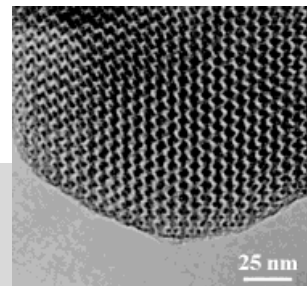# Ordered Mesoporous Carbons**

By *Ryong Ryoo,* *Sang Hoon Joo*, *Michal Kruk*, and *Mietek Jaroniec**

Ordered mesoporous carbons have recently been synthesized using ordered mesoporous silica templates. The synthesis procedure involves infiltration of the pores of the template with appropriate carbon precursor, its carbonization, and subsequent template removal. The template needs to exhibit three-dimensional pore structure in order to be suitable for the ordered mesoporous carbon synthesis, otherwise disordered microporous carbon is formed. MCM-48, SBA-1, and SBA-15 silicas were successfully used to synthesize carbons with cubic or hexagonal frameworks, narrow mesopore size distributions, high nitrogen Brunauer–Emmett–Teller (BET) specific surface areas (up to $1800 \ m^2 \ g^{-1}$), and large pore volumes. Ordered mesoporous carbons are promising in many applications, including adsorption of large molecules, chromatography, and manufacturing of electrochemical double-layer capacitors.

1. Introduction

Porous carbonaceous materials are important in many areas of modern science and technology, including water and air purification, gas separation, catalysis, chromatography, and energy storage.[1,2] This wide-spread use of porous carbons results from their remarkable properties, such as high specific surface areas, large pore volumes, chemical inertness, and good mechanical stability. Most porous carbons are primarily microporous[1–3] (pores will be classified herein, depending on their width, as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm)). Porous carbons are usually obtained via carbonization of precursors of natural or synthetic origin, followed by activation.[1] The microporous nature of the majority of porous carbons is well-suited to many applications, including molecular sieving, adsorption, and catalytic reactions of small molecules.[1,2] However, there are numerous other potential applications in which materials with carbonaceous surfaces would be attractive, for instance adsorption of large hydrophobic molecules (such as vitamins, dyes, humic acids, dextrins), chromatographic separations, electrochemical

double-layer capacitors, and lithium batteries. In these cases, the presence of wider pores, preferably in the mesopore range, would be advantageous.[3–9] Therefore, there has been recently a considerable interest in the synthesis of mesoporous carbons. There are several methods to achieve this goal, including: i) activation to high burn-off degrees;[10] ii) catalytic activation in the presence of certain metals;[11] iii) combination of physical and chemical activation;[6] iv) carbonization of polymer aerogels[12] or cryogels;[13] v) carbonization of polymer blends with one thermally unstable component;[3,14] vi) synthesis of multiwalled nanotubes;[15] and vii) infiltration of an appropriate template by carbon precursors, followed by carbonization and template dissolution.[16] Until recently, none of these synthesis approaches was shown to be suitable for the synthesis of mesoporous carbons with monodisperse pores of well-defined size and shape. Even multiwalled nanotubes that may exhibit the high degree of uniformity of internal diameter of single tubes were found to exhibit broad pore size distribution in the micropore and mesopore ranges, and relatively small surface areas, the latter being not only attributable to adsorption inside the tubes, but also to a large extent to adsorption on the external surface of the tubes.[17]

2. Templated Porous Carbons

Two decades ago, Knox et al. reported that silica gel can be impregnated with polymer precursors that can be polymerized to form a continuous network surrounding the silica particles.[16] The carbonization of the polymer coating and the subsequent dissolution of the silica gel template rendered a mesoporous carbon with a rigid structure featuring also some micropores. The material exhibited a specific surface

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area on the order of 500 m^{2}g^{-1} and a large total pore volume (2 cm^{3}g^{-1}). The carbon can be further graphitized, affording a rigid carbon structure of appreciable degree of graphitization and a specific surface area of about 150 m^{2}g^{-1}. Since the carbon retained the particle shape of the template, it was possible to prepare the graphitized carbon in the form of spherical particles of size suitable for high-performance liquid chromatography (HPLC) applications. This type of HPLC packing is currently commercially available. Subsequent studies showed that preformed silica gels[7,18,19] as well as silica gels formed in-situ via sol–gel processing[9] are suitable templates for the synthesis of carbons with high surface areas and large mesopore volumes.

