

PREPARATION OF POROUS CARBON WITH PERIODIC ORDERING STRUCTURE BY USING ZEOLITES AS TEMPLATE

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Introduction

Porous carbon materials or activated carbons have been widely used in gas separation, purification and catalysts. If the pore structure of porous carbon materials could be well-tailored, new applications of these materials would be expected due to interesting physical, magnetic and electronic properties that these novel materials would possess. Lots of approaches to control pore structure have been proposed and the detailed features of these techniques were recently reviewed by Kyotani [1]. Among these approaches, a template carbonization method is one of the most important and elegant techniques. Two Korean research groups have independently obtained mesoporous carbon with ordered structure using mesoporous silica (MCM-48) as a template [2,3]. However, none of these porous carbons has a regular microporous structure. Very recently, by using Y zeolite as a template, we prepared a high surface area carbon materials with long-range periodic ordering which reflects the crystal structure of Y zeolite [4]. In this study, an optimized synthesis condition for preparing such porous carbon material was further investigated. In addition, an attempt was made to synthesize porous carbon having structural regularity by using beta zeolite as a template.

Experimental

The pyrolytic carbon was introduced into zeolite channels by the following method. Dried Y zeolite (Na-form, $\text{SiO}_2/\text{Al}_2\text{O}_3=5.6$, Tosoh Inc., HSZ-320NAA) or beta zeolite (H-form, $\text{SiO}_2/\text{Al}_2\text{O}_3=37.1$, Tosoh Inc., HSZ-940HOA) powder was impregnated with furfuryl alcohol (FA) under reduced pressure at room temperature. The mixture of FA and zeolite was stirred for 8 h and then filtered, followed by washing the product with mesitylene to remove FA on the external surface of zeolite powder. The zeolite/FA composite was then placed in a

vertical quartz reactor and FA in zeolite was polymerized by heating the composite at 150 °C under N_2 flow. After the polymerization for 8 h, the reactor temperature was raised to 700 or 800 °C, and then propylene gas (2.0 % in N_2) was passed through the reactor at a total flow rate of 150 cm^3/min . After a desired period of time, propylene gas was cut off and the reactor was cooled to room temperature. Some of the resultant zeolite/carbon composites were subjected to further heat-treatment at 900 °C for 3 h under N_2 flow without propylene gas. Then, the zeolite framework in composite was dissolved by successive washing with HF and HCl solution. Carbon was obtained as an insoluble fraction. The crystallinity and the microscopic feature of the carbon were examined with an X-ray diffractometer (XRD) and a transmission electron microscope (TEM).

Results and discussion

The XRD patterns of Y zeolite and the resultant carbons are given in Figure 1. The carbon prepared from the propylene CVD at 700 °C (Figure 1b) showed a peak at small angle side around 6°, indicating that this carbon has a structural regularity with a periodicity of about 1.4 nm which corresponds to the spacing of the (111) plane of Y zeolite. But its ordering was rather poor judging from the peak width. For the carbon obtained from the propylene CVD at 800 °C (Figure 1c), a very sharp peak appeared around 6°, which manifests highly ordered structure of this carbon material. In addition, a broad peak around 25°, which is hardly found in the XRD pattern of the carbon from the CVD at 700 °C (Figure 1b), is also observed. This broad peak can be ascribed to the carbon layers deposited on the external surface of zeolite particles based on our previous work [5] and a dense envelope originated from such carbon deposition was viewable for every carbon particle with a high-resolution TEM [4]. The presence of this kind of carbon envelope

would give some disadvantages to the practical use of this carbon material because of the difficulty in accessing the pores of carbon particles.

According to the above results, the CVD at 800 °C would not be suitable for preparing long-range ordered carbon without the envelopes outside of carbon particles. On the other hand, the CVD at 700 °C gave no obvious peak around 25°. Furthermore, the TEM observation of the carbon prepared at this CVD condition evidenced the absence of thick envelopes. Thus, the CVD at 700 °C would be a better condition. Then the composite obtained from the CVD at 700 °C was further heat-treated at 900 °C with carbon remained inside the zeolite channels. The XRD pattern of the carbon liberated from the heat-treated composite is given in Figure 1d, where a very sharp peak is observed around 6° whereas there is no peak around 25°, suggesting highly ordered structure without dense envelopes. This finding implies that, during the heat-treatment, the carbon inside zeolite channels was more carbonized, consequently its structure became more rigid and stable. Therefore, the long-range ordering of carbon particles might be kept better than that of carbon without heat-treatment. Considering these results, the process as: 1) FA impregnation and polymerization, 2) propylene CVD at 700 °C, and 3) the heat-treatment of zeolite/carbon composite, would be an optimized procedure for preparation of the carbon material with highly ordered periodic structure by using Y zeolite as a template.

Using the same process mentioned above, an attempt was also made to synthesize porous carbon by using beta zeolite as a template. The XRD patterns of beta zeolite and the resultant carbon are shown in Figure 2. Compared with Y zeolite, the XRD peak appeared around 8° in beta zeolite (Figure 2a) is broad, indicating relatively poor crystallinity of beta zeolite. In the XRD pattern of carbon (Figure 2b), a peak around 8° was distinctly visible. It indicates that the carbon prepared by using beta zeolite also has a periodic ordering structure. However, compared with the carbon obtained from Y zeolite, the carbon from beta zeolite showed a broad peak, which implies the ordering of this carbon was not so good. The poor crystallinity of parent beta zeolite should be one of

the reasons. The optimum conditions for Y zeolite might not be an optimum one for beta zeolite.

Conclusions

The procedure for preparing the carbon material with highly ordered periodic structure by using Y zeolite as a template was optimized. In addition, the carbon prepared by using beta zeolite as a template also showed a periodic ordering structure.

References

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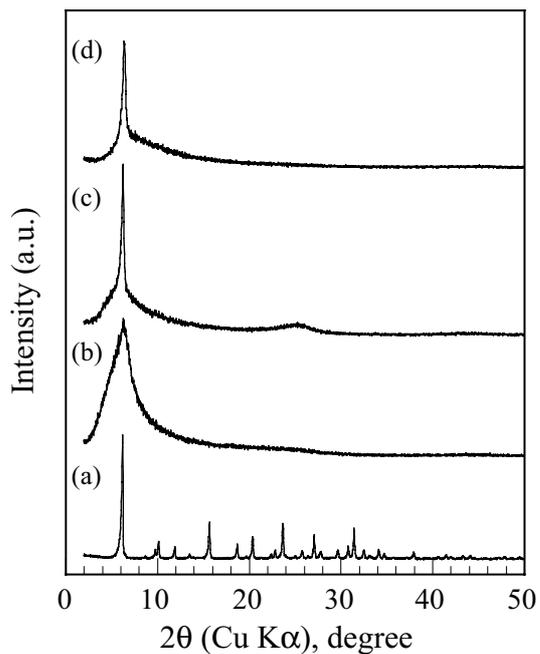


Figure 1. XRD patterns of Y zeolite and the resultant carbons. a: Y zeolite, b: carbon from the CVD at 700 °C, c: carbon from the CVD at 800 °C, d: carbon from the CVD at 700 °C followed by the heat-treatment at 900 °C

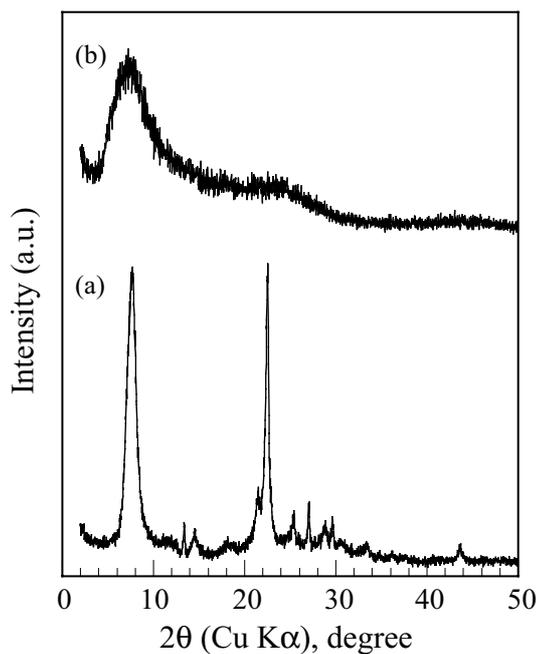


Figure 2. XRD patterns of beta zeolite and the resultant carbon. a: beta zeolite, b: carbon from the CVD at 700 °C followed by the heat-treatment at 900 °C

Note: The scales of the intensity from all of the carbons shown in Figure 1 and Figure 2 were expanded by two times.