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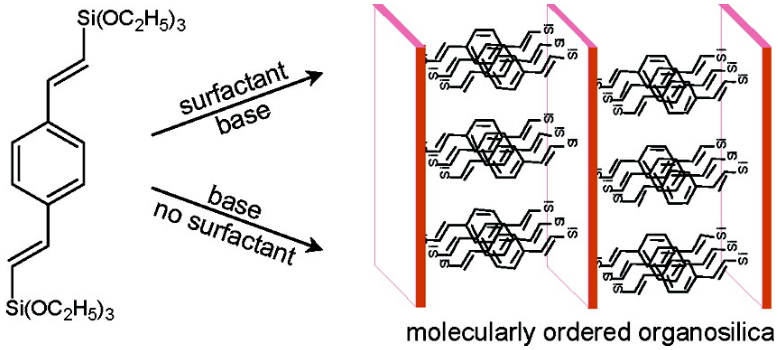

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COMMUNICATIONS

Molecularly Ordered Nanoporous Organosilicates Prepared with and without Surfactants

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Although work on periodic mesoporous organosilicas (PMOs) dealt overwhelmingly with ethanesilicas,[1] PMOs based on silsesquioxane precursors with organic spacers originating from methane, ethylene, acetylene, butene, benzene and substituted benzene, biphenyl, thiophene, bithiophene, ferrocene, and others have been achieved.[1−8] However, there are hardly any studies on pure PMOs with spacers containing more than a single organic functional group. Burleigh et al.[9] approached this issue by using mixtures of ethane and phenylene-containing silsesquioxane precursors. Another important aspect of PMOs containing aromatic linkers is the occurrence of molecular order within the pore walls. Inagaki et al.[3] found that periodic mesoporous 1,4-phenylene-bridged organosilica prepared under basic condition using octadecyltrimethylammonium chloride (ODTMACl) as structure-directing template exhibits, in addition to the (100), (110), and (200) reflections associated with the long-range order of the material with hexagonal symmetry, a series of XRD peaks at 7.6, 3.8, 2.5, and 1.9 Å. The latter were attributed to an additional structural periodicity with a spacing of 7.6 Å along the channel direction due to the $\pi-\pi$ stacking of bridging phenylene groups. Similar observations were made for phenylene-bridged PMOs prepared in the presence of alkyltrimethylammonium surfactants with different carbon chain lengths.[4] Moreover, Inagaki et al. found that other aromatic-containing precursors also lead, under basic conditions, to PMOs with similar molecular order.[5,6,10] However, molecular order within the pore walls of PMOs prepared under acid conditions was less striking,[2,7] but it could be improved by postsynthesis hydrothermal treatment in the presence of bases.[11]

The objective of the current investigation was 3-fold: (i) synthesize for the first time a PMO which contains an aromatic ring and two ethylene groups using BTSEB, bis(triethoxysilylethen-2-yl)benzene ($(C_2H_5O)_3Si-CH=CH-C_6H_4-CH=CH-Si(OC_2H_5)_3$), as a single precursor; (ii) establish the occurrence of molecular order within the pore walls of the PMO; (iii) demonstrate for the first time that the long-range molecular order may occur without surfactant templating effect and in the absence of a periodic pore system.

The precursor BTSEB was synthesized via the Heck reaction using vinyltriethoxylsilane and 1,4-dibromobenzene.[12] The BTSEB-derived PMO was prepared in the presence of ODTMACl using a gel with the following molar composition BTSEB:ODTMACl:NaOH:H_2O = 1:1.27:11.91:1318 (see Supporting Information). This sample will be referred to as **S**-BTSEB. Another sample denoted **NS**-BTSEB was prepared using the same procedure, except that no surfactant was added. A third sample designated **SG**-BTSEB was prepared in the absence of surfactant using a sol−gel method as described elsewhere.[13]

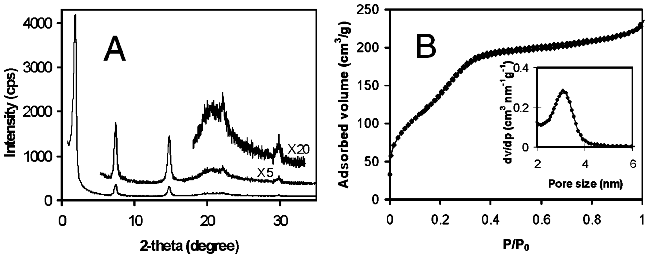

Figure 1. (A) X-ray diffraction pattern for **S**-BTSEB. (B) Nitrogen adsorption−desorption isotherm and pore size distribution (inset) for **S**-BTSEB.

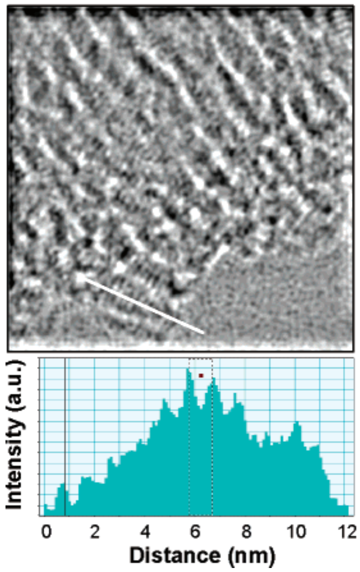

Figure 2. High-resolution TEM image for **S**-BTSEB and intensity across parallel fringes along the white line.

