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Very High Surface Area Microporous Carbon with a Three-Dimensional Nano-Array Structure: Synthesis and Its Molecular Structure

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In recent years, there has been growing interest in new applications of porous carbons, for example, the storage of natural gas and use as electrodes of an electric double-layer capacitor. These kinds of applications require porous carbons to have a tailored micropore structure.[1−4] To meet the requirement, many novel approaches to control pore structure have been proposed.[5] Among them, great attention has been paid to the template carbonization method. So far, many researchers have prepared novel porous carbons with this technique using a variety of inorganic porous templates.[6−16] Recently, two Korean research groups independently obtained mesoporous carbons with an ordered structure using a silica mesoporous molecular sieve as a template and demonstrated that their method is quite effective for the control of carbon mesoporosity.[17−23] However,such mesoporous silica templates cannot be used for the synthesis of microporous carbon. We had been investigating the synthesis of porous carbon using zeolite Y as a template[24] and last year we prepared microporous carbon with the structural regularity of zeolite Y.[25] Since then, we have made great efforts to improve the template method using zeolite Y. Finally, we could synthesize microporous carbon with a three-dimensional nano-array structure, whose arrangement is identical to that of supercages of zeolite Y. Surprisingly, the BET surface area was found to be as high as 3600 m^2/g. Here, we report the details of the extraordinary features of the present microporous carbon and discuss how the carbon structure can accommodate itself into such a narrow space as in the nanochannels of zeolite Y.

In the previous work,[25] the two step method was employed for the filling of carbon into the nanochannels of zeolite Y, the carbon deposition from propylene at 800 °C for 4 h after the heat treatment of the zeolite/poly(furfuryl alcohol) (PFA) composite at 700 °C for 4 h. In the present method,[26] the zeolite/PFA composite was heated to 700 °C in N_2. As soon as the temperature reached 700 °C, propylene CVD was carried out at this temperature. After the CVD, the composite was further heat-treated at 900 °C under a N_2 flow. The resultant carbon was liberated from the zeolite framework by acid washing.

Figure 1 shows X-ray diffraction (XRD) patterns of the carbons prepared by the previous and present methods, together with the pattern of zeolite Y. Both of the carbons show a sharp peak around 6°, indicating that these carbons have a structural regularity with a periodicity of about 1.4 nm that corresponds to the spacing of the {111} plane of zeolite Y. It is clear that the peak of the present carbon is more intense than that of the previous one, indicating the presence of a larger amount of highly ordered parts in the former carbon. In the present method, the carbon/zeolite composite was further heat-treated at 900 °C in N_2. During this

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(26) Powdery zeolite Y (Na form, $SiO_2/Al_2O_3 = 5.6$, HSZ-320NAA, Tosoh Co. Ltd.) was placed in a flask and kept at 150 °C under vacuum. Liquid furfuryl alcohol (FA) was introduced into the flask under reduced pressure at room temperature after the zeolite was dried. The mixture of zeolite and FA was stirred for 8 h under a N_2 flow and then filtered, followed by washing with mesitylene to remove FA on the external surface of zeolite powder. The polymerization of FA in zeolite was carried out by heating the powder under a N_2 flow at 80 °C for 24 h and then at 150 °C for 8 h. The resultant zeolite/PFA composite was placed in a quartz reactor (i.d., 20 mm) and the reactor temperature was raised to 700 °C at a heating rate of 5 °C/min under a N_2 flow. When the temperature reached 700 °C, propylene gas (2.0% in N_2) was passed through the reactor at a total flow rate of 150 cm^3/min and kept there for 4 h. After the propylene CVD, the zeolite/carbon composite was further heat-treated at 900 °C for 3 h under a N_2 flow. Then, the zeolite/carbon composites were treated with an excess amount of 46% aqueous HF solution at room temperature for 3 h and subsequently refluxed in concentrated HCl solution at 60 °C for 3 h to dissolve the zeolite framework. The solution was filtered and the insoluble carbon was washed with copious quantities of water.

