Preparation of Novel Mesoporous Carbon Materials with Tunable Pore Diameters Using Directly Synthesized AlSBA-15 Materials

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Large pore mesoporous carbon materials (MCA) have been prepared from AlSBA-15 templates synthesized at different temperatures. The obtained materials have been unambiguously characterized by XRD, HRTEM, and N_2 adsorption. It has been found that the specific surface area, pore volume and pore diameter of the MCA materials are higher as compared to CMK-3 mesoporous carbon.

Porous carbon materials have been received much attention in recent years because of their applications in many areas, such as gas separation, adsorption of small gas molecules, catalysis, energy storage, and capacitors.[1] Especially the development of mesopores in the carbon materials has attained significant importance because it allows the adsorption and separation of large biomolecules and ions that are too large to enter micropores.[2] The porous carbons with uniform and tunable mesopore sizes are indispensable not only for the adsorption of large biomolecules but also for a new applications such as electrical double layer capacitors. Recently, Ryoo et al. prepared ordered mesoporous carbons (CMK-x) from mesoporous silica templates such as MCM-48, SBA-1, and SBA-15 using sucrose as the carbon source.[2–6] Independently and somewhat later, similar approaches were published by Hyeon et al. (the materials were designated SNU-x.)[7,8] However, the preparation of well-ordered large pore mesoporous carbon with reliable control of pore structure parameters, such as specific pore volume, specific surface area and pore diameter, is critical for the envisaged application in the adsorption and separation of giant molecules such as proteins and enzymes.[9–12]

Recently, Vinu et al. have reported the synthesis of large pore mesoporous silica, SBA-15 and aluminosilicates, AlSBA-15 with variable pore diameters prepared by changing the synthesis temperature.[13,14] These materials possess well-ordered pore structure, high specific pore volume, surface area, and large pore diameter. We have also transformed the mesoporous silica into mesoporous carbons with various pore diameters using SBA-15 as the template and studied their protein adsorption capacity.[2] In this communication, we report for the first time the preparation of highly ordered large pore mesoporous carbons with fine tunable pore diameters using directly synthesized AlSBA-15 with various pore diameters as the template. In this case, AlSBA-15 acts as both an acid catalyst for carbon source polymerization as well as the template.

The large pore mesoporous carbons were prepared by using AlSBA-15 materials as templates synthesized at different temperatures and sucrose as the carbon source. The obtained materials were designated MCA-100, MCA-120, and MCA-130 where the number indicates the synthesis temperature of the AlSBA-15 template. In a typical synthesis of mesoporous carbon, 1 g of template (mesoporous silica material) was added to a solution obtained by dissolving 1.25 g of sucrose in 5 g of water, and keeping the mixture in an oven for 6 h at 100 °C. Subsequently, the oven temperature was raised to 160 °C for another 6 h. In order to obtain fully polymerized and carbonized sucrose inside the pores of the silica template, 0.8 g of sucrose, 0.09 g of H_2SO_4 and 5 g of water were again added to the pretreated sample and the mixture was again subjected to the thermal treatment described above. The template–polymer composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 6 h to carbonize the polymer. The mesoporous carbon was recovered after dissolution of the silica framework in 5 wt % hydrofluoric acid, by filtration, washed several times with ethanol and dried at 120 °C. Thermogravimetric analysis of all the mesoporous carbon samples up to 900 °C in flowing air found less than 1.5% residue, indicating that almost all silica is removed from the carbon after the HF treatment.

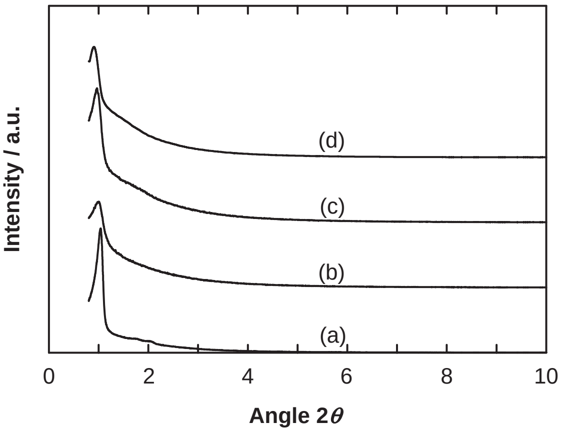

Figure 1. XRD powder patterns of different mesoporous carbon samples: (a) CMK-3,[5] (b) MCA-100, (c) MCA-120, and (d) MCA-130.

Figure 1 shows the powder XRD patterns of MCA samples prepared using AlSBA-15 templates synthesized at different temperature. All exhibit XRD patterns with a very strong intense diffraction peak, which is characteristic of unidimensional hexagonal structure (*P*6*mm*).[14] The result also shows that the obtained materials are a replica of the parent AlSBA-15 template. The length of the hexagonal unit cell a_0 is calculated using the formula $a_0 = 2d_{100}/\sqrt{3}$. It is interesting to note that the unit cell constant of the MCA materials increases with increasing the pore diameter of the template. It can also be seen from the Table 1 that the unit cell constant of MCA-130 is higher as compared to that of MCA-100.

