

Reversible replication between ordered mesoporous silica and mesoporous carbon

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Received (in Cambridge, UK) 23rd April 2002, Accepted 18th July 2002

First published as an Advance Article on the web 31st July 2002

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} 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 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.^{7–9} 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 possibility to use 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.^{7,10} A triblock polymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, M_{av} = 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

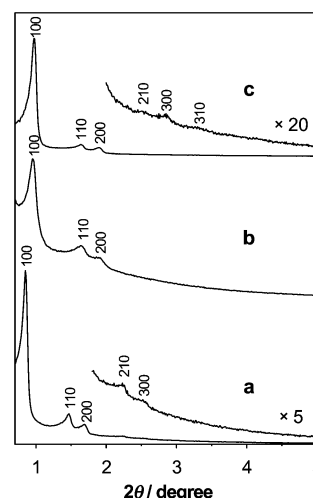


Fig. 1 XRD patterns for mesoporous materials: (a) SBA-15, (b) CMK-3 and (c) silica replica from the CMK-3. XRD patterns were collected with a Cu K α X-ray source using a MAC instrument at room temperature.

Table 1 Physical properties of SBA-15, CMK-3 and silica replica

Material	Lattice parameter ^a /nm	Surface area ^b /m ² g ⁻¹	Pore volume ^c /cm ³ g ⁻¹	Pore size ^d /nm	Wall thickness ^e /nm
SBA-15	11.99	776	1.27 (0.23)	8.11	3.88
CMK-3	10.69	1603	1.48 (0.46)	3.43	—
Silica replica	10.20	685	0.90 (0.21)	6.47	3.73

^a Lattice parameters calculated from d_{100} spacing in XRD patterns. ^b Surface areas calculated with the BET method. ^c Total pore volume calculated at $p/p_0 = 0.99$. Values in parentheses are microporous volumes (< 1.0 nm) of the materials. ^d Pore sizes obtained from N₂ adsorption isotherms following BdB analysis with a cylindrical model. ^e Wall thickness calculated by subtraction of pore sizes from lattice parameters.

very narrow pore size distribution. A well defined step in the adsorption and desorption curve appears between partial pressures p/p_0 of 0.6–0.7. The pore size distribution curve shows a mesopore with the pore diameter of 6.47 nm at the maximum of the distribution. The peak width of 0.40 nm, measured on the basis of the width at half-maximum for the pore size distribution, indicates that the material has well defined uniform pore dimensions.

It is noteworthy to look at the physical properties of the present materials in Table 1. A decrease in the lattice parameters of the materials can be expected due to the thermal treatment at high temperatures. The pore size of the CMK-3 is very similar to the wall thickness of the SBA-15 and the silica replica. These results indicate the reversible replications from silica to carbon and from carbon to silica materials. Carbon sources can be placed within the void mesoporous channels of the SBA-15, and subsequent removal of the silica framework results in the mesopores of CMK-3. In an opposite way, the void space of the CMK-3 is filled with silica species and the carbon rods give the mesopores in the silica replica by calcination. It is reasonable that the silica species are filled into the mesopores of the CMK-3 during the impregnation and become the silica framework of the silica replica material upon calcination. Based on the mesopores volume of the CMK-3 in Table 1 and the amount of the silica precursor, the wall density of the silica replica material

thus obtained can be calculated as 1.0 g cm³. This estimated wall density is in good agreement with the range of 0.8–1.6 g cm³ found for mesoporous materials, which is obtained from gas sorption and neutron diffraction measurements.¹¹ Additionally, the micropore volume of the SBA-15 is mostly maintained in the silica replica material (Table 1). This result indicates that the connecting carbons⁷ between the 1-D carbon rods of CMK-3, which are generated by micropores in the SBA-15, result in the micropore formation in the silica replica.

This novel reversible replication technique for the preparation of mesoporous materials is a remarkable achievement in the field of porous materials. Most researches have focused on silica as the framework constituent.³ The synthesis of mesoporous materials constructed with transition metal oxide frameworks has been less successful. One difficulty may be a facile crystallization of most transition metal oxides during the mesostructure formation and the removal of the organic templates.¹² In the present work, the CMK-3 can be successfully used as a rigid template for the formation of mesoporous silica. Various types of mesoporous inorganic materials such as alumina, titania, zirconia, *etc.* can also be obtained from the carbon template by using the present synthetic strategy. We are developing the optimum conditions in order to obtain highly ordered mesoporous inorganic materials. We believe that the rigid nature and well-defined mesoporosity of the mesoporous carbon help to form and stabilize inorganic frameworks before removal of the templates. Moreover, this technique promises the successful preparation of inorganic mesoporous materials with different pore connectivity and sizes, if carbon templates have different structures such as CMK-1, CMK-4 and CMK-5.^{8,9}

The authors are grateful for support by the Research Initiation Program at Ajou University (20012010) and the Department of Molecular Science & Technology through the Brain Korea 21 Project. Professor R. Ryoo at the Korea Advanced Institute of Science and Technology is acknowledged for the supply of the CMK-3 sample and fruitful discussions.

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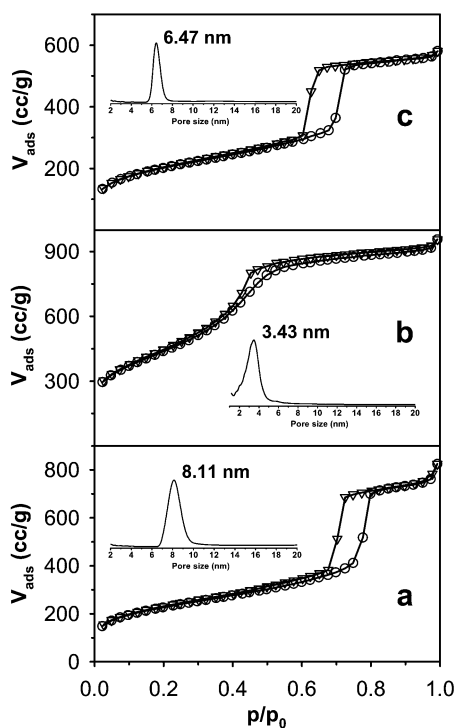


Fig. 2 N₂ adsorption-desorption isotherms and corresponding pore size distribution curves for the mesoporous materials: (a) SBA-15, (b) CMK-3, (c) CMK-3 filled with silica and (d) silica replica from the CMK-3. The isotherms were obtained using an Autosorb-1 apparatus (Quantachrome) at liquid-N₂ temperature and pore size distributions were calculated by the BdB (Broekhoff and de Boer) method.¹⁰ Before the measurements, samples were degassed for 12 h at 550 K.