

Synthesis of Periodic Mesoporous Phenylsilica under Acidic Conditions with Novel Molecular Order in the Pore Walls

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Periodic mesoporous organosilicates are one of the latest innovations in the field of ordered mesoporous materials.^{1,2} Similarly to their silica counterparts, they are prepared in the presence of amphiphile supramolecular templates using bridged silsesquioxane molecules, $(R'O)_3Si-R-Si(OR')_3$, as precursors. Through proper design of the organic linker R, such materials offer unique opportunities for controlling their surface and chemical properties at the molecular level. This is in addition to the inherent advantages of periodic mesoporous materials such as their high surface area and narrow pore size distribution (PSD). In a recent development, Inagaki et al.³ showed that using 1,4-bis-(triethoxysilyl)benzene under basic conditions in the presence of octadecyltrimethylammonium chloride affords a material which exhibits both long- and short-range order. In addition to the periodic system of 4.5-nm-diameter hexagonally packed cylindrical pores, the pore walls exhibited also a structural periodicity with a spacing of 0.76 nm along the channel direction due to the $\pi-\pi$ stacking of bridging phenylene groups. Using similar preparation conditions, Bion et al.⁴ synthesized phenyl-bridged organosilicas with comparable order using alkyltrimethylammonium surfactants with 14, 16, and 18 carbon atom alkyl chains. Similar molecular-scale periodicity with 1.16-nm spacing occurred also within the pore walls of biphenylene-bridged mesoporous organosilica.⁵ However, prepared under acidic conditions using the triblock copolymer Pluronic P123 as the structure-directing agent, phenylene-bridged organosilica showed little evidence of molecular order within the pore walls.⁶ Periodic mesoporous organosilicates with aryl groups such as tolyl, xylyl, and dimeth-

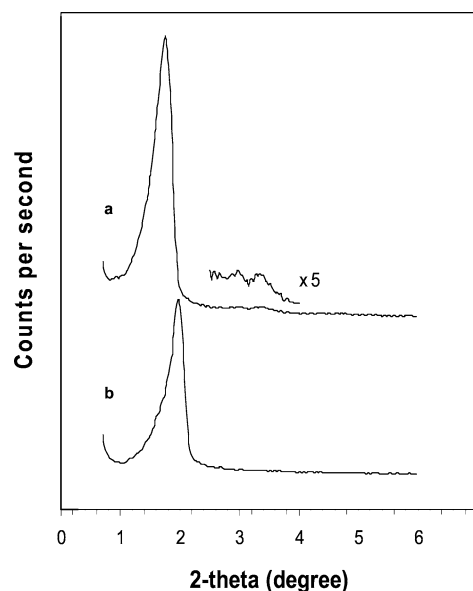


Figure 1. XRD patterns for phenylene-bridged mesoporous organosilica (after extraction) prepared in the presence of (a) Brij 76 and (b) Brij 56.

oxyphenyl prepared under acidic conditions in the presence of cetylpyridinium chloride also gave indication of arylsilica ordering in the channel walls.⁷

Oligomeric surfactants such as nonionic alkyl poly-(oxyethylene) surfactants $C_nH_{2n+1}(OCH_2CH_2)_{10}OH$, denoted C_nOE_m , proved to be excellent supramolecular templates for the synthesis of highly ordered mesoporous silicas⁸ and ethanesilicas⁹ under acidic conditions. The purpose of the current investigation is to extend this synthetic approach to phenylsilica and to check if there is any structural ordering of the aromatic rings within the channel walls.

Phenylene-bridged mesoporous materials were synthesized using 1,4-bis(triethoxysilyl)benzene (BTEB) as precursor in the presence of oligomeric surfactants Brij 56 ($C_{16}EO_{10}$) and Brij 76 ($C_{18}EO_{10}$) under acidic conditions. BTEB was prepared and purified according to the literature.¹⁰ In a typical synthesis of mesoporous phenylsilica, 2 g of surfactant was dissolved in 10 g of distilled water and 50 g of 2 M hydrochloric acid. After 30 min of stirring at 50 °C, BTEB (4.225 g) was added to the solution and then stirred for 20 h at 50 °C. The molar composition of the reaction mixture was BTEB: Brij 76:HCl:H₂O = 1:0.27:7.7:53. A white precipitate was recovered by filtration, washed thoroughly with water, and dried. The surfactant was removed by two consecutive solvent extractions using 150 mL of ethanol and 2 g of concentrated HCl for 1 g of sample at 50 °C for 5 h.

XRD patterns (Figure 1) of the surfactant-free materials revealed a strong peak at $2\theta = ca. 1.7^\circ$ and two

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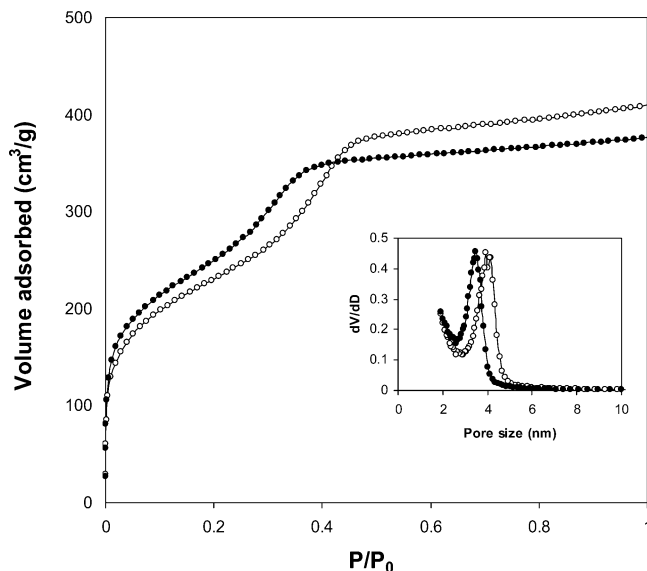


Figure 2. Nitrogen adsorption isotherms for phenylene-bridged mesoporous organosilica prepared in the presence of (○) Brij 76 or (●) Brij 56 as a structure-directing agent.

Table 1. N₂ Adsorption Data for Samples Prepared in a Single Step

surfactant used	pore volume (cm ³ /g)	surface area (m ² /g)	pore size (nm)	pore wall thickness (nm)
Brij 76	0.63	840	3.9	1.9
Brij 56	0.58	899	3.5	1.6

minor peaks in the 2θ range of 3–3.5°. These features are consistent with the occurrence of a two-dimensional hexagonal structure, akin to MCM-41 or SBA-15 mesophases. They correspond to the (100), (110), and (200) reflections. The unit cell dimension was 5.83 and 5.13 nm, for samples prepared in the presence of Brij 76 and Brij 56, respectively.

Nitrogen adsorption isotherms (Figure 2) were typical of periodic mesoporous materials. They exhibited a steep increase in adsorption at $P/P_0 = 0.25$ – 0.45 due to capillary condensation of nitrogen in the mesopores. The pore size distributions were narrow, particularly for the sample prepared in the presence of Brij 76. The KJS (Kruk-Jaroniec-Sayari) pore diameter, BET surface area, and pore volume were calculated from the adsorption isotherms as reported elsewhere.¹¹ These data are shown in Table 1. The pore wall thickness calculated using the equation $b = 2d_{100}/(3)^{1/2} - w_{KJS}$ was also included.

A typical ²⁹Si MAS NMR spectrum for the current phenylene-bridged mesoporous materials is shown in Figure 3a. It exhibited three main signals at –62.01, –70.35, and –79.21 ppm, assigned to Si species covalently bonded to carbon atoms T¹ [*Si*C(OH/OEt)₂(OSi)], T² [*Si*C(OH/OEt)(OSi)₂], and T³ [*Si*C(OSi)₃], respectively. These data are consistent with the occurrence of the organic linker within the material framework. Small signals between –90 and –120 ppm attributable to condensed SiO₄ species (*Si*(OSi)_{*n*}(OH)_{4–*n*}) were also present. The overall relative intensity of such signals was below 8%. The ¹³C CP NMR spectra (Figure 3b) were dominated by a peak at 134 ppm, which

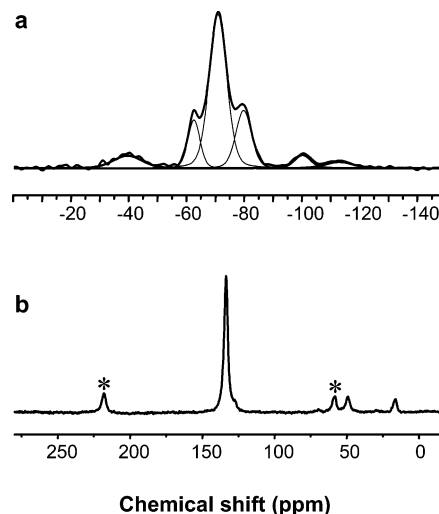


Figure 3. (a) ²⁹Si NMR and (b) ¹³C NMR data for the phenylene-bridged mesoporous organosilica prepared in the presence of Brij 76. * refers to spinning sidebands.

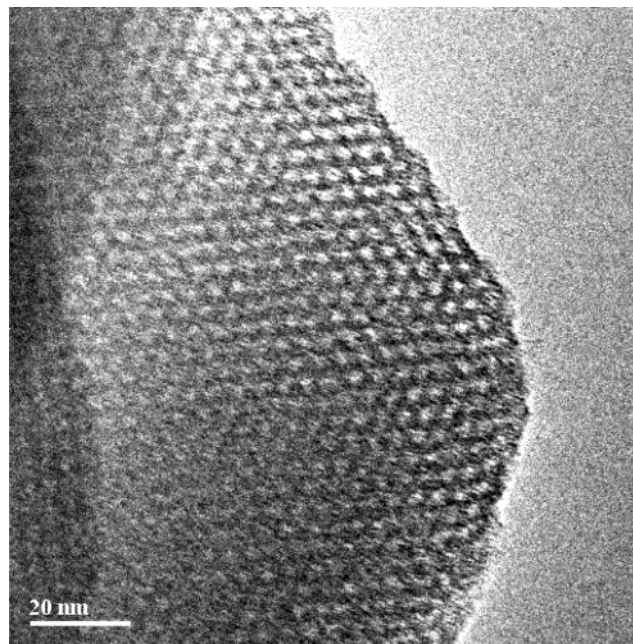


Figure 4. TEM image of the mesoporous product viewed down the [001] zone axis for samples prepared in the presence of Brij 76. The white spots are the direct images of the pores.

corresponds to the superposition of unresolved signals from *o*- and *m*-carbons in the phenylene ring. This peak exhibited a shoulder attributable to carbon atoms in positions 1 and 4, which are bonded to Si. There were two additional peaks at 16.2 and 58.8 ppm, which were assigned to nonhydrolyzed Si–O–CH₂CH₃ groups. These were estimated to be less than 3% of the ethoxy species in the starting amount of BTEB. The ²⁹Si and ¹³C NMR data are consistent with each other and provide strong evidence for the occurrence of a network composed of O_{1.5}Si–C₆H₄–SiO_{1.5} units.

Transmission electron microscopic (TEM) images of the specimens were obtained on a JEOL JEM-2010 electron microscope operating at 200 kV. When looking down the pore axis, the hexagonal arrangement of the mesopores was confirmed (Figure 4). The pore center to pore center distance was about 5 nm, being consistent with the XRD results. When viewed down the [100]

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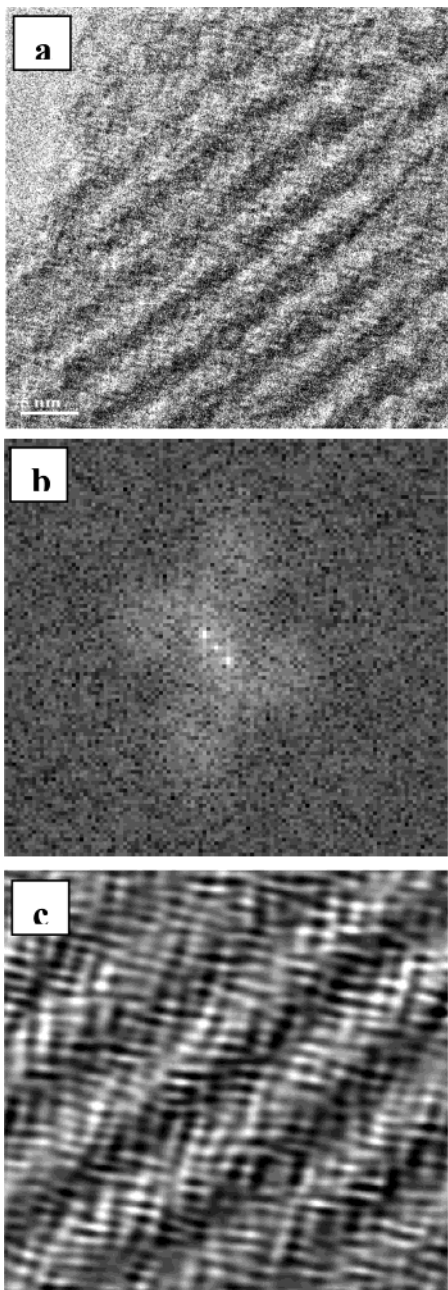


Figure 5. (a) TEM image of the mesoporous phase viewed down the [100] zone axis for the sample prepared in the presence of Brij 76. (b) Diffraction pattern made by the Fourier transform of (a). (c) TEM image created by the inverse Fourier transform of (b) when the sharp spots and two pairs of diffused spots were considered.

