

# SYNTHESIS AND CHARACTERIZATION OF NITROGEN-CONTAINING MICROPOROUS CARBON WITH A THREE-DIMENSIONAL NANO-ARRAY STRUCTURE

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## Introduction

High specific surface area microporous carbon with a three-dimensional nano-array structure has been synthesized by using zeolite Y as a template in our laboratory [1]. This kind of carbon, which has high surface area and large microporous volume, is extremely attractive in a variety of fields, and now is in great demand for the application to the electrodes of electric double-layer capacitors [2]. One of the important factors for such electrodes is the affinity to the solvent in the capacitor. In order to increase the affinity to solvent, introduction of heteroatoms would be effective. Moreover, such introduction could further create electro-chemically active sites, resulting in the increase of capacitance. Here, by using acetonitrile as one of carbon sources, we attempted to fabricate N-containing microporous carbon with a three-dimensional nano-array structure using zeolite Y as a template

## Experiments

A two-step method was applied in the preparation of N-containing microporous carbon. In the first step, zeolite Y (Na-form,  $\text{SiO}_2/\text{Al}_2\text{O}_3=5.6$ , Tosoh Inc., HSZ-320NAA) channels were filled with furfuryl alcohol (FA) by impregnation and then FA was polymerized at 150 °C. The resultant polyfurfuryl alcohol (PFA)/zeolite composite was placed in a vertical quartz reactor (20 mm I.D.) and heated up to a fixed temperature under a  $\text{N}_2$  flow at a heating rate of 5 °C/min. The second step was acetonitrile chemical vapor deposition (CVD), in which N-containing carbon is deposited into zeolite channels. As soon as the temperature reached the fixed temperature just after the first step, acetonitrile vapor (4.2 % in  $\text{N}_2$  of 150  $\text{cm}^3$  (STP)/min) was introduced into the reactor. The vapor was generated by bubbling  $\text{N}_2$  through acetonitrile liquid in a saturator at 0 °C. This acetonitrile CVD was performed for a given time. After the CVD, the composite was further heat-treated at 900 °C

under a N<sub>2</sub> flow for 1 h. For clarity, each reaction step was defined by using the following abbreviations: acetonitrile-CVD at 800 °C for 2 h or 900°C for 1 h = A8(2) or A9(1). The detailed experimental conditions are summarized in Table 1.

The resultant carbons were liberated from the zeolