Preparation of a high surface area microporous carbon having the structural regularity of Y zeolite

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An ordered microporous carbon that preserves the structural regularity of Y zeolite has been prepared by a template carbonization technique using Y zeolite.

The synthesis of porous carbon materials is of great importance for both practical and fundamental reasons. The recent development of industrial technology requires porous carbons to have a tailored pore structure. The importance of pore structure control has been pointed out for applications such as electrode materials for electric double-layer capacitors and adsorbents for methane storage. To meet the requirements, many novel approaches to control pore structure have been proposed. The detailed features of these techniques have been recently reviewed by Kyotani.[1] One of the most important and elegant techniques is a template carbonization method,[2–7] which utilizes the inorganic templates whose opening or pores are controlled at the nanometer level. We demonstrated that porous carbons with a surface area as high as 2200 $m^2\ g^{-1}$ could be prepared using Y zeolite as a template.[8] There were also a few other reports on such carbon formation in zeolite channels.[9,10] Recently, two Korean research groups have independently obtained mesoporous carbon with ordered structure using mesoporous silica (MCM-48) as a template.[11,12] Their works are the first example of synthesizing an ordered mesoporous carbon. However, none of these porous carbons has a regular microporous structure. Here, by filling as much carbon as possible into the channels of Y zeolite template, we attempted to prepare an ordered microporous carbon that retains the structural regularity of Y zeolite. The obtained microporous carbon has a periodical ordering of 1.4 nm, which is the same as the spacing of (111) plane of Y zeolite.

A two-step method was used in the preparation of carbon material. In the first step, dry Y zeolite powder (Na-form, $SiO_2/Al_2O_3 = 5.6$, Tosoh Inc., HSZ-320NAA) was impregnated with furfuryl alcohol (FA) under reduced pressure at room temperature. The mixture of FA and zeolite powder was stirred for 5 days and then filtered, followed by washing the product with mesitylene. The FA/zeolite composite was placed in a vertical quartz reactor and FA was polymerized in zeolite by heating the composite at 150 °C under N_2 flow. The resultant PFA (polyfurfuryl alcohol)/zeolite composite was heat-treated at 700 °C for 4 h to carbonize the polymer in the zeolite channels. After this first carbon filling, the reactor temperature was raised to 800 °C and then propylene gas (2.0% in N_2) was passed through the reactor for 4 h. This second step resulted in pyrolytic carbon deposition into the remaining opening of the composite. After the propylene CVD, the zeolite framework in the carbon/zeolite composite was dissolved by successive washing with HF and HCl solution. Carbon was obtained as an insoluble fraction. The elemental analysis of the carbon was as follows: C, 94 wt%; H, 2 wt%; O, 4 wt% (difference). The ash content was nearly zero with an experimental error of ±0.1 wt%, indicating almost perfect removal of zeolite template.

The crystallinity and the microscopic features of the carbon were examined using an X-ray diffractometer (XRD, Shimadzu, XD-D1, Cu-Kα radiation) and transmission electron microscopy (TEM, JEOL, JEM-2010). The pore structure was investigated with an automatic volumetric sorption analyzer (Quantachrome, Autosorb-1) using N_2 as the adsorbate at −196 °C. The micropore and mesopore volumes were determined from methods describe elsewhere.[8]

Fig. 1 shows the XRD patterns of the original Y zeolite and the carbon liberated from the carbon/zeolite composite. The former pattern [Fig. 1(a)] is characterized by the appearance of many sharp peaks due to the framework topology of Y zeolite. Among these peaks, the strongest appearing at $2\theta = 6.19°$ can be indexed as the diffraction from the (111) plane. In the XRD pattern of the carbon [Fig. 1(b)], a sharp peak appeared at $2\theta = 6.26°$, together with a very broad and weak peak in the range $2\theta = 23–27°$. This type of broad peak is often observed as the (002) diffraction from carbonaceous materials with poor crystallinity. However, a sharp peak at 2θ *ca.* 6° as observed in Fig. 1(b) has not, to our knowledge, been reported. The presence of the sharp peak indicates that this carbon has a long-range ordering with a periodicity of 1.41 nm, almost the same as the spacing of the (111) plane in Y zeolite (1.43 nm). The presence of such periodical ordering was further confirmed by the lattice fringe image discussed below.

