

LETTERS

Synthesis of Highly Ordered Carbon Molecular Sieves via Template-Mediated Structural Transformation

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Ordered carbon molecular sieves exhibiting Bragg diffraction of X-ray lines have been synthesized for the first time, using mesoporous silica molecular sieves as the template. Sucrose was converted to carbon inside the mesopores of the silica molecular sieves through a mild carbonization process using a sulfuric acid catalyst. The carbon molecular sieves were obtained after the removal of the silica framework using an aqueous solution of sodium hydroxide. The X-ray diffraction, transmission electron microscopy, and pore size analysis showed that the structure of the carbon molecular sieves consisted of a three-dimensional regular array of uniform mesopores 3 nm in diameter. The structure was not simply a negative replica of the used silica template, but the synthesis mechanism involved the unique transformation into a new ordered array that was triggered by the removal of the silica frameworks. The highly ordered mesoporous texture suggested its scientific and technological importance as a new shape-selective catalyst, adsorbent, sensor, and electrode material.

The molecular sieves with ordered micropores such as zeolites have been used widely as catalysts, adsorbents and ion-exchange media.¹ Recently, there have been growing interests in the synthesis of new molecular sieves extending the pore diameter to the mesoporous region.²⁻⁴ The mesoporous molecular sieves are obtained with various structures and pore diameters that can be controlled over a wide range (1.6–30 nm). These new molecular sieves offer great potential for the shape-selective sensing, adsorption, and catalysis of large species that were limited by the micropores (typically less than 1 nm) of zeolites.^{1,5} Such materials attract also much attention as a new type of host for quantum particles and wires in nanotechnology.⁶

We report the first composition of ordered mesoporous molecular sieves with carbon framework. The synthesis was performed using sucrose as the carbon source and the cubic (*1a3d*) mesoporous silica molecular sieve referred to as MCM-

48⁷ as the template. Briefly, the mesopores in the silica molecular sieve were impregnated with sucrose and sulfuric acid using their aqueous solution. The silica material after the impregnation was heated to a desired temperature in the range of 1073–1373 K under vacuum or in an inert atmosphere. The sucrose was converted to carbon by such a process using sulfuric acid as the catalyst. Finally, the silica framework was removed by dissolution typically in aqueous solution containing NaOH and ethanol.⁸ The resultant porous carbon material is referred to as CMK-1. Elemental analysis gave the empirical formulas of C₁₂H₁O₁ and C₁₆H₁O₁ for CMK-1 materials obtained after heating at 1073 and 1373 K, respectively. These materials showed the complete loss of weight in air at 773 K during the thermogravimetric analysis, due to the combustion of carbon.

The transmission electron microscopy (TEM) for the carbon materials gave the regular pore image shown in Figure 1a. The TEM image from thin edges of the carbon particles shows that the carbon molecular sieve has a uniform pore distribution,

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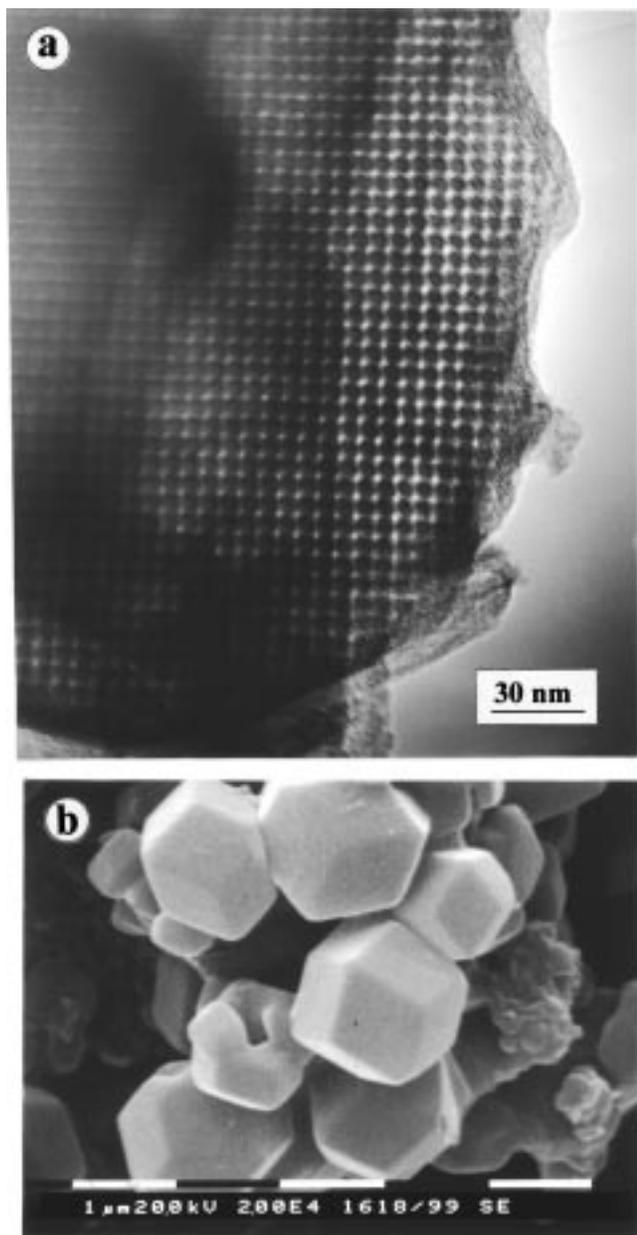


