Electronic Supplementary Information

Preparation of Periodic Mesoporous Organosilica with Large Mesopores Using Silica Colloidal Crystals as Templates

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Additional experimental details

Hydrolysis behavior of BTEE1

The mixture of BTEE1 (150 µL), EtOH (71.8 µL), H₂O (84.6 µL), and 0.1 M HCl (4.10 µL) (molar ratio of 1 BTEE1:3 EtOH:12 H₂O:0.001 HCl) was stirred at room temperature for 15 min. For ¹H NMR and ²⁹Si NMR measurements, 200 µL of this mixture, 400 µL of THF-d₈, 50 µL of TMS, and a small amount of Cr(acac)₃ (acac: acetylacetonate) were mixed in an NMR sample tube (5 mm φ). The measurement was started from ¹H NMR (accumulation number of 16 with a recycle delay of 5 s), followed by ²⁹Si NMR (accumulation number of 64 with a recycle delay of 10 s).

Treatment of SCC43-organosiloxane composite with NaOH aq. for varied durations.

Five sample bottles (volume 15 mL) were put on a hot plate placed within a filtration bell. SCC43 was added to each sample bottle and vacuum dried at 120 °C for 3 h. BTEE1 was partially hydrolyzed by stirring a mixture of BTEE1 2000 µL, EtOH 957 µL, H₂O 1128 µL, and 0.1 M HCl 54.7 µL (molar ratio of 1 BTEE1:3 EtOH:12 H₂O:0.001 HCl) at room temperature for 15 min. This hydrolyzed BTEE1 solution (190 µL) was added to each sample bottle containing dried SCC43 (1.00 g). After the evacuation at room temperature for 3 min, the same amount of hydrolyzed BTEE1 solution was added and vacuum dried for 1 h. The hydrolyzed solution of BTEE1 was prepared again and the same procedures for filling and drying were repeated. Subsequently, 13.3 mL of 1 M NaOH aq. (molar ratio of NaOH to SiO₂ in the template was 0.8:1.0) was added and the mixtures were heated at 80 °C for y hour(s) (y = 1, 8, 24, 96, and 167 h) in an oven. The samples were recovered by filtration and white solids were finally obtained.

Preparation of PMO43_BTEE1 (extended hydrolysis time of BTEE1)

BTEE1 was hydrolyzed by stirring a mixture of BTEE1 (380 µL), EtOH (182 µL), pure water (214 µL), and 0.1 M HCl (10.4 µL) (molar ratio of 1 BTEE1:3 EtOH:12 H₂O:0.001 HCl) at room temperature for 4 h. 197 µL (1/4 of the total amount) of this hydrolyzed solution was added to the dried SCC43 under a nitrogen atmosphere and was infiltrated and vacuum dried in the voids of the colloidal crystals for 3 min at room temperature. Then 197 µL of the same hydrolyzed solution was subsequently infiltrated and vacuum dried for 1 h. The same procedures for filling and drying were repeated using the rest of the hydrolyzed solution of BTEE1 (5 h after starting the hydrolysis reaction). Other procedures and conditions were same as those used for preparing PMO43_BTEE1.
**Calculation of residual ratio of silica and organosiloxane**

The mass ratio of organosiloxane and silica is calculated to be organosiloxane:silica = 1.00:1.01 on the basis of the integration ratio of T:Q = 1.00:1.11.

(Assuming that all added BTEE and Q species derived from silica colloidal crystals were hydrolyzed and polycondensed)

- Organosiloxane
  - Mass of organosiloxane in the obtained sample (0.3408 g)
  
  \[
  0.3408 \, g \times \frac{1.00}{1.00 + 1.01} = 0.1696 \, g 
  \]
  
  - Residual ratio of Si species of organosiloxane
  
  \[
  \frac{0.1696 \, g \times \frac{354.59}{132.22}}{0.566 \, g \text{ (Added BTEE1)}} \times 100 = 80 \%
  \]

- Silica
  - Mass of the silica in the obtained sample (0.3408 g)
  
  \[
  0.3408 \, g \times \frac{1.01}{1.00 + 1.01} = 0.1712 \, g 
  \]
  
  - Residual ratio of Si species of silica
  
  \[
  \frac{0.1712 \, g}{1.5359 \, g \text{ (Added Silica colloidal crystals)}} \times 100 = 11.1 \%
  \]
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Table S1 Integral ratio, and residual ratios of organosiloxane and silica.

<table>
<thead>
<tr>
<th>Hydrolysis time of BTEE1</th>
<th>T:Q (integration ratio)</th>
<th>Residual ratio of organosiloxane / wt%</th>
<th>Residual ratio of silica / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>1.0:1.2</td>
<td>21</td>
<td>3</td>
</tr>
<tr>
<td>15 min (normal condition)</td>
<td>1.0:1.1</td>
<td>80</td>
<td>11</td>
</tr>
<tr>
<td>4 and 5 h</td>
<td>1.0:1.6</td>
<td>69</td>
<td>14</td>
</tr>
</tbody>
</table>

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