From TEM observation, it was found that each carbon particle consists of a thin and dense envelope with straight lattice fringes present inside each envelope. Fig. 2(a) shows a typical image of lattice fringes, which run along the envelope located on the upper part of this picture. The regular spacing of the observed lattice planes is about 1.3 nm and the diffraction from these planes was clearly observed as a pair of sharp spots in the corresponding electron diffraction pattern [Fig. 2(b)].

Taking the results of our previous work[8] into consideration, we can ascribe the envelopes observed in the particles to the carbon deposited on the external surface of the zeolite particles. When we prepared porous carbon with a shorter CVD period (2 h), many of the resultant carbon particles had no envelope

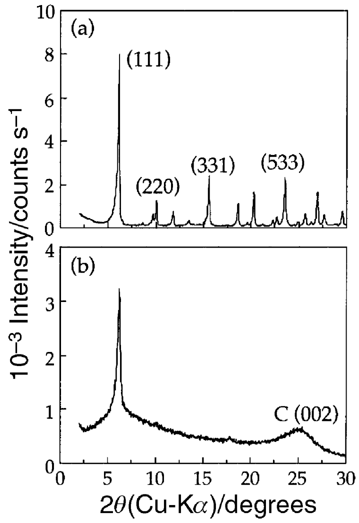

Fig. 1 XRD patterns of Y zeolite (a) and carbon liberated from the carbon/zeolite composite (b).

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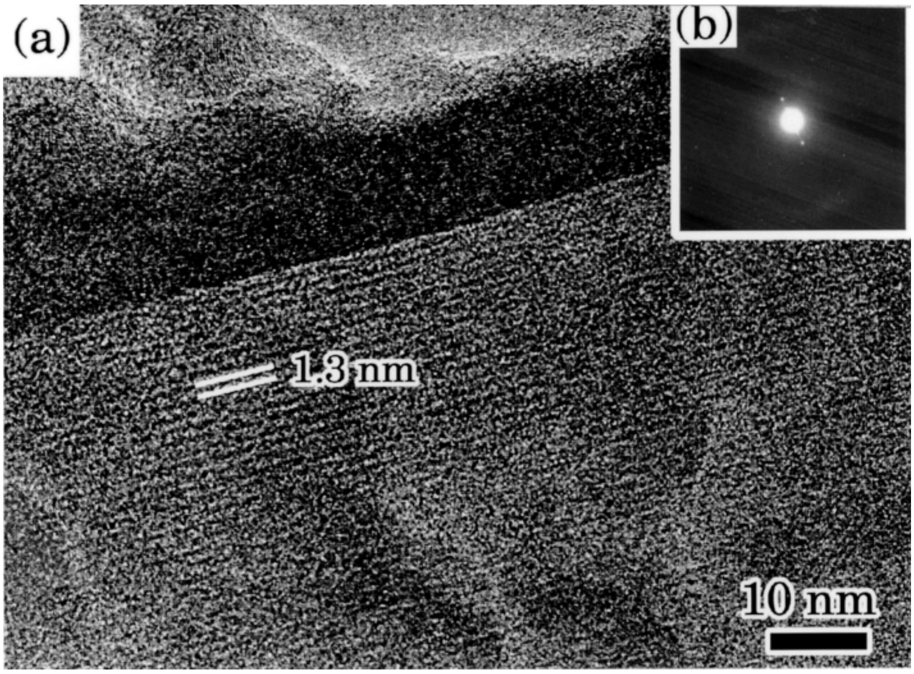

Fig. 2 (a) High-resolution TEM image of part of a carbon particle. (b) Electron diffraction pattern taken from the image of (a).

and the XRD pattern of this carbon did not show such a broad (002) XRD peak as in Fig. 1(b). This finding indicates that the broad XRD peak arises from the envelopes and there is no stacking structure of (002) layers in the ordered carbon.