The work on carbon templating using amorphous silica gels was followed by the successful synthesis of microporous carbons using layered materials,[20] and templating with anodic alumina with disconnected nanochannels afforded carbon nanotubes.[21] Zeolites with three-dimensional pore structures were also found to be suitable as templates,[22–24] whereas zeolites with one-dimensional structures were not effective.[23] Some of the resulting carbons exhibited remarkably high specific surface areas despite the fact that the carbonization was not followed by activation, usually necessary to develop such well-accessible microporous structures. These carbons obtained using zeolite templates with three-dimensional pore structures retained the shapes of zeolite particles, but did not retain their internal periodic structure (the method to circumvent the latter problem has been reported very recently, as will be discussed later). In contrast, templating with synthetic siliceous opals with ordered structures was successful in providing ordered macroporous carbons,[25] but unfortunately there is currently no clear way to prepare such templates suitable for the synthesis of ordered mesoporous carbons.

3. Ordered Mesoporous Carbons

The recent discovery of ordered mesoporous materials (OMMs) provided a new generation of silica templates[26–30] suitable for the synthesis of mesoporous carbons, possibly with ordered mesoporous structures. Ryoo et al. first realized this opportunity,[31] synthesizing ordered mesoporous carbon (denoted CMK-1) using MCM-48 silica of *Ia*3*d* symmetry,[26] which exhibits porous structures consisting of two disconnected interwoven three-dimensional pore systems.[27,32] MCM-48 was impregnated with sucrose in the presence of sulfuric acid, the resulting mixture was dried at 373 K and subsequently at 433 K, and then the impregnation/drying step was repeated once. The obtained sample was carbonized under vacuum at 1173 K and finally the silica template was dissolved at 373 K in aqueous/ethanol solution of NaOH. Other carbon

precursors were also found to be suitable for CMK-1 synthesis, including glucose, xylose, furfuryl alcohol, and in-situ polymerized phenol resin. In the case of the latter two precursors, the aluminosilicate form of the template was required to ensure facile carbonization, and sulfuric acid was not used. CMK-1 carbon exhibits an X-ray diffraction (XRD) pattern with several sharp low-angle reflections (Fig. 1) corresponding to cubic structure[31] with a unit cell parameter of about 8–9.5 nm.[33] The periodic nature of CMK-1 was confirmed using transmission electron microscopy (TEM)[31] (see Fig. 2). CMK-1 exhibits a high nitrogen Brunauer–Emmett–Teller (BET) specific surface area (1500–1800 m^{2}g^{-1}) and a large total pore volume (0.9–1.2 cm^{3}g^{-1}),[31,33] and its adsorption capacity is comparable or larger than that of MCM-48 template (see Fig. 3). Argon[31] and nitrogen[33] adsorption isotherms of CMK-1 featured well-pronounced capillary condensation steps similar (although somewhat less steep) to those observed on adsorption isotherms of ordered mesoporous silicas[26,29,30] (see Fig. 3) and indicative of a high degree of mesopore size uniformity. Typical CMK-1 has uniform mesopores about 3 nm in size (Fig. 4), which are accompanied by a certain amount of micropores. The periodic structure of CMK-1
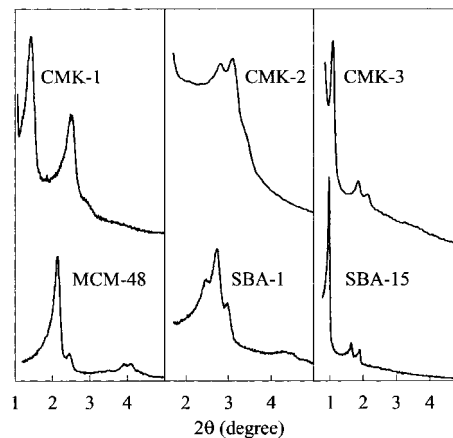

Fig. 1. Powder XRD patterns for the ordered mesoporous silica templates and the corresponding templated ordered mesoporous carbons (data taken from [33,36,40]).
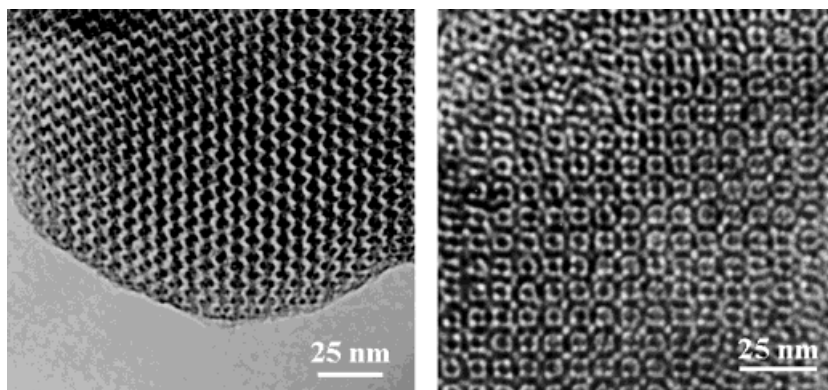

