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## Communications

### Periodic Mesoporous Organosilica with Large Cagelike Pores

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After the recent discovery of periodic mesoporous organosilicas (PMOs),<sup>1–4</sup> their synthesis, reactivity, structural characterization, and prospective applications

have received much attention.<sup>5–14</sup> PMOs were already found to be promising as catalysts,<sup>11</sup> templates for nanostructure synthesis,<sup>12</sup> and selective adsorbents.<sup>14</sup> There is currently a quest for expanding the pore size domain attainable for PMOs<sup>15–18</sup> because large-pore PMOs are of kin interest from the point of view of immobilization and encapsulation of large molecules.<sup>17,18</sup> Standard PMO synthesis using alkylammonium surfactants affords pore diameters below about 5 nm,<sup>1–4</sup> and pore diameters of PMOs templated by neutral amines<sup>19</sup> and oligomeric surfactants<sup>9,19–22</sup> were also found to be below this limit.<sup>9,19</sup> So the only large-pore

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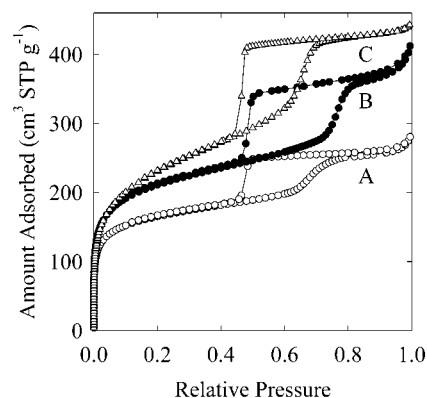
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PMOs reported to date were those templated using triblock copolymers.<sup>15–18</sup> With one exception,<sup>18</sup> these materials were either poorly ordered (as inferred from the reported data)<sup>15,17</sup> or it was necessary to mix the organosilicate precursor with an appreciable amount of silicate precursor to achieve structural ordering.<sup>16</sup> The only highly ordered large-pore PMO reported was ethanesilica with two-dimensional (2-D) hexagonal structure.<sup>18</sup> Herein, we report the successful synthesis of the first pure organosilica PMO with very large (about 10 nm) cage-like pores.

The PMO with large cage-like pores was synthesized using bis(triethoxysilyl)ethane (BTSE) precursor and poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) triblock copolymer template (B50-6600, EO<sub>39</sub>–BO<sub>47</sub>EO<sub>39</sub> from Dow Chemicals). This template was already employed in the synthesis of ordered FDU-1 silicas with cage-like pores using TEOS<sup>23</sup> and sodium silicate<sup>24</sup> as precursors. However, to achieve a well-ordered organosilicate structure, lower amounts of acid and polymer (relative to silicon content in the framework precursor), sufficiently high initial temperature, and subsequent aging at 373 K had to be employed; otherwise, products with poor adsorption properties (small adsorption capacity and/or broad pore size distribution) were obtained. The molar composition in the synthesis mixture was 1:0.00735:1:310 BTSE:B50-6600:HCl:H<sub>2</sub>O. For the synthesis, 0.5 g of the polymer was added to 5 g of 2 M HCl and 56 g of water and mixed at room temperature using magnetic stirring until a homogeneous solution was obtained. To this solution was added 3.54 g of BTSE and then the mixture was heated at 313 K for 24 h under stirring, during which time precipitation took place. The mixture was then transferred into a Teflon-lined autoclave and heated at 373 K for 6 or 12 h. Then, the precipitate was filtered and dried at room temperature to obtain as-synthesized material or washed with water, dried at room temperature, and calcined under nitrogen at 573 K for 10 h to remove the surfactant.

