[10] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.

[11] J. S. Binkley, J. A. Pople, W. J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939; M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, W. J. Hehre, *J. Am. Chem. Soc.* **1982**, *104*, 2797; M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265, and references therein; K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.* **1986**, *7*, 359; K. D. Dobbs, W. J. Hehre, *J. Comput. Chem.* **1987**, *8*, 861, 880.

Room-Temperature Synthesis in Acidic Media of Large-Pore Three-Dimensional Bicontinuous Mesoporous Silica with *Ia*3*d* Symmetry**

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Since the discovery of a new family of mesoporous silicate materials, denoted M41S and including MCM-41, MCM-48, and MCM-50, by researchers at Mobil,[1] major developments have been made in this field. A great variety of mesostructures has been obtained, including mesoporous silica, metal oxides, metals, carbon, and hybrid organosilicates.[2] Up to now, the main research efforts have concentrated on the MCM-41 silica structure, which consists of a hexagonal packing of one-dimensional (1D) channels (*p6mm*), and fewer investigations have been reported on mesoporous MCM-48, which has a 3D bicontinuous mesostructure (*Ia*3*d*). This may result from the small domain of this cubic phase (*Ia*3*d*) of MCM-48 in phase diagrams. Several methodologies have been developed for the syntheses of mesoporous silica MCM-48 by using a cationic alkylammonium surfactant,[1,3] mixed cationic/anionic surfactants,[4] or cationic/nonionic surfactants as templates.[5] Generally, these syntheses were carried out under the severe conditions of high-temperature ($\geq 100\,°C$) hydrothermal synthesis in alkaline aqueous media. Relatively expensive ionic surfactants were employed, and the resulting mesostructures have a limited range of small pore sizes (pore diameter 1.5–4.5 nm). These restrictions may limit the potential applications of 3D bicontinuous mesoporous materials as adsorbents, separators, and catalysts.

Here we report the synthesis of large-pore 3D bicontinuous mesoporous silica (designated FDU-5) at room temperature in acidic media by using a commercial nonionic triblock copolymer as template and an organosiloxane or organic compound as additive. To the best of our knowledge, this is the first preparation of *Ia*3*d* mesostructured material at room temperature under acidic conditions. The FDU-5 products have uniform large pores (4.5–9.5 nm). Such mesoporous materials with large 3D bicontinuous pores could have applications in sorption and transport, especially of large molecules.

Large-pore 3D bicontinuous mesoporous FDU-5 was synthesized at room temperature in ethanol solution by a solvent-evaporation method. Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer ($EO_{20}PO_{70}EO_{20}$, P123) was used as template, tetraethyl orthosilicate (TEOS) as silica source, and a small amount of 3-mercaptopropyltrimethoxysilane (MPTS), benzene, or a benzene derivative (methyl-, ethyl-, dimethyl-, or trimethylbenzene) as additive.

Transmission electron microscopy (TEM) images and corresponding Fourier diffractograms recorded along the [100], [111], [110], and [331] directions of calcined FDU-5 silica prepared with P123 as template and MPTS as additive in acidic medium at room temperature are shown in Figure 1. These images clearly show that the products have large domains of ordered 3D bicontinuous mesostructure. The two principal directions displaying continuous pores are [100] and [111] (Figure 1 a,b), and two types of hexagonally packed dots with different sizes and darknesses (Figure 1 b) are clearly observed. The images shown in Figure 1 are beautiful representative packing patterns for bicontinuous cubic mesostructures (*Ia*3*d*).[6,7] The cell parameter *a* calculated from these TEM images is 18.0 nm. On the basis of these TEM

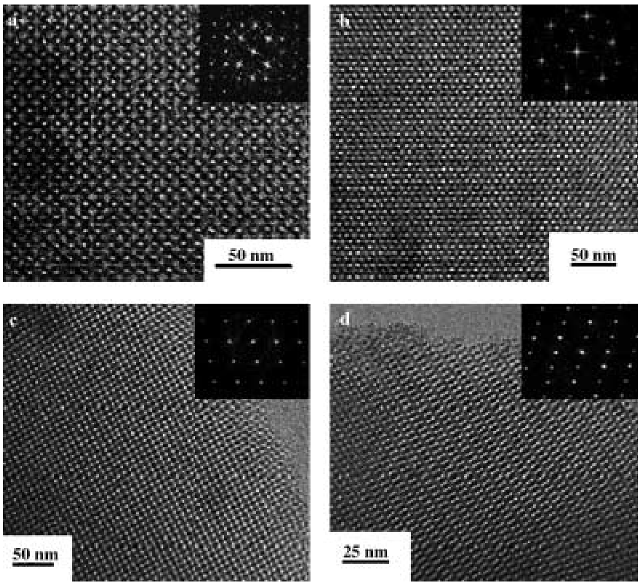

Figure 1. TEM images and corresponding Fourier diffractograms of calcined FDU-5 prepared at room temperature under acidic conditions with triblock copolymer P123 as template and MPTS as additive. The images were recorded along the directions [100] (a), [111] (b), [110] (c), and [331] (d).

