

Synthesis of ordered mesoporous carbon molecular sieves CMK-1

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Abstract

Highly ordered mesoporous carbon molecular sieves designated as CMK-1 were synthesized using mesoporous MCM-48 silica with various pore diameters as templates, sucrose as a carbon source and sulfuric acid as the carbonization catalyst. The effect of the sucrose-to-sulfuric acid ratio on the structure of the resultant carbon, the effect of the pyrolysis temperature, and the optimum amounts of sucrose for MCM-48 with various pore diameters have been investigated. These results show that the synthesis method can be accurately controlled to obtain the highly ordered mesoporous carbon molecular sieves in a large scale. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, Ryoo et al. [1] reported the synthesis of mesoporous carbon molecular sieves exhibiting highly ordered X-ray powder diffraction (XRD) pattern. One member of this new series of mesoporous carbon materials, designated as CMK-1, was synthesized by using sucrose, furfuryl alcohol or phenol resin as the carbon source inside the cubic mesoporous silica molecular sieve MCM-48 [2] used as the template. Later, similar materials were reported using phenol resin as the carbon source [3,4]. Among the carbon sources, sucrose gave the best structurally ordered and the most easily reproducible results. In the synthesis, the sucrose was

impregnated into the mesopores of the MCM-48 silica with aqueous solution containing sulfuric acid. The impregnated sucrose was converted to carbon inside the MCM-48 pores under pyrolysis conditions. The sulfuric acid was added as the carbonization catalyst. After the carbonization was completed, the silica framework was removed using aqueous solution of NaOH or HF. The resultant CMK-1 carbon showed three distinct Bragg lines in the $1 \sim 4^\circ 2\theta$ region. The XRD pattern, transmission electron microscopy (TEM) and pore size analysis revealed that the porous texture of the carbon was not the negative replica of the MCM-48 silica but changed to a new cubic I4₃₂ structure [5] consisting of three-dimensional regular array of uniform mesopores 3 nm in diameter. The CMK-1 carbon also contained micropores in the mesopore walls [1,6]. Typically, the BET specific surface area was in the range of $1300 \sim 1800 \text{ m}^2 \text{ g}^{-1}$.

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The simplicity of the CMK-1 synthesis and the recent development of a facile method for the synthesis of MCM-48 silica template [7] have opened an opportunity of the large-scale production of CMK-1. More recently, the synthesis using mesoporous silica template has been extended to produce other CMK members such as of cubic Ia3d and hexagonal structures [8,9]. The carbon frameworks are hydrophobic and have great stability under hydrothermal conditions. The highly ordered mesoporous textures of these CMK carbons show new possibilities for applications as the shape-selective catalysts, adsorbents, separation materials, sensors, hydrogen container and electrode materials.

The outline of the CMK-1 synthesis was described in a previous communication paper [1]. The pore size distribution for CMK-1 was analyzed in a more recent report [6]. However, these reports dealt with the synthesis conditions only very briefly, skipping many important points such as the effect of the sucrose-to-sulfuric acid ratio on the structure of the resultant carbon, the effect of the pyrolysis temperature, and the optimum amounts of sucrose for MCM-48 with various pore diameters. We have therefore investigated these effects in the present work, and report here the results and the synthesis details.

2. Experimental

2.1. Preparation of MCM-48 template

Pure silica MCM-48 samples were obtained following the recently developed facile synthesis