The bridging ethane groups in calcined products were intact, as shown using <sup>13</sup>C and <sup>29</sup>Si CP MAS NMR spectroscopy (Supplementary Figure 1, see Supporting Information). <sup>13</sup>C CP MAS NMR spectra provided evidence for the removal of most of the template during calcination, which was confirmed by thermogravimetry. The calcination is a convenient method for template removal,<sup>9</sup> but solvent extraction can also be employed.<sup>1–4</sup> Nitrogen adsorption isotherm for the material heated for 6 h at 373 K (Figure 1B) featured a broad hysteresis loop with a sharp capillary condensation step at a relative pressure of 0.77, and a very sharp capillary evaporation step centered at 0.485, which coincides with the lower limit of adsorption–desorption hysteresis.<sup>24</sup> The sharpness of the capillary condensation step indicates the narrow mesopore size distribution, whereas the location of the step at such high pressure provides evidence of a large pore diameter. Similar shapes of adsorption isotherms have been reported for FDU-1 silicas<sup>23,24</sup> and other ordered silicas with large cage-like mesopores.<sup>25,26</sup> This attests to the cage-like nature of the



**Figure 1.** Nitrogen adsorption isotherms for PMOs templated by poly(ethylene oxide)–poly(butylene oxide)–poly(ethylene oxide) copolymer at 313 K (A) and at 313 K and subsequently heated at 373 K for 6 h (B). Nitrogen adsorption isotherm for PMO templated by poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) copolymer, synthesized at 313 K, and further heated at 373 K for 24 h (C) is shown for comparison.

pores in the organosilica under study. The sample exhibited a BET specific surface area of 750 m<sup>2</sup> g<sup>−1</sup>, total pore volume of 0.62 cm<sup>3</sup> g<sup>−1</sup>, and pore diameter of about 10 nm (calculated from adsorption branches of isotherms as reported in ref 27). These structural parameters are similar to those reported for FDU-1 silicas.<sup>23,24</sup> In the case of the PMO studied here, it is not possible to exactly determine the pore entrance size on the basis of its nitrogen adsorption isotherm because capillary evaporation takes place at the lower limit of adsorption–desorption hysteresis, which merely indicates that the pore entrances are of diameter below about 5 nm.<sup>24</sup> However, it should be noted that, in the case of FDU-1 silica, the average pore entrance size was found to be in the range from 1 to 3 nm and increased as the synthesis temperature increased.<sup>28</sup> The height of the capillary condensation step was much smaller than the amount adsorbed at the onset of the step (Figure 1B), which strongly suggests that multilayer adsorption is not the only adsorption process occurring before capillary condensation commences. It is known that FDU-1 silica<sup>24</sup> and other polymeric-templated silicas<sup>29</sup> have microporous frameworks, and thus the presence of microporosity is the most likely factor that contributes to this adsorption behavior in the polymeric-templated PMOs. Figure 2 and Supplementary Figure 2 (see Supporting Information) show TEM images of selected areas of the large-pore PMO studied. Hexagonal arrays of dots and parallel lines, which are typical for a 2-D hexagonal structure, were observed, but fine contrast of TEM images suggests that the structure is three-dimensionally ordered. Although a definite assignment of the structure is very difficult because of the small ordered domain size, the images may be explained as projections of a cubic structure. Four peaks corresponding to the interplanar spacing of 13.8, 8.4, 5.3, and 4.8