Fig. 3 shows a N_2 adsorption–desorption isotherm of the carbon. In the relative pressure range of > 0.2, the isotherm shows an almost flat sorption characteristic. Furthermore, there is almost no hysteresis loop in the isotherm. These findings clearly indicate the absence of mesoporosity in the carbon. The BET surface area, the micropore and mesopore volumes were calculated from this isotherm to be 1910 $m^2 g^{-1}$, 1.1 $cm^3 g^{-1}$ and 0 $cm^3 g^{-1}$, respectively. In our previous study,[8] we prepared high surface area carbons by a one-step carbon filling method, *via* propylene CVD over Y zeolite. The resultant carbons had both micro- and meso-porosity. The porosity of the carbon obtained here, however, shows highly developed microporous structure without any mesopores.

In conclusion, a microporous carbon with a long-range periodic ordering ($d = 1.4$ nm) has been synthesized for the first time. Such structural periodicity in the carbon would originate from the structural ordering in Y zeolite. It is well known that Y zeolite consists of a tetrahedral network structure of sodalite units, which results in a supercage, *i.e.* a large cavity with a diameter of 1.3 nm. Each supercage is connected to four other supercages by an opening with a diameter of 0.74 nm. Due to this framework topology, many sharp XRD peaks appeared as in Fig. 1(a). However, the carbon gave only one sharp XRD peak at the angle corresponding to the (111) diffraction [Fig. 2(b)]. No other peak was observed at the angles where sharp peaks from the zeolite appeared. This implies that the carbon retains only the structural ordering of (111) plane stacking of Y zeolite.

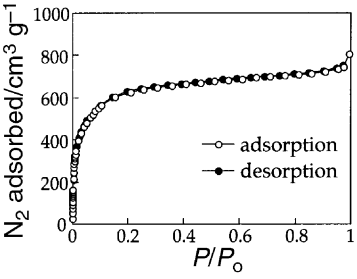

Fig. 3 N_2 adsorption–desorption isotherm at −196 °C for the carbon. The adsorption and desorption curves are plotted using open and filled circles, respectively.

The formation of the ordered microporous carbon suggests that the amount of carbon filled into the zeolite channels by the present method was sufficient to preserve the network structure reflecting the zeolite template. Also, if one can fill zeolite channels with a sufficient amount of carbon for other types of zeolites with three-dimensional structures such as ZSM-5, ZMS-11 and A zeolite, this opens up a possibility for the preparation of a series of microporous carbons having the structural regularity of template zeolites.

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Notes and references

1 T. Kyotani, *Carbon*, 2000, **38**, 269.
2 T. Kyotani, N. Sonobe and A. Tomita, *Nature*, 1988, **331**, 331.
3 T. Bandosz, K. Putyera, J. Jagiello and J. A. Schwarz, *Carbon*, 1994, **32**, 659.
4 M. T. Gilbert, J. H. Knox and B. Kaur, *Chromatographia*, 1982, **16**, 138.
5 A. A. Zakhidov, R. Baughman, Z. Iqbal, C. Cui, I. Khayrullin, S. O. Dantas, J. Marti and V. G. Ralchenko, *Science*, 1998, **282**, 897.
6 T. Kyotani, L. Tsai and A. Tomita, *Chem. Mater.*, 1995, **7**, 1427.
7 G. Che, B. B. Lakshmi, C. R. Martin, E. R. Fisher and R. S. Ruoff, *Chem. Mater.*, 1998, **10**, 260.
8 T. Kyotani, T. Nagai, S. Inoue and A. Tomita, *Chem. Mater.*, 1997, **9**, 609.
9 S. A. Johnson, E. S. Brigham, P. J. Ollivier and T. E. Mallouk, *Chem. Mater.*, 1997, **9**, 2448.
10 J. Rodriguez-Mirasol, T. Cordero, L. R. Radovic and J. J. Rodriguez, *Chem. Mater.*, 1998, **10**, 550.
11 R. Ryoo, S. H. Joo and S. Jun, *J. Phys. Chem. B*, 1999, **103**, 7743.
12 J. Lee, S. Yoon, T. Hyeon, S. M. Oh and K. B. Kim, *Chem. Commun.*, 1999, 2177.