method, which used Na silicate ($\text{Si/Na} = 2$) and cationic–nonionic surfactant mixtures [7]. The MCM-48 samples were denoted as $\text{C}_n\text{MCM-48}$ (where n is varied from 12 to 20) depending on the number of carbon atoms in the tail of the cationic surfactant. The syntheses were performed under different optimum conditions depending on C_n as given in Table 1. For example, the synthesis of $\text{C}_{16}\text{MCM-48}$ was carried out with $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$ and $\text{C}_{12}\text{H}_{25}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$. Aqueous solution of these surfactants was rapidly combined with the sodium silicate solution using a polypropylene bottle. The bottle was immediately capped and shaken vigorously for 2 ~ 5 min. This mixture was continuously stirred for a period of 30 ~ 60 min, using a magnetic or mechanical stirrer. The molar composition of the starting mixture was 5.0 SiO_2 :1.25 Na_2O :0.85 $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}$:0.15 $\text{C}_{12}\text{H}_{25}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$:400 H_2O . The mixture was then heated in an oven under atmospheric pressure at 373 K. No aging periods were given, and after heating for 60 h in the oven, the reaction mixture was cooled to room temperature for pH adjustment. The pH adjustment was performed by the addition of 0.58 mol of CH_3COOH per total Na present in the mixture, in a drop-by-drop manner with vigorous stirring. The reaction mixture after the pH adjustment was heated again for 48 h at 373 K. The product was filtered, washed with distilled water, dried at 393 K, washed with HCl–ethanol and finally calcined in air at 823 K, as reported previously [7].

2.2. Synthesis of CMK-1 using sucrose

The CMK-1 carbons are denoted as $\text{C}_n\text{CMK-1}$ with the same C_n notation as for MCM-48. Car-

Table 1
Optimum synthesis conditions for $\text{C}_n\text{MCM-48}^a$

Sample	Cationic surfactant	Neutral surfactant ^b	x^a	y^a	Reaction time before pH adjustment (h)
$\text{C}_{12}\text{MCM-48}$	$\text{C}_{12}\text{TMABr}$	$\text{C}_{12}(\text{EO})_3$	0.25	400	72
$\text{C}_{14}\text{MCM-48}$	$\text{C}_{14}\text{TMABr}$	$\text{C}_{12}(\text{EO})_4$	0.20	400	60
$\text{C}_{16}\text{MCM-48}$	$\text{C}_{16}\text{TMABr}$	$\text{C}_{12}(\text{EO})_4$	0.15	400	60
$\text{C}_{18}\text{MCM-48}$	$\text{C}_{18}\text{TMACl}$	TX-100	0.08	400	40
$\text{C}_{20}\text{MCM-48}$	$\text{C}_{20}\text{TMABr}$	TX-100	0.08	300	43

^a MCM-48 materials were obtained by the hydrothermal reaction at 373 K from the starting molar composition of $5\text{SiO}_2:1.25\text{Na}_2\text{O}:x$ neutral surfactant: $(1-x)$ cationic surfactant: $y\text{H}_2\text{O}$.

^b $\text{C}_{12}(\text{EO})_3$, $\text{C}_{12}(\text{EO})_4$ and TX-100 mean $\text{C}_{12}\text{H}_{25}\text{O}(\text{C}_2\text{H}_4\text{O})_3\text{H}$, $\text{C}_{12}\text{H}_{25}\text{O}(\text{C}_2\text{H}_4\text{O})_4\text{H}$ and $i\text{-C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}(\text{C}_2\text{H}_4\text{O})_{10}\text{H}$, respectively.

bonization experiments were performed with various amounts of sucrose and sulfuric acid per silica under various conditions. The synthesis parameters were individually optimized for each C_n so that the carbon product gave highest possible line intensity and resolution in the XRD pattern. For example, the optimum synthesis procedure for C_{16} CMK-1 was to dissolve 1.25 g sucrose and 0.14 g H_2SO_4 in 5.0 g H_2O , and to add this solution with 1 g MCM-48 [1]. The sucrose solution corresponded approximately to the maximum amount of sucrose and sulfuric acid that could be contained in the pores of 1 g MCM-48. The resultant mixture was dried in an oven at 373 K, and subsequently, the oven temperature was increased to 433 K. After 6 h at 433 K, the MCM-48 silica containing the partially carbonizing organic masses was added with an aqueous solution consisting of 0.75 g sucrose, 0.08 g H_2SO_4 and 5.0 g H_2O . The resultant mixture was dried again at 373 K, and subsequently the oven temperature was increased to 433 K. The color of the sample turned very dark brown or nearly black. This powder sample was heated to 1173 K under vacuum using a fused quartz reactor equipped with a fritted disk. The carbon–silica composite thus obtained was washed with 1 M NaOH solution of 50% ethanol–50% H_2O twice at 363 K, in order to dissolve the silica template completely. The silica removal was performed as rapidly as possible because prolonged contact of the carbon with the NaOH solution resulted in a significant loss of the XRD intensity, due to the absorption of NaOH. The removal of the silica template was also performed with HF solutions instead of NaOH. The carbon samples obtained after the silica removal were filtered, washed with ethanol and dried at 393 K.