Fig. 2. TEM images of CMK-1 viewed from the (111) direction (left), and CMK-2 viewed from the (100) direction (right).
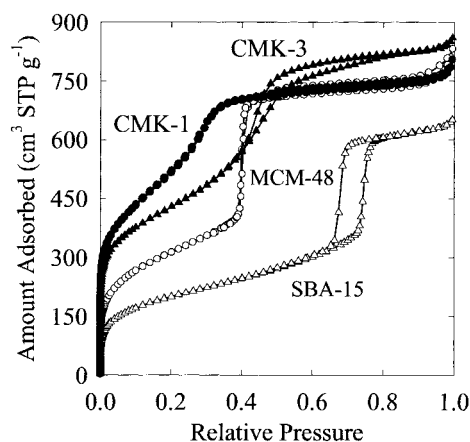
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Fig. 3. Nitrogen adsorption isotherms of selected ordered mesoporous carbons and the corresponding silica templates (data taken from [33,36]).
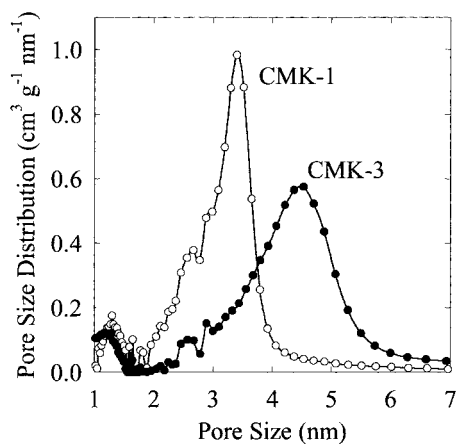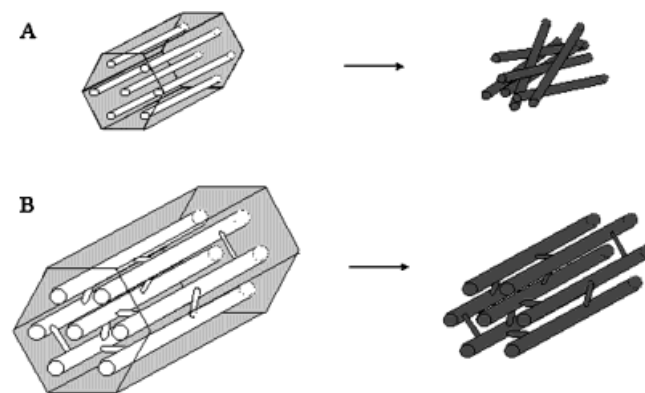

Fig. 4. Pore size distributions of selected ordered mesoporous carbons (data for CMK-3 taken from [36]).

is somewhat different from that of the MCM-48 template (see XRD patterns shown in Fig. 1). Apparently, a structural transformation accompanies the template dissolution,[31] as can be expected[31,33] from the fact that the template features two disconnected porous systems separated by the silica wall.[27,32] The carbon structures formed in these two porous systems are obviously also disconnected and are capable of changing their position with respect to one another when the template is removed.[31,33] An additional drawback of MCM-48 templating is that it is difficult to tailor the size of ordered pores. It is expected to be possible to tailor the CMK-1 pore size by varying the template pore wall thickness, but the latter was found to be relatively constant for different MCM-48 samples and therefore such templates of different pore sizes and unit-cell sizes afforded ordered carbons of very similar mesopore size.[33] The synthesis of MCM-48-templated ordered mesoporous carbon was also accomplished by another research group[34] and the account of their work was submitted for publication just three months after the submission of the original work of Ryoo et al.[31]

As expected from earlier studies on zeolites,[22–24] the most popular OMM, i.e., MCM-41 silica with a hexagonally or-

dered structure of approximately cylindrical one-dimensional pores, was found unsuitable as a template for ordered mesoporous carbon synthesis, and indeed its application yielded disordered high-surface-area microporous carbon[33,35] (see Scheme 1).

Scheme 1. Schematic illustration of formation of A) disordered carbon using a template with disconnected pores (MCM-41, or alternatively SBA-15 calcined at temperatures of about 1243 K), and B) ordered CMK-3 carbon using a template with an interconnected pore system (for instance SBA-15 calcined at temperatures below about 1173 K).