direction, straight lattice fringes were observed with a separation of 4.3 nm, which is the d spacing of the (010) planes (Figure 5a). In addition, some fine lattice fringes were also visible, although the contrast was very low. To study the detailed structure, a Fourier transform of the image in Figure 5a was performed (Figure 5b). The sharp diffraction spots resulted from the ordering of the mesopores with the d spacing of 4.3 nm. Two pairs of greatly diffused diffraction disks were also visible, indicating partial ordering in the wall structure in two dimensions. An inverse Fourier transform of Figure 5b by removing the background noise enabled us to see the structural details of the framework as shown in Figure 5c. Wavelike lattice fringes were

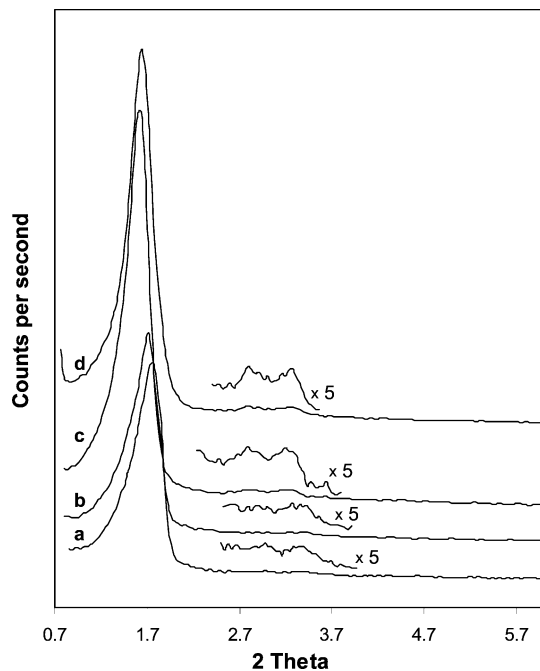


Figure 6. XRD patterns for phenylene-bridged mesoporous organosilica (after extraction) prepared in the presence of Brij 76 in a single step at 50 °C (a) or with use of a second hydrothermal stage for 20 h at (b) 50 °C, (c) 70 °C, and (d) 95 °C.

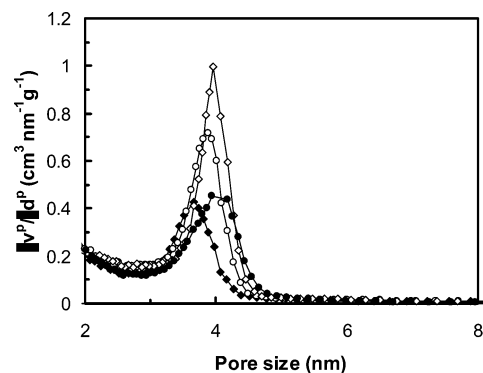


Figure 7. Pore size distribution for phenylene-bridged mesoporous organosilica prepared in the presence of Brij 76 in a single step (◆) or with use of a second hydrothermal stage for 20 h at (●) 50 °C, (○) 70 °C, and (◇) 95 °C.

revealed along two directions. Calculated from both the image and the diffraction pattern, the d spacings of these fringes were about 1.2 and 0.8 nm, respectively. The latter is similar to the d spacing observed by Inagaki et al.,³ from their crystal-like benzene-silica prepared under basic conditions and it is believed that the periodicity is related to the separation of the phenylene bridging molecules. The spacing of 1.2 nm must relate to the length of the molecules, that is, partial ordering parallel to the molecules. Unlike the observed wall structure of similar materials prepared under basic conditions,³ the ordering of the bridged molecules is not parallel to the pore axis, but with an angle of about 57°. Furthermore, there was only partial ordering of the molecules. This is why no sharp diffraction peaks of such ordering were observed in the XRD pattern.

Attempts to prepare samples with improved ordering within the pore walls were made by adding to the

synthesis procedure described above, another hydrothermal treatment whose duration and temperature were varied from 20 to 48 h and from 50 to 95 °C, respectively. This also included the preparation of samples under the same conditions as described above to check the reproducibility of the molecular order in the pore walls. Figure 6 shows the XRD patterns for samples prepared using an additional hydrothermal stage for 20 h at different temperatures. The XRD pattern of a sample prepared under the same conditions as above, that is, a single step at 50 °C for 20 h, is also shown (Figure 6a). The intensity of the XRD peaks was found to increase with the temperature of the additional hydrothermal treatment. This indicates that the long-

range order of the material improved; however, no extra sharp peaks appeared. Consistent with this observation, the corresponding PSDs (Figure 7) showed also a clear improvement as the temperature of the additional synthesis step increased. However, despite their enhanced long-range order, these materials exhibited no order within the pore walls. Nonetheless, the sample prepared with no additional hydrothermal treatment showed the same ordering in the pore walls as described above, indicating that the synthesis of periodic phenyl-bridged silica with novel ordering in the pore walls is reproducible.

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