Figure 1. (a) Representative transmission electron micrograph of the ordered carbon molecular sieve CMK-1, obtained by the template synthesis with the mesoporous silica molecular sieve MCM-48. This image was obtained with a Philips CM20 transmission electron microscope operated at 100 kV from thin edges of a particle supported on porous carbon grid. (b) Scanning electron micrograph of a CMK-1 sample. This image was obtained on a Philips SEM-535M microscope using an acceleration voltage of 20.0 kV.

without carbon deposition on the external surface. The scanning electron microscopy showed that the porous carbon particles retained the crystal morphologies for the silica template as in Figure 1b.⁹ However, the template synthesis did not follow a simple replication process for the structure of the mesoporous silica. A systematic transformation of structure occurred during the removal of silica framework as revealed by its change in the powder X-ray diffraction (XRD) patterns obtained during the framework removal as in Figure 2. The XRD pattern taken prior to the framework removal was identical to that of the silica template MCM-48 except for lattice contraction and intensity loss. The lattice contraction usually occurs when the MCM-48 structure is subjected to heating at high temperature even without sucrose, while the intensity loss can be attributed to the pore

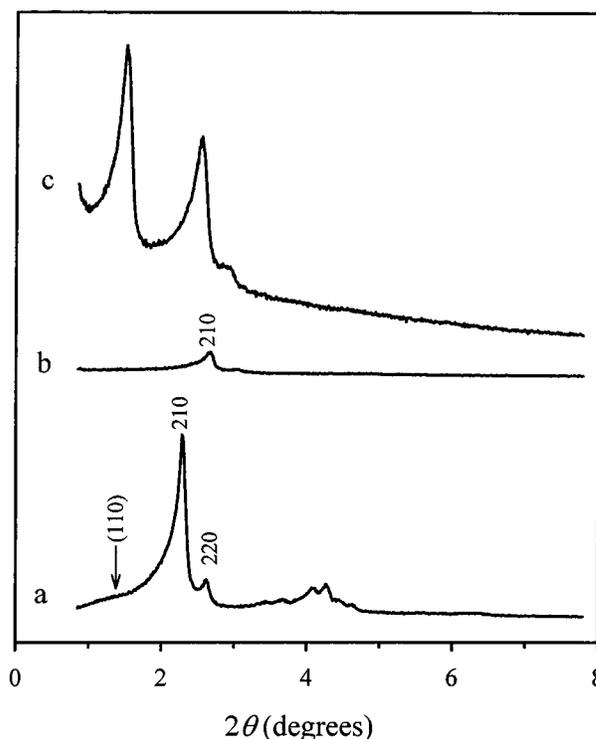


Figure 2. Changes in powder X-ray diffraction patterns during synthesis of the carbon molecular sieve CMK-1 with its silica template MCM-48: (a) The mesoporous silica molecular sieve MCM-48, (b) MCM-48 after completing carbonization within pores, and (c) CMK-1 obtained by removing silica wall after carbonization. These XRD patterns were obtained using a Rigaku D/MAX-III (3 kW).

filling with carbon. The intensity change in the XRD pattern indicates that both enantiomeric channel systems separated by the silica walls corresponding to periodic G-surface¹⁰ were statistically equally filled with carbon, maintaining the cubic *Ia3d* space group with inversion centers on the original G-surface. The removal of the silica wall caused a new peak to appear, which corresponded to the position of the (110) reflection for *Ia3d* (The (110) reflection is symmetrically forbidden for *Ia3d*). This change indicated that the structure of the resultant carbon underwent a systematic transformation to a new ordered structure that allowed this reflection such as cubic *I4₁32* or another as in Figure 3. The XRD pattern of CMK-1 showed no Bragg lines in the region 2θ greater than 10° , indicating that the carbon framework was atomically disordered.