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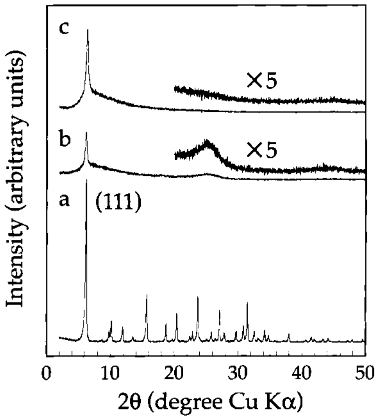

Figure 1. XRD patterns of zeolite Y and the resultant carbons: (a) zeolite Y; (b) the carbon prepared by the previous procedure;[25] (c) the carbon from the present method.[26]

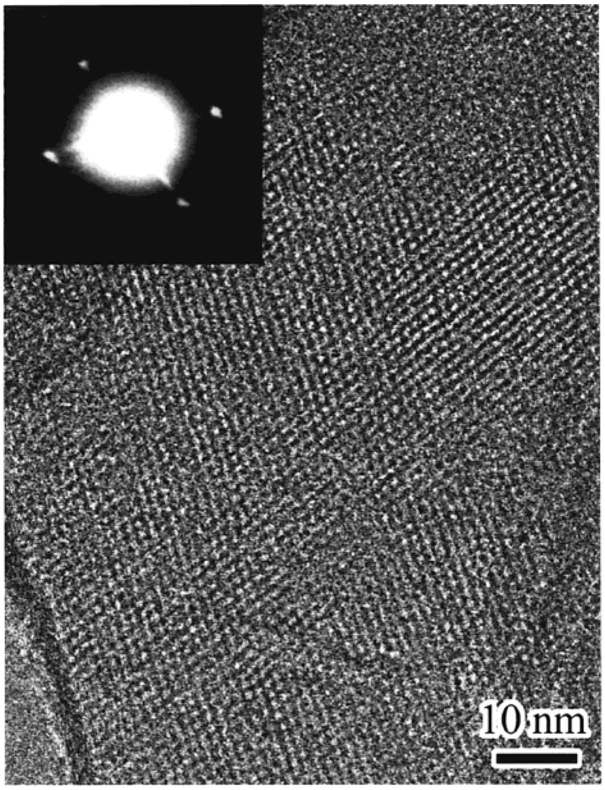

Figure 2. HRTEM image of the carbon prepared by the present method. The inset corresponds to a diffraction pattern taken from this image.

treatment, the carbon inside the channels may be more carbonized and its structure would become more rigid and stable as a result. Therefore, the long-range ordering of carbon particles might be kept better than that of the carbon without such heat treatment at 900 °C. In addition, a broad peak around 25° that was observed in the previous carbon (Figure 1b) is not detected in the present one. This finding indicates that the present carbon does not have any stacking structure of carbon layers, even though it was heat-treated at a temperature as high as 900 °C.

The excellent three-dimensional ordering of the present carbon was revealed by high-resolution transmission electron microscope (HRTEM) observation. An HRTEM image of the present carbon is shown in Figure 2, where a periodically ordered array can be seen from the image. The arrangement and periodicity (about 1.3 nm) of this array structure correspond to those of supercages on a {110} plane of zeolite Y. The diffraction pattern (an inset in Figure 2) is characterized by two pairs of spots and the arrangement of these spots corresponds to the pattern of four spots from a {111} reflection of fcc zeolite Y with a ⟨110⟩ zone axis. In addition to these four spots, sometimes we could observe another pair of very weak spots at the positions corresponding to {220} reflection of zeolite Y. However, all these spots could be observed only in the diffraction with a ⟨110⟩ zone axis and any diffraction spots did not appear in the case of other zone axes. This finding suggests that the carbon inherited its regular ordering only from the zeolite crystal planes parallel to the ⟨110⟩ direction, mostly from the ordering of {111} planes which directly correspond to a row of supercages in zeolite Y crystal.