2.3. Characterization

XRD patterns were obtained with a CuK_α source (Rigaku Miniflex instrument, 450 W). The BET specific surface area and the pore size distribution were determined by the N_2 adsorption isotherm measured at liquid nitrogen temperature. TEM images were obtained with a Phillips CM 20 transmission electron microscope operating at 100 kV. Powder samples were dispersed in ethanol for

the TEM measurement. One drop of the ethanol dispersion was dried on a porous carbon grid. Thin edges of the dispersed CMK-1 particles were taken for the TEM images.

3. Results and discussion

Fig. 1 shows the XRD patterns of high-quality C_n CMK-1 samples, which were obtained by the impregnation of sucrose in two steps under the optimum synthesis conditions given in Table 2. Fig. 2 shows a typical TEM image for the C_{16} CMK-1 sample. The XRD patterns and the TEM image indicate that the CMK-1 samples were composed with highly ordered uniform mesopores.

Carbon samples with completely featureless XRD patterns were obtained irrespective of the amount of sucrose when the sucrose impregnation was finished in a single step. This result indicates that the pore volume of the MCM-48 silica is not large enough to contain a sucrose quantity that

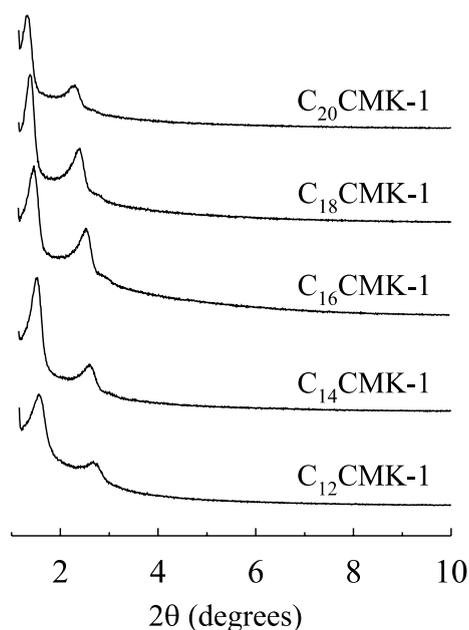


Fig. 1. XRD patterns for C_n CMK-1 ordered mesoporous carbon synthesized with sucrose and MCM-48 silica.

Table 2
Optimum synthesis conditions for C_n CMK-1^a

Sample	First step			Second step		
	Sucrose	H ₂ SO ₄	H ₂ O	Sucrose	H ₂ SO ₄	H ₂ O
C ₁₂ CMK-1	1.20	0.14	5	0.65	0.07	5
C ₁₄ CMK-1	1.25	0.14	5	0.65	0.07	5
C ₁₆ CMK-1	1.25	0.14	5	0.75	0.08	5
C ₁₈ CMK-1	1.50	0.17	5	0.80	0.09	5
C ₂₀ CMK-1	1.50	0.17	5	0.90	0.10	5

^a Numbers mean quantities in g per g MCM-48.