Further structural information was provided by comparing the pore diameter of CMK-1 with that of the silica wall thickness in MCM-48. Argon adsorption–desorption isotherm and the corresponding pore size distribution for CMK-1 gave an inflection of the desorption characteristic of the capillary condensation within pores 3.0 nm in diameter, as shown in Figure 4. This pore diameter should have been equal to the wall thickness of MCM-48 if the carbon synthesis had followed simply a geometrical replication process. The silica wall thickness of MCM-48 was 1.3 nm as determined from the electron diffraction of MCM-48 single crystals.¹¹ However, the pore diameter of carbon was approximately twice the silica wall thickness. This difference showed that the structural transformation of the carbon frameworks took place upon the removal of the silica wall. The cause of the structural transformation might be attributed to strain in the carbon frameworks. A large contraction of volume might well occur if pyrolysis of organic compounds to carbon took place without the external constraints.

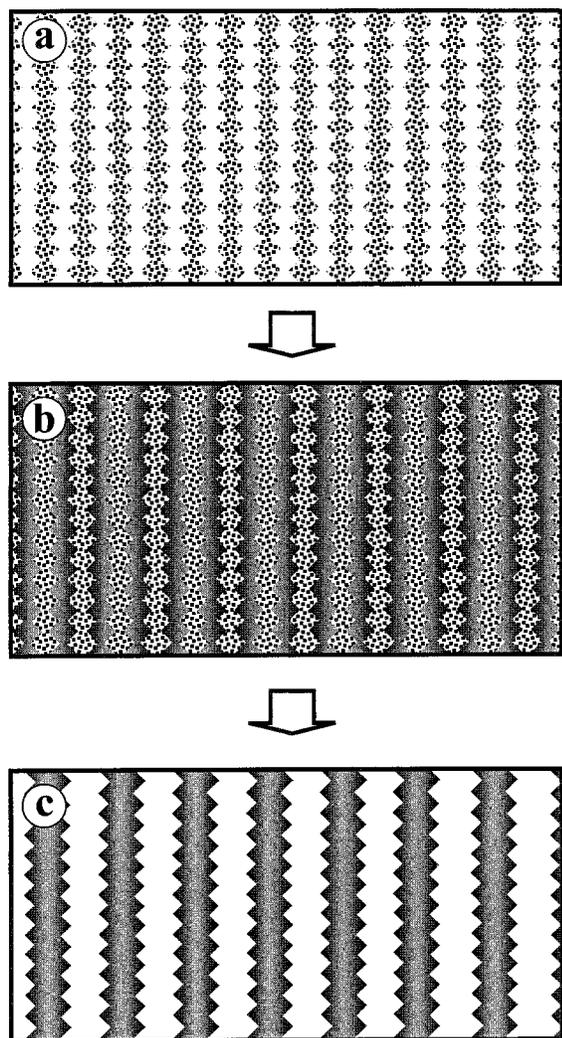


Figure 3. Schematic outline of the template synthesis procedure with silica molecular sieve: (a) The mesoporous silica molecular sieve MCM-48, (b) MCM-48 after completing carbonization within pores, and (c) CMK-1 obtained by removing the silica wall after carbonization.

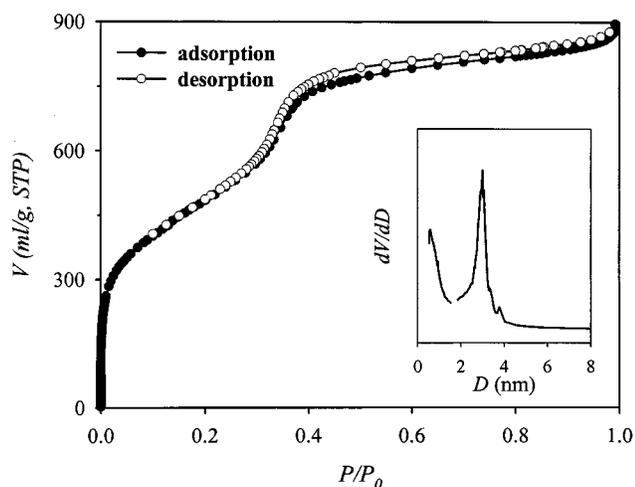


Figure 4. Argon adsorption-desorption isotherms at 87 K for the carbon molecular sieve CMK-1. Inset: The corresponding pore size distribution curves obtained from the desorption by the Barrett-Joyner-Halenda method (>1.7 nm), and the Horvath-Kawazoe analysis ($0.5-1.7$ nm).