Another noticeable characteristic of this ordered carbon is its high surface area. From N_2 adsorption experiments at −196 °C, the BET surface area was determined using the data in the relative pressure range of 0.01−0.05, as Kaneko et al. recommended.[27] The calculated surface area was found to be 3600 m^2/g, which is much higher than that of the carbon prepared by the previous method (2200 m^2/g). Generally, microporous carbons with a surface area more than 3000 m^2/g can be produced only by the chemical activation using KOH. Thus, the present study is the first example to prepare such high surface area carbon without using the conventional chemical activation method. Moreover, the KOH-activated carbons always suffer from the presence of some mesoporosity and wide pore distribution,[28,29] which should be avoided for the application of gas storage. On the other hand, the present carbon has almost no mesoporosity (its micropore and mesopore volumes are 1.52 and 0.05 cm^3/g, respectively[30]).

It is very likely that these extraordinary characteristics of this carbon are the result of better filling of carbon into the zeolite nanochannels under the present synthesis conditions. It is, however, very hard to imagine how macro carbon molecular structure can accommodate itself into the zeolite nanochannels. To obtain the information on carbon molecular structure, the present carbon was subjected to ^{13}C solid-state NMR measurement. Figure 3 shows NMR spectra with the following two different measurement modes: cross-polarization with magic-angle spinning (CP/MAS) and single-pulse excitation with magic-angle spinning (SPE/MAS) using longer pulse delay. In these two NMR spectra, one broad peak with a chemical shift of about 130 ppm was observed, together with two small peaks around 60 and 200 ppm. The large peak can be attributed to sp^2-hybridized carbon atoms in condensed aromatic rings and the latter two are spinning sidebands from the aromatic band. There is no clear peak from the aliphatic carbon, which would appear in the range of 10−50 ppm.

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[30] The micropore volume was calculated from the Dubinin−Radushkevich equation and the mesopore volume was determined by subtracting the micropore volume from the volume of N_2 adsorbed at a relative pressure of 0.95.

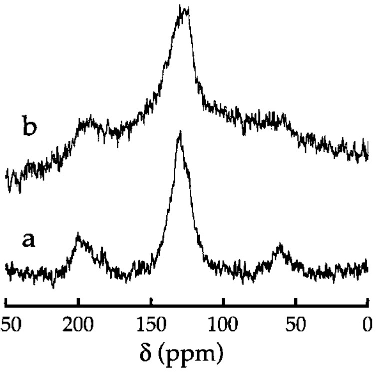

Figure 3. ^{13}C solid-state NMR spectra of the present carbon with two different measurement modes: (a) CP/MAS with a pulse delay of 10 s; (b) SPE/MAS with a pulse delay of 100 s.

From the results of the NMR analysis, it is concluded that the molecular structure of the present carbon consists of a condensed aromatic ring system. With HRTEM, we made every effort to observe the stacking of graphene sheets inside carbon particles. However, we have never seen any stacking structure or even any single layers, but only the long-range ordering as mentioned above. This is in accord with the XRD pattern in Figure 1, where there is no peak due to such stacking. Because the size of a supercage (1.3 nm) is so small that, for example, it can hold only one coronene molecule ($C_{24}H_{12}$), the presence of a large planar graphene sheet in a supercage is impossible. Thus, it is unlikely that there is parallel stacking of planar graphene sheets in the zeolite nanochannels. Considering that the size of a supercage is large enough to encapsulate a single fullerene molecule of C_{60}, we can conjecture that in the nanochannels carbon is present as curved graphene sheets, rather than planar ones. The carbon might have pentagons and heptagons distributed through a hexagonal network to adapt the structure to the zigzagged pores in zeolite Y.

In conclusion, the resultant carbon has a three-dimensional nano-array structure with surprisingly regular ordering. It was found that this carbon possesses a very high surface area such as 3600 m^2/g. Because of such highly ordered structure, there is almost no mesoporosity. One of the possible structures of the carbon is a curved graphene structure whose faceting and curvature are accommodated to the curved inner surface of the zeolite nanochannels.

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