The first ordered mesoporous carbon that was a faithful replica of the template was synthesized[36] using SBA-15 silica[30] as a template. This choice of the template was far from obvious, since SBA-15 was initially reported[30] and later widely believed to exhibit a structure with disconnected channel-like pores, similar to MCM-41. Surely, such a structure would not be suitable for templating an ordered mesoporous carbon, as discussed above and additionally demonstrated below. However, our studies of SBA-15 silica provided strong evidence that the aforementioned initial identification of SBA-15 actually missed one important structural detail—the existence of connecting micropores and small mesopores in the walls of large-pore channels of SBA-15.[37] This identification of the SBA-15 structure facilitated the synthesis of the first ordered mesoporous carbons (referred to as CMK-3), whose structure was a faithful replica of the ordered silica template, as shown by XRD (see Fig. 1) and high-resolution TEM.[36] The material consisted of uniformly sized carbon rods arranged in a hexagonal pattern (see Scheme 1). The arrangement of connections between these rods will require further studies. Similarly to CMK-1, CMK-3 exhibited large adsorption capacity (see Fig. 3), with a nitrogen BET specific surface area of about 1500 $m^2 g^{-1}$ and total pore volume of about 1.3 $cm^3 g^{-1}$. CMK-3 has a primary pore size of about 4.5 nm, as was consistently determined by TEM and nitrogen adsorption. The primary pores were accompanied by micropores and some secondary mesopores. As expected from the fact that the SBA-15 pore wall is thicker than that of MCM-48, the CMK-3 pore size was larger than that of CMK-1 (see Fig. 4).

CMK-3 can be obtained when the SBA-15 template is calcined at 1153 K prior to carbon precursor infiltration even though this calcination procedure leads to a large structural

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shrinkage and to significant depletion of the micropores and small mesopores that are responsible for the connectivity between the SBA-15 large pore channels.[38] In contrast, SBA-15 calcined at somewhat higher temperature (1243 K) afforded disordered carbon.[38] Apparently, the connecting pores in the SBA-15 structure were so depleted that the formation of connections between carbon rods was prevented and the carbon structure collapsed upon silica template dissolution, as illustrated in Scheme 1. It is interesting to note that the suitability of SBA-15 template for CMK-3 carbon synthesis can be assessed by examining a relation between the pore size, specific surface area, and pore volume for a given SBA-15 sample. If this relation is similar to that for MCM-41, the CMK-3 structure is not expected to form. On the other hand, if SBA-15 exhibits a larger specific surface area than that characteristic of uniform approximately cylindrical pores of the particular size and volume, the presence of connecting pores is indicated and the formation of three-dimensional CMK-3 carbon is expected.[38]

The initial studies on ordered mesoporous carbon synthesis[31] showed that it is possible to obtain such material using an SBA-1 template of *Pm3n* cubic structure with two different kinds of mesoporous cages.[28,39] However, the resultant carbon exhibited a low degree of structural ordering, which manifested itself in the occurrence of only one peak in the XRD pattern for this material. Since then, the synthesis procedure has been improved and an SBA-1-templated carbon (denoted CMK-2) with an XRD pattern similar to that of SBA-1 has been obtained (Fig. 1).[40] The TEM image of CMK-2 clearly shows retention of the cubic structure characteristic of the SBA-1 template (see Fig. 2).

Other recent developments in the field of templated carbons include the syntheses of i) disordered mesoporous carbon with narrow pore size distribution[35] using an HMS silica template[29] and ii) ordered zeolite-templated microporous carbon.[41] The successful synthesis of the latter was achieved by improving carbon loading through two-step infiltration via impregnation with furfuryl alcohol and subsequent carbonization, followed by chemical vapor deposition of additional amount of carbon from propylene pyrolysis. This led to the formation of carbon that retained the (111) plane ordering of zeolite Y template, as seen from XRD and TEM, and exhibited a nitrogen BET specific surface area as high as 1900 $m^2 g^{-1}$. Clearly, there are vast opportunities in the synthesis of mesoporous and microporous carbons with narrow pore size distributions using the templating procedures.

The templated synthesis of ordered mesoporous carbons, and in particular those constituting faithful replicas of the templates, is a remarkable achievement in the field of porous materials. The resulting high-surface-area materials with uniform pores promise to be suitable as adsorbents, catalyst supports, and materials for advanced electronics applications. Their remarkable performance as electrochemical double-layer capacitors has already been reported.[34,35] The methods developed for the synthesis of ordered mesoporous carbons are simple and cost-efficient.[31] CMK-3 carbon is particularly

promising because of the fact that SBA-15 template is inexpensive[42] and easy to synthesize,[30] and its pore wall thickness can be readily tailored,[30] the latter feature being promising for the point of view of CMK-3 pore size tailoring. Recent work on the synthesis of MCM-48[43] and SBA-1[44] has also brought about much improvement in the cost-effective and custom-tailored syntheses of these templates. Moreover, advances in the methodology of structural characterization of ordered mesoporous silicas[32,37–39] are expected to largely facilitate the identification of additional promising templates for the mesopore carbon synthesis. On the other hand, examination of the carbon synthesized using a given silica template provides a lot of information about the structure of that template, and therefore this approach can be used as a powerful tool to characterize ordered mesoporous silicas.[35,38]

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