Since silica frameworks in the MCM-48 channels prevented this kind of volume contraction, the resultant carbon frameworks

could be physically “frustrated”. When the silica framework was removed, the structural transformation might take place in order to relieve the “frustration” or strain. The strain-caused transformation was reasonable, similar to the mesophase transition to relieve the “frustration” in surfactant micelles in the liquid-crystalline state.¹²

The structure of CMK-1 contained micropores 0.5–0.8 nm in diameter in addition to the 3.0 nm mesopores. The total pore volumes corresponding to the micropores and mesopores were 0.3 and 1.1 $\text{cm}^3 \text{g}^{-1}$, respectively. The pore size distribution analyzed at various steps of the template synthesis showed that the micropores were formed in the amorphous carbon framework prior to the removal of silica wall, while the mesopores were formed upon the removal of the silica wall. The atomically disordered nature of the carbon framework was confirmed by Raman spectroscopy (broad lines at 1350 and 1590 cm^{-1}). Its chemical composition containing oxygen and hydrogen was similar to that of active carbon materials containing hydroxyl groups and carboxylic groups, which may be used to graft various organic and inorganic functional groups within the carbon pores. These structural properties with large specific surface area (BET area 1380 $\text{m}^2 \text{g}^{-1}$) suggest that the carbon molecular sieves can be useful as catalytic materials in the hydrophobic applications and adsorbents for the removal of organic pollutants, as well as the organic-sampling applications. Other applications such as for batteries and fuel cells may also be considered although their electrical properties have yet to be investigated.

The present synthesis technique is suitable for the production of carbon molecular sieves in a large industrial scale.¹³ The synthesis strategy can also be extended to the synthesis of other members of the carbon molecular sieves. For example, we have obtained a mesoporous carbon exhibiting a single XRD peak at $2\theta = 2.5^\circ$ using the mesoporous silica molecular sieve referred to as SBA-1. It has been confirmed that the sucrose can be substituted with various other organic compounds such as glucose, xylose, furfuryl alcohol, and in-situ polymerized phenol resin. When the furfuryl alcohol and phenol resin are used as the carbon source, the sulfuric acid catalyst should be substituted with the aluminum solid acid grafted on the mesopore wall. However, the structural order has not been so good in our experiment using the furfuryl alcohol and phenol resin as compared with the case of sugar.

Porous silica materials exhibiting structural periodicity are synthesized typically using organic amines, surfactants, block copolymers, or polymer beads as the template. Since nature favors the formation of a highly condensed phase, it becomes more difficult to achieve the periodicity as the diameter of the silica pore increases. In this regard, many recent research works are aimed at increasing the length scale of periodicity from that of zeolite to micrometers. On the contrary, the synthesis of porous carbon with structural periodicity becomes increasingly difficult as the pore diameter of the silica template decreases. This is because relatively larger amounts of organic carbon source per surface area of the pore wall can be infiltrated into macropores than micropores. The carbonization in macropores leads to a thick carbon coat that can remain stable and undergo no structural transformations upon the removal of the silica wall. Thus, the carbonization using organic polymer resins and hydrocarbon vapors is a convenient method for obtaining macroporous carbon nanotubes above 30 nm in diameter¹⁴ or arrays.¹⁵ However, if these carbon sources are used for the synthesis of microporous carbon, the resultant carbon framework tends to lose the structural order similar to previous results with

faujasite-type zeolites.^{16–18} In this case, the uniform infiltration of carbon is inhibited due to the pore blockage and limited space within the micropores.

Compared to the difficulty with the organic polymer resins and hydrocarbon vapors, the present carbonization process using sucrose and sulfuric acid is suitable for the facile and uniform infiltration of carbon into mesoporous silica. The carbonization technique may be comparable to the sol–gel process applied for the synthesis of metal oxides,¹⁹ in that the formation of the solid phase occurs uniformly under mild conditions at low temperature. The carbonization process may be suitable for extending the present research limit for carbon structures exhibiting three-dimensional periodicity toward the microporous region, as well as obtaining various new carbon structures.

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