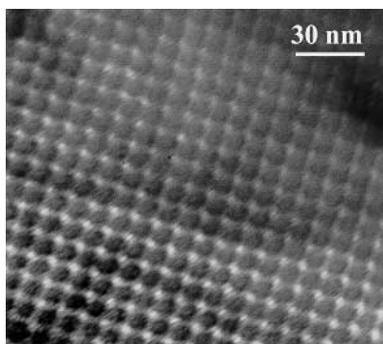


Fig. 2. Typical transmission electron micrograph of CMK-1 carbon.

can form a rigid carbon structure in the case of the single step impregnation. The pore volume of 1 g C₁₆MCM-48 silica is approximately 1 cm³ [10]. Theoretically, this pore volume can take up about 1.6 g of solid sucrose. However, since the sucrose was given as an aqueous solution containing sulfuric acid, the actual amount of the maximum quantity decreased to 1.25 g. Gravimetric analysis indicated that the 1.25 g sucrose was converted to 0.38 g carbon by the carbonization process. When sucrose more than 1.25 g was used in the single step, the carbon source exceeding 1.25 g could not enter the MCM-48 pores. The excess sucrose caused coagulation of the MCM-48 particles and consequently formation of nonporous amorphous carbon. Here, it is noteworthy that the sample was able to take up an additional quantity (0.75 g as given in Table 2) of sucrose after the 1.25 g sucrose was partially decomposed at 433 K inside the pores of the template. The 0.75 g quantity seemed to correspond to the maximum amount of sucrose that could be added into the pore volume gener-

ated by the sucrose decomposition at 433 K. When sucrose more than 0.75 g was impregnated, the resultant carbon showed a decrease in the XRD intensity.

The synthesis results using various amounts of sulfuric acid are shown in Fig. 3. These syntheses were performed following the same optimum two-step impregnation, as given in Section 2.2, except that the ratios between sulfuric acid and sucrose were varied. The XRD patterns show that the ordered porous structure was not obtained without

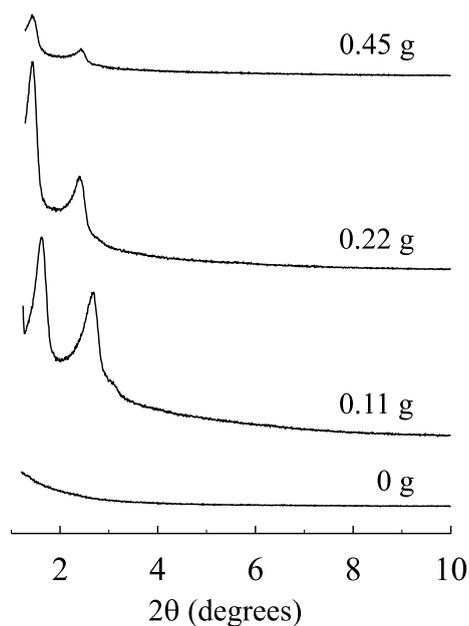


Fig. 3. XRD patterns for carbon synthesized with various amounts of H₂SO₄ per g sucrose.

sulfuric acid. The structural order was dramatically improved when 0.11 g sulfuric acid was added per g sucrose. This change seemed to be related to the conversion of sucrose to less hydrophilic species in the aqueous solution. As discussed above, 1.25 g sucrose was used per g MCM-48. This quantity of sucrose, which was somewhat less than to fill the total pore volume of MCM-48, was added to the template as dissolved in about four times the volume of the sucrose. While this sucrose solution was evaporated without sulfuric acid, a significantly large fraction of the sucrose was solidified outside the silica particles. This could be due to the strongly hydrophilic nature of sucrose. That is, the sucrose seemed to be too hydrophilic to enter the pores surrounded by the less hydrophilic silica frameworks. On this ground, we propose that the initial role of the sulfuric acid should be to convert the sucrose to less hydrophilic substances that can enter the silica pore during the evaporation of solvent in a drying oven. However, we believe that rapid decomposition of sucrose and subsequent polymerization to bulky polymers would make the precursor difficult to enter the pore if the amount of sulfuric acid exceeds the optimum point. A large part of the silica pore volume will also be occupied by the sulfuric acid. A large portion of carbon will then be formed outside the silica pores, resulting in a decrease in the XRD intensity. Thus, the amount of sulfuric acid is an important factor controlling the formation of the carbon inside the MCM-48 template. Although the carbonization starts under at low temperatures due to the sulfuric acid catalyst, the pyrolysis temperature should still be increased to at least 873 K. The pyrolysis below 773 K resulted in a featureless XRD pattern or weak diffraction intensities as shown in Fig. 4.