To further confirm the mesoporous nature of the different mesoporous carbon adsorbents, we have observed HRTEM of

Table 1. Textural parameters of MCA mesoporous carbons prepared using AlSBA-15 templates

Materials	T/ °C[b]	a_o/ nm	A_{BET}/ m^2/g	d_p, BJH/ nm	$V_p/cm^3/g$
CMK-3[a]	100	10.1	1260	3.0	1.10
MCA-100	100	10.2	1700	3.6	1.50
MCA-120	120	10.5	1630	4.0	1.55
MCA-130	130	11.3	1605	4.9	1.65

[a] Prepared using SBA-15 template; [b] Temperature used for the synthesis of AlSBA-15 templates.

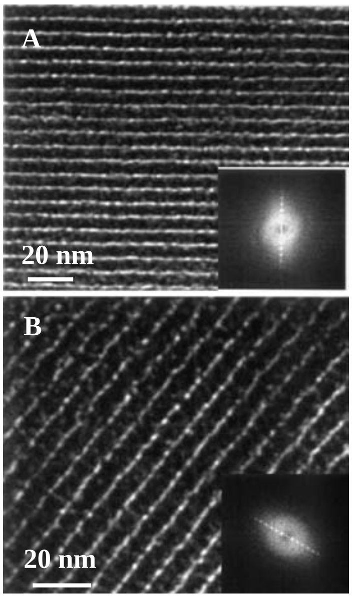

Figure 2. HRTEM images of (A) MCA-100 and (B) MCA-130.

different mesoporous carbon samples. Figure 2 shows the HRTEM images for MCA-100 and MCA-130 with the corresponding Fourier transforms in the lower right corners. Both materials show the well-ordered mesoporous channels that are arranged in the linear way and are separated by thick walls. These results also support the conclusion from XRD analysis that all the materials have well-ordered mesoporous structure.

Figure 3 shows the nitrogen adsorption–desorption isotherms and the corresponding BJH adsorption pore size distribution curves for MCA-100, -120, and -130 in comparison to CMK-3[5] which was prepared using pure silica SBA-15 as the template. All the isotherms in Figure 3 are of type IV with H1 hysteresis loops and exhibit a high degree of structural ordering, as indicated by the steep capillary condensation step of the respective adsorption isotherm. Specific surface area and specific pore volume significantly change with increasing the pore diameter of the AlSBA-15 template. The specific surface area amounts to 1700 m^2/g for MCA-100 and decreases to 1605 m^2/g for MCA-130, while the specific pore volume increases from 1.5 to 1.65 cm^3/g for the same samples. Pore size distribution curves show that all the MCA materials possess well-ordered mesopores with uniform pore dimensions. The pore diameter of MCA-130 is 4.9 nm which is 1.3 nm higher than the pore diameter of MCA-100, while the pore diameter of MCA-120 is 4.0. These results indicate that one can finely tune

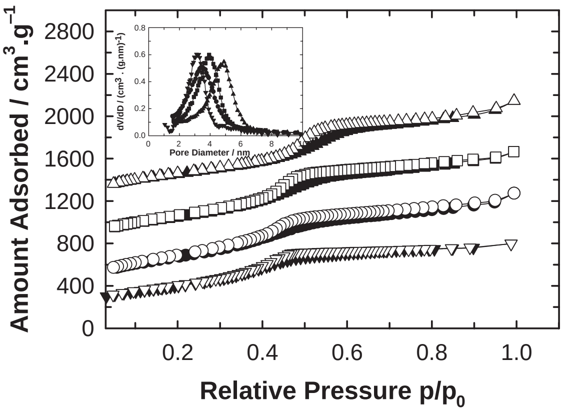

Figure 3. Nitrogen adsorption isotherm (adsorption: closed symbols; desorption: open symbols) of MCA mesoporous carbons: (▼) CMK-3, (●) MCA-100, (■) MCA-120, and (▲) MCA-130.

the pore diameter of MCA mesoporous carbon materials by choosing the suitable AlSBA-15 template. It is also interesting to note that the specific surface area, specific pore volume and pore diameter of MCA-100 are significantly higher as compared to that of CMK-3.

In summary, we have successfully prepared the large pore novel mesoporous carbon materials (MCA) from AlSBA-15 templates synthesized at different temperatures. The textural parameters of the MCA can be easily tuned. The specific surface area, pore volume, and pore diameter of the obtained materials are higher as compared to CMK-3 which was prepared from SBA-15 template. The well-ordered mesoporous carbon materials with tunable pore diameters will definitely find many applications in the field of adsorption and separation.

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