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images, corresponding Fourier diffractograms, and the results of simulations,[6] we assign the mesoporous silica a 3D cubic *Ia*3*d* mesostructure.

X-ray powder diffraction (XRD) patterns (Figure 2) further confirm the cubic *Ia*3*d*-type mesostructure of FDU-5 prepared in acidic medium at room temperature. Although only two diffraction peaks can be observed for the as-made sample (Figure 2a), their *d*-spacing ratio is exactly 0.866, which implies that these two peaks can be indexed as (211) and (220) diffraction peaks of mesoporous bicontinuous cubic space group *Ia*3*d*. The unit cell parameter *a* of the as-made sample, calculated from XRD data, is as large as 21.1 nm. After extraction by ethanol, the two diffraction peaks merge into one broad reflection peak. The additional broad diffraction peak in the range of $2\theta = 1.5$–2.2 may arise from overlapping of (321), (400), (420), and (332) diffraction peaks of the *Ia*3*d* space group. The XRD pattern of the calcined sample (Figure 2c) features one high-intensity Bragg peak and a shoulder peak, which can be indexed as (211) and (220) and show a typical pattern for *Ia*3*d* mesostructures. Similar to that observed for the extracted sample, a broad diffraction peak in the range of $2\theta = 1.7$–2.4 is also observed. The cell parameter *a* of the calcined sample was calculated to be 18.2 nm, in good agreement with the value estimated from TEM images, and suggests that the mesoporous silica FDU-5 has a bicontinuous cubic *Ia*3*d*-type mesostructure.

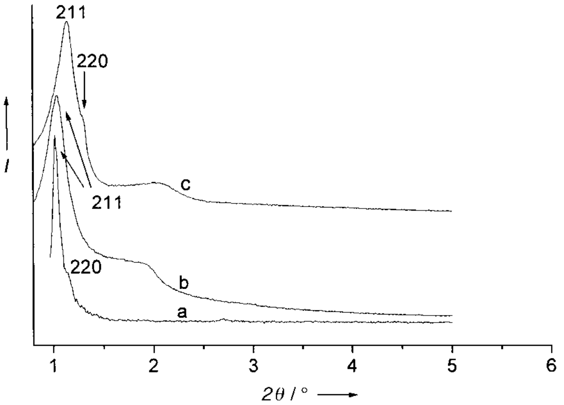

Figure 2. XRD patterns for a) as-made, b) ethanol-extracted, and c) calcined mesoporous FDU-5 synthesized at room temperature under acidic conditions with P123 as template and MPTS as additive.

Nitrogen adsorption–desorption isotherms (Figure 3) for both extracted and calcined samples show type IV curves with typical H_1 hysteresis loops, and this implies that the samples have large 3D bicontinuous mesopores without windows or necks. The calcined mesoporous FDU-5 has a narrow pore size distribution with a mean value of 8.1 nm, a BET surface area of $804\,m^2g^{-1}$, and a pore volume of $1.04\,cm^3g^{-1}$. The ethanol-extracted mesoporous FDU-5 has also a narrow pore size distribution, but with a relatively small mean value of 5.9 nm, a BET surface area of $399\,m^2g^{-1}$, and a pore volume of $0.55\,cm^3g^{-1}$. The relatively small pore diameter, surface area, and pore volume of the extracted sample may result from the organic functional groups that remain in the channels.

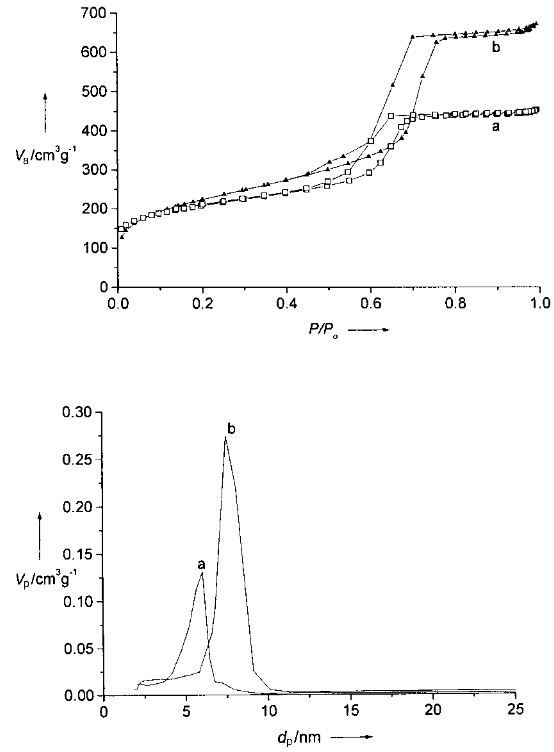

Figure 3. Nitrogen adsorption–desorption isotherms (top) and pore size distribution curves (bottom) calculated from the adsorption branch of the isotherms for a) extracted and b) calcined FDU-5 synthesized at room temperature under acidic conditions with P123 as template and MPTS as additive. The pore size was calculated by Barrett–Joyner–Halenda (BJH) analysis. V_a: volume adsorbed, V_p: pore volume, d_p: pore diameter.

The organosiloxane or organic additive plays an essential role in the formation of *Ia*3*d*-type mesostructures under acidic conditions at room temperature. With MPTS as additive, mesoporous FDU-5 is formed only for an MPTS/TEOS molar ratio of 0.046–0.058. Without organosiloxane, 2D hexagonal (*p*6*mm*) mesostructure is obtained from TEOS as sole silica source.[8] With MPTS/TEOS ratios smaller than 0.046, the products consisted of a mixture of hexagonal (*p*6*mm*) and cubic (*Ia*3*d*) mesostructured phases (see Supporting Information), and this suggests that a phase transition occurs. The addition of organosiloxane or small organic molecules may increase the hydrophobic/hydrophilic ratio and result in a transition of the cooperatively assembled inorganic–organic mesostructure from high-curvature hexagonal *p*6*mm* to low-curvature bicontinous cubic *Ia*3*d*.[9,10] An analogous phase transition was also observed in previous syntheses of *Ia*3*d* mesostructured MCM-48 in an aqueous system during hydrothermal treatment owing to the increase in the hydrophobic portion caused by the hydropobicity of organic co-solvents such as alcohols.[3a,c,e,f,11] Moreover, high-curvature cubic *Pm*3*n* mesostructures can be transformed into low-curvature hexagonal *p*6*mm* mesostructures by increasing the hydrophobic/hydrophilic ratio in an aqueous reaction system by addition of co-solvents.[3e,12] However, previous methodologies[3a,c,e,f,11] for obtaining *Ia*3*d* mesostructures by phase transition required high-temperature processes (≥100 °C) and alkaline media. In our procedure, such a conversion can be attained economically (cheap template) with the aid of an additive under mild conditions (low temperature).

The solid-state ^{29}Si magic-angle spinning (MAS) NMR spectrum (see Supporting Information) of as-made mesoporous FDU-5 prepared by using MPTS as an additive under acidic conditions at room temperature exhibits four signals corresponding to T_2 ($\delta = -53$), T_3 ($\delta = -66$), Q_3 ($\delta = -101$), and Q_4 ($\delta = -111$ ppm), where T_2 and T_3 represent the species $RSi(OSi)_2OH$ and $RSi(OSi)_3$, and Q_3 and Q_4 correspond to $Si(OSi)_3OH$ and $Si(OSi)_4$ moieties. The results suggest that large-pore 3D bicontinuous mesoporous material with functional organic groups can be formed in one step under acidic conditions at room temperature. The $(T_3 + Q_4)/(T_2 + Q_3)$ ratio of 3.77 suggests a high degree of framework cross-linking.[13] The amount (4.6%) of organic moieties incorporated in the mesostructure, calculated by the ratio $T/(T+Q)$ ($T = T_2 + T_3$, $Q = Q_3 + Q_4$), is in accordance with that calculated from the initial composition (5.1%).

In summary, 3D bicontinuous cubic *Ia*3*d*-type mesoporous silica has been synthesized for the first time in acidic medium at room temperature by using a nonionic triblock copolymer as template. The resulting FDU-5 materials have extra-large pores (4.5–9.5 nm) with narrow size distributions. Such materials could have promising applications for the sorption, transport, and separation of large molecules.

Experimental Section

Typical synthesis of FDU-5: P123 (1 g, $M_w = 5800$, Aldrich) was dispersed with HCl solution (0.1 g, 2 M) and H_2O (0.9 g) in EtOH (10 g). After stirring vigorously at room temperature for 2 h, MPTS (0.106 g, 5.4 mmol) was added. After a further 2 h of stirring, TEOS (2.08 g, 10 mmol) was added. Then the mixture was stirred for 1 h. The resulting solution was dried in air for 2 d, and a solid white product was obtained. The surfactant P123 was removed from the as-synthesized material by washing with ethanol under reflux for 40 h or by calcining the product at 823 K for 6 h. The molar composition of the reaction mixture TEOS/P123/HCl/H_2O/EtOH/additive was 1/0.015–0.020/0.018–0.096/2.44–6.97/11–52/*x*, where *x* varied in the ranges of 0.046–0.058, 0.048–0.66, 0.042–0.60, 0.035–0.54, and 0.030–0.47 for MPTS, benzene, methylbenzene, 1,4-dimethylbenzene, and 1,3,5-trimethylbenzene as additive, respectively.

