ASAP 2000 instrument on samples degassed at 180 °C under high vacuum for several hours.
13. a) J.C.P. Brockhoff and J.H. de Boer, *J. Catal.* **9**, 8 (1967); *J. Catal.* **10**, 153 (1968); *J. Catal.* **10**, 368 (1968). b) W.W. Lukens Jr., P. Schmidt-Winkel, D. Zhao, G.D. Stucky, *Langmuir* (1999), in press.
14. a) S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed. (Academic Press, New York, 1982), Ch. 3. b) S.J. Gregg, K.S.W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed. (Academic Press, New York, 1982), p. 287.
15. TEM was performed on a JEOL 2000 microscope at 200 kV using copper grids.
16. For recent reviews, see: a) H. Hüsing, U. Schubert, *Angew. Chem. Int. Ed.* **37**, 22 (1998). b) M. Schneider, A. Baiker, *Catal. Rev.-Sci. Eng.* **37**, 515 (1995).
17. A.A. Zakhidov, R.H. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S.Q. Dantas, J. Marti, V.G. Ralchenko, *Science* **282**, 897 (1998).
18. For recent reviews, see: a) D. Langevin, *Acc. Chem. Res.* **21**, 255 (1988). b) A. Kabalnov, B. Lindman, U. Olsson, L. Piculell, K. Thuresson, H. Wennerström, *Colloid Polym. Sci.* **274**, 297 (1996).
19. A. Imhof and D.J. Pine, *J. Colloid Interface Sci.* **192**, 368 (1997).