The XRD profile of the surfactant-free **S**-BTSEB sample (Figure 1A) exhibited a strong peak at 2θ = ca. 1.95° (d_{100} spacing of 4.82 nm) characteristic of long-range order in 2D hexagonal mesostructures. In addition, four other peaks at d spacings of 11.9, 6.0, 4.0, and 3.0 Å occurred. They were assigned to a periodicity with a spacing of 11.9 Å and higher-order harmonics. High-resolution TEM images provided direct evidence of such a molecular order (Figure 2) as lattice fringes with 12 Å spacing, close to the length of the organic linker, were clearly observed. This indicates that, driven by the $\pi-\pi$ interactions, the flat organic spacers are stacked parallel to each other, thus forming a lamellar structure within the PMO pore walls.

The nitrogen adsorption isotherm (Figure 1B) for **S**-BTSEB was typical of periodic mesoporous materials. It exhibited a sharp uptake at P/P_0 = 0.1−0.3 due to capillary condensation of nitrogen in the mesopores. The KJS (Kruk−Jaroniec−Sayari)[14] pore diameter (w_{KJS}), BET surface area, and pore volume were 3.06 nm, 563 m^2/g, and 0.34 cm^3/g, respectively. The pore wall thickness calculated using the equation $b = 2d_{100}/(3)^{1/2} - w_{KJS}$ was 2.51 nm.

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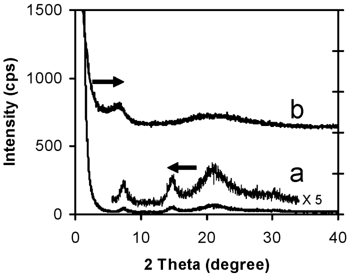

Figure 3. X-ray diffraction patterns for (a) **NS**-BTSEB and (b) **SG**-BTSEB (shifted upward by 200 units for clarity).

The ^{13}C CP MAS NMR spectra (Figure S1, Supporting Information) exhibited four strong peaks at 120.0, 126.7, 137.3, and 147.8 ppm. The peak at 120.0 ppm was assigned to the two carbon atoms of the ethylene groups, which bond to the silicon atoms. The peak at 126.7 ppm was due to the four carbon atoms of the phenylene ring, which are not connected to the ethylene groups. The peaks at 137.3 and 147.8 ppm were attributed, respectively, to the carbon atoms of the phenylene ring, which are connected to the ethylene groups, and the carbon atoms of the ethylene groups, which are linked to the phenylene ring. The ^{29}Si CP MAS NMR spectra (Figure S2, Supporting Information) exhibited only two main signals at −69.29 and −79.44 ppm, assigned to Si species covalently bonded to carbon atoms T^2 [C-***Si***(OH)(OSi)$_2$] and T^3 [C-***Si***(OSi)$_3$], respectively. The absence of SiO_4 species at ca. −100 ppm confirms that no carbon−silicon bond cleavage occurred during the synthesis or solvent extraction.

Surprisingly, sample **NS**-BTSEB prepared in the absence of the supramolecular templating effect of an amphiphile molecule also showed a distinct series of weak, but clearly visible diffraction peaks at 11.7, 5.9, 3.9 (shoulder), and 2.95 Å (Figure 3a), consistent with the occurrence of molecular order of the bis(ethene-2-yl)benzene moieties. However, no low-angle diffraction peak was observed, indicating the absence of mesoscopic structure. This material had a broad distribution of mesopores and exhibited a surface area of 202 m^2/g. Moreover, using sol−gel condensation in the presence of tetrabutylammonium fluoride catalyst at 55 °C, as described by Corriu et al.,[13] also afforded a high surface area (440 m^2/g) organosilica whose XRD pattern showed a broad, yet distinct peak at ca. 12.5 Å, indicative of a long-range molecular order (Figure 3b). Corriu et al. carried out extensive work on the anisotropic organization of organosilicas with rigid (e.g., aromatic) organic spacers prepared by sol−gel polymerization. As shown by small-angle X-ray scattering and birefringence measurements, these materials often exhibit only short-range order as no Bragg diffractions were observed.[13,15] However, long-range order was achieved only under special conditions, such as the occurrence of strong interactions by H-bonding[16] or of mesogen-like organic spacers.[17] Though more highly ordered, the lamellar structure of the pore walls described here is reminiscent of the structure obtained by solid-state thermal polycondensation of lamellar organo bis-silanetriols.[16d,e,18]

In conclusion, we reported the first example of pure PMO using a single precursor containing aromatic and olefinic functional groups. The occurrence of carbon−carbon double bonds and phenylene groups provides new opportunities for further chemical transformations within the pore walls. Moreover, we found for the first time that long-range molecular order can be achieved, regardless of the occurrence of a periodic pore system. Several other organosilicates containing aromatic rings exhibited similar behavior. These findings will be reported in a forthcoming paper.

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Supporting Information Available: Synthesis of BTSEB (precursor), synthesis of **S**-BTSEB organosilica, ^{13}C and ^{29}Si CP MAS NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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