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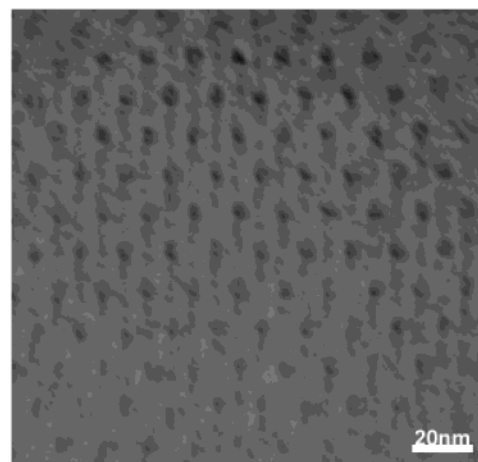
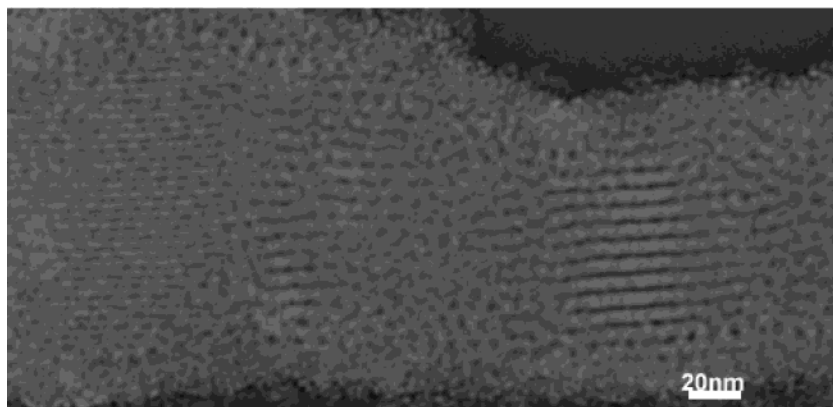
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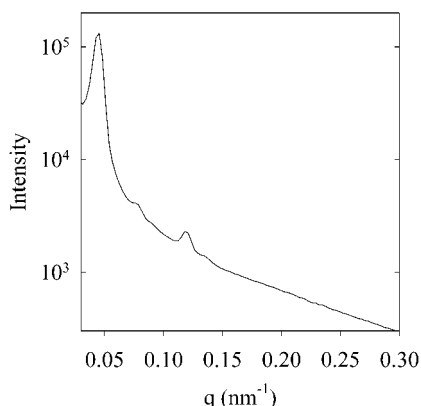
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**Figure 2.** TEM image of PMO from Figure 1B.



**Figure 3.** SAXS pattern for PMO from Figure 1B.

nm were observed on the small-angle X-ray scattering (SAXS) pattern (Figure 3) for this PMO (a detailed description of setup for the SAXS measurements can be found in ref 30), but no definite structural assignment can be made, although the pattern itself was quite similar to that acquired for FDU-1 silica.

The increase in aging time at 373 K to 12 h did not result in any appreciable changes in adsorption properties. However, the sample synthesized without aging at 373 K exhibited lower adsorption capacity and a broader capillary condensation step (Figure 1A). Moreover, when the initial 24-h stirring step was carried out at room temperature instead of 313 K, PMOs with less pronounced capillary condensation steps on their adsorption isotherms were obtained, indicating smaller volume and/or broader size distribution of ordered pores. But in all the cases, the hysteresis loops were broad, so the mesopores appeared to be cagelike.

Ethanesilica PMOs can also be synthesized using Pluronic P123 poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) template ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ; BASF) using the following synthesis mixture: 1:0.02:

5.81:200 BTSE:P123:HCl:H<sub>2</sub>O. After the synthesis mixture was heated at 313 K and the template was removed via calcination (essentially no cleavage of Si–C bonds was observed) or Soxhlett extraction, a product with a rather narrow capillary condensation step on the adsorption isotherm (Figure 1C) at pressure corresponding to the pore diameter of about 6.5 nm was obtained. The pore diameter was slightly enlarged to about 7 nm and the adsorption capacity was increased after aging at 373 K. This material exhibited an X-ray diffraction peak corresponding to an interplanar spacing of about 10.4 nm. A similar material was recently synthesized by others using P123 template.<sup>15</sup> The pore diameter of PMO synthesized using triblock copolymer P123 with poly(propylene oxide) block at 373 K is much lower than that of SBA-15 silica synthesized using the same template under similar conditions, whereas the pore diameter of PMO synthesized using the B50-6600 template with poly(butylene oxide) block is similar to that of FDU-1 silicas. This suggests that the organosilicate structure has a higher tendency than the silicate structure to occlude hydrophobic polymer chains, and thus the template with a more strongly hydrophobic block, such as the poly(butylene oxide) block, appears to be advantageous in the synthesis of large-pore PMOs, consistent with the results reported for mixed organosilicate–silicate frameworks.<sup>16</sup>

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**Supporting Information Available:** Figures (2) with <sup>13</sup>C and <sup>29</sup>Si CP MAS NMR spectra and TEM image (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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