Reversible replication between ordered mesoporous silica and mesoporous carbon

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Highly ordered mesoporous silica can be regenerated from a mesoporous carbon CMK-3 that is a negative replica of mesoporous silica SBA-15, indicating reversible replication between carbon and inorganic materials.

Ordered mesoporous materials such as MCM-41, MCM-48, SBA-15, etc.1,2,7 have attracted much attention due to their large pore diameters (2–30 nm),3 compared with those of conventional microporous zeolites (< 1 nm). It is well known that mesoporous materials are synthesised by the synergistic self-assembly between surfactant micelles and inorganic species to form mesoscopically ordered composites.1,4 Other templates assembly between surfactant micelles and inorganic species to mesoporous materials are synthesised by the synergistic self-assembly of surfactant micelles and inorganic species to form mesoscopically ordered composites.1,4 Other templates such as polymer beads,5 emulsions,6 etc. can be used for the generation of porous materials instead of the surfactant micelles. It is reasonable to divide the templating materials into two types: one is soft such as surfactant micelles and emulsions and the other is rigid such as polymer beads. The rigid templates are supposed to have excellent structure-directing abilities since it is not necessary to control the synthetic conditions (temperature, pH, concentration, etc.) for the pore formation. Therefore, the rigid templates are expected to be useful for the preparation of various types of mesoporous inorganic materials, especially transition metal oxides. However, it is difficult to find good rigid templates, in order to obtain mesoporous inorganic materials with well-ordered structure and high surface area.

Recently, a new series of ordered mesoporous carbons has been obtained by using mesoporous silica materials as templates.7,8,9 The mesoporous carbons exhibit ordered X-ray powder diffraction peaks indicating a highly ordered pore arrangement. This new type of materials with high surface area and uniform pores promise to be suitable as adsorbents, catalyst supports and materials for advanced electronics applications. Among the mesoporous carbon materials, CMK-3, obtained from SBA-15 mesoporous silica, is a precise inverse replica retaining the structural symmetry of the silica template.7 The CMK-3 is constructed with uniformly sized 1-D carbon rods, arranged in a hexagonal pattern and connected with each other.7 It is interesting to investigate the possibilities to employ the mesoporous carbons as templates for mesoporous inorganic materials because the carbons have well-ordered mesostructures and rigidity. Here, we present reversible replication between ordered mesoporous silica and ordered mesoporous carbons. We have explored the possibility that the mesoporous carbons can be used as templating materials for ordered mesoporous inorganic materials.

Mesoporous silica SBA-15 and mesoporous carbon CMK-3 were obtained following the procedures described elsewhere.7,8 A triblock polymer Pluronic P123 (EO20PO70EO20, Mn = 5800, BASF) was used as the structure-directing agent and anhydrous sodium metasilicate (Na2SiO3, Aldrich) was used as the silica source for the SBA-15 material.10 For CMK-3, calcined SBA-15 and sucrose were used as the template and the carbon source, respectively.7 The mesopores of the CMK-3 material were filled with Na2SiO3 by the wetness impregnation method. Typically, 1.0 g of the CMK-3 was slurried in an aqueous solution containing 2.0 g of Na2SiO3 at room temperature and subsequently the water was removed at 333 K by using a rotary evaporator. In order to polymerise the silica species and obtain inorganic frameworks, the samples were treated with HCl vapour in the chamber containing 1 M HCl aqueous solution at 373 K for 1 day. The products were washed with doubly distilled water, dried at 373 K in an oven and calcined at 823 K in air under static conditions to remove carbon templates.

Fig. 1(a), (b) and (c) show powder X-ray diffraction (XRD) patterns for the SBA-15, CMK-3 and silica replica from the CMK-3, respectively. All exhibit XRD patterns with a very intense diffraction peak and two or more weak peaks, which are characteristic of 2-D hexagonal (P6mm) structure.1,2,7 It is very interesting that the silica replica (Fig. 1(c)) obtained from the mesoporous carbon exhibits a highly ordered 2-D hexagonal structure. Moreover, the XRD pattern in Fig. 1(c) shows (210), (300) and (310) peaks, which indicates excellent textural uniformity of the silica replica. The result shows that the mesoporous silica can be regenerated by faithful negative replication from the mesoporous carbon. Further evidence for the 2-D hexagonal mesostructures of the silica replica is provided by the TEM images.

Fig. 2 shows nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves for the present mesoporous materials. All the isotherms in Fig. 2 are type IV with hysteresis loops. The isotherms for the SBA-15 and CMK-3 materials coincide with the data reported elsewhere.7,10 CMK-3, with mesopores of narrow size distribution, has well ordered hexagonal structures corresponding to the replication of the SBA-15. The silica replica obtained from the CMK-3 exhibits a

Fig. 1 XRD patterns for mesoporous materials: (a) SBA-15, (b) CMK-3 and (c) silica replica from the CMK-3. XRD patterns were collected with a Cu Kα X-ray source using a MAC instrument at room temperature.
Table 1 Physical properties of SBA-15, CMK-3 and silica replica

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice parameter/Å</th>
<th>Surface area/m² g⁻¹</th>
<th>Pore volume/cm³ g⁻¹</th>
<th>Pore size/Å</th>
<th>Wall thickness/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>11.99</td>
<td>776</td>
<td>1.27 (0.23)</td>
<td>8.11</td>
<td>3.88</td>
</tr>
<tr>
<td>CMK-3</td>
<td>10.69</td>
<td>1603</td>
<td>1.48 (0.46)</td>
<td>3.43</td>
<td></td>
</tr>
<tr>
<td>Silica replica</td>
<td>10.20</td>
<td>685</td>
<td>0.90 (0.21)</td>
<td>6.47</td>
<td>3.73</td>
</tr>
</tbody>
</table>

Notes and references


**Fig. 2** N₂ adsorption–desorption isotherms and corresponding pore size distribution curves for the mesoporous materials: (a) SBA-15, (b) CMK-3, (c) CMK-3 filled with silica and (d) silica replica from the CMK-3. The isotherms were obtained using an Autosorb-1 apparatus (Quantachrome) at liquid-N₂ temperature and pore size distributions were calculated by the BdB (Broekhoff and de Boer) method.™ Before the measurements, samples were degassed for 12 h at 550 K.