Characterization: TEM photographs were obtained on a JEOL 2010 microscope operated at 200 kV. XRD patterns were obtained on a Bruker D4 X-Ray diffractometer with $Cu_{K\alpha}$ radiation. Nitrogen adsorption–desorption isotherms were acquired on a Micromeritics Tristar 3000 system at 77 K. ^{29}Si NMR experiments were performed on a Bruker DSX300 spectrometer with a frequency of 59.63 MHz, a recycling delay of 600 s, and a radiation frequency intensity of 62.5 KHz.

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[1] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Varuli, J. S. Beck, *Nature* **1992**, *359*, 710; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

[2] a) A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F. Chmelka, *Science* **1993**, *261*, 1299; b) P. T. Tanev, T. J. Pannavaia, *Science* **1995**, *267*, 865; c) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548; D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024; d) S. A. Bagshaw, T. J. Pinnavaia, *Angew. Chem.* **1996**, *108*, 1180; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1102; e) D. M. Antonelli, J. Y. Ying, *Angew. Chem.* **1995**, *107*, 2202; *Angew. Chem. Int. Ed.* **1995**, *34*, 2014; f) G. S. Attard, P. N. Bartlett, N. R. B. Coleman, J. M. Elliott, J. R. Owen, J. H. Wang, *Science* **1997**, *278*, 838; g) R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743; h) T. Asefa, M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *402*, 867; i) C. Yu, Y. Yu, D. Zhao, *Chem. Commun.* **2000**, 575.

[3] a) J. M. Kim, S. K. Kim, R. Ryoo, *Chem. Commun*, **1998**, 259; b) Y. Liu, A. Karkamkar, T. J. Pinnavaia, *Chem. Commun.* **2001**, 1822; c) K. W. Gallis, C. C. Landry, *Chem. Mater.* **1997**, *9*, 2035; d) O. Collart, P. Van Der Voort, E. F. Vansant, D. Desplantier, A. Galarneau, F. Di Renzo, F. Fajula, *J. Phys. Chem. B* **2001**, *105*, 12771; e) Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147; f) A. A. Romero, M. D. Alba, W. Zhou, J. Klinowski, *J. Phys. Chem. B* **1997**, *101*, 5294; g) A. Sayari, *J. Am. Chem. Soc.* **2000**, *122*, 6504.

[4] F. Chen, L. Huang, Q. Li, *Chem. Mater.* **1997**, *9*, 2685.

[5] R. Ryoo, S. H. Joo, J. M. Kim, *J. Phys. Chem. B* **1999**, *103*, 7435.

[6] a) V. Alfredsson, M. W. Anderson, *Chem. Mater.* **1996**, *8*, 1141; b) J. N. Thomas, O. Terasaki, P. L. Gai, W. Z. Zhou, J. G. Calbet, *Acc. Chem. Res.* **2001**, *34*, 583.

[7] V. Alfredsson, M. W. Anderson, T. Ohsuna, O. Terasaki, M. Jacob, M. Bojrup, *Chem. Mater.* **1997**, *9*, 2066.

[8] D. Zhao, P. Yang, N. Melosh, J. Feng, B. F. Chmelka, G. D. Stucky, *Adv. Mater.* **1998**, *10*, 1380.

[9] M. Clerc, A. M. Levelut, J. F. Sadoc, *J. Phys. II* **1991**, *1*, 1263.

[10] V. Luzzati, *J. Phys. II* **1995**, *5*, 1649.

[11] C. C. Landry, S. H. Tolbert, K. W. Gallis, A. Monnier, G. D. Stucky, P. Norby, J. C. Hanson, *Chem. Mater.* **2001**, *13*, 1600.

[12] S. Che, S. Kamiya, O. Terasaki, T. Tatsumi, *J. Am. Chem. Soc.* **2001**, *123*, 12089.

[13] D. W. Sindorf, G. E. Maciel, *J. Am. Chem. Soc.* **1983**, *105*, 3767.

Transmembrane Signalling[**]

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Cells are separated from their surroundings by a lipid bilayer membrane, yet their survival depends on their ability to sense and respond to changes in the environment such as the levels of extracellular hormones, growth factors, cytokines, nutrients, and pathogens. One way in which these molecular signals can change the intracellular chemistry is by being transported into the cell through active transport or pores in the membrane. To date, synthetic approaches to communication across lipid membranes have relied on mimicking this direct physical transport of the molecular signal across the

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