Fig. 5 shows synthesis results obtained by using furfuryl alcohol as a carbon source and the aluminosilicate form of MCM-48 as the template. In this synthesis, the MCM-48 template was first synthesized in the pure silica form. An aqueous solution of AlCl_3 corresponding to the Si/Al ratio of 20 was subsequently impregnated into the silica MCM-48 using the excess-solution wet impregnation technique [11]. This MCM-48 was calcined at 823 K before use as the template. The

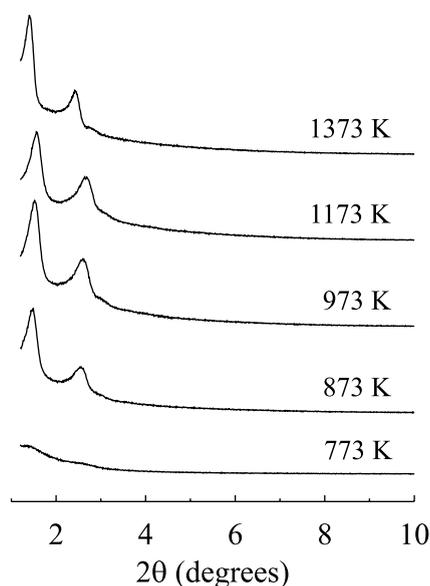


Fig. 4. XRD patterns for carbon obtained with various maximum pyrolysis temperatures.

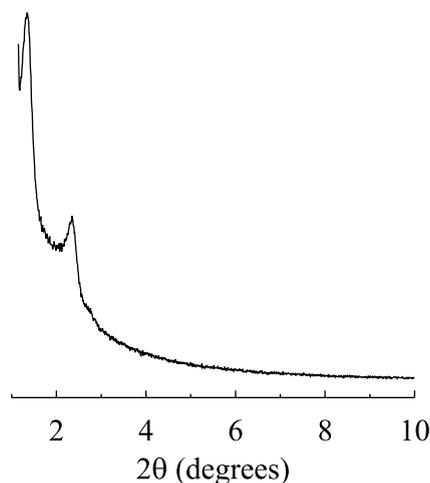


Fig. 5. XRD patterns for CMK-1 carbon synthesized from furfuryl alcohol and aluminosilicate MCM-48.

aluminosilicate template thus prepared was wetted with a sufficient amount of the liquid furfuryl alcohol. The carbon source was first polymerized and then converted to carbon while the temperature

was increased to 1173 K in N₂ flow or vacuum. Compared with this synthesis using furfuryl alcohol, the carbonization of sucrose had several advantages. First, the carbon source was impregnated using aqueous solution. Second, the template in the pure silica form was easier to synthesize than the aluminosilicate form. More importantly, the structural order of CMK-1 was better, which was probably due to the flexibility in controlling the amounts of sucrose through the two-step impregnation.

4. Conclusion

We investigated the various experimental parameters such as the sucrose-to-sulfuric acid ratio, the pyrolysis temperature and the optimum amount of sucrose for the synthesis of the CMK-1 mesoporous carbon. The well-defined synthesis information reported by the present work will be useful for obtaining the novel carbon materials for future applications. It is also expected that the facile synthesis method will be suitable for obtaining other carbon molecular sieves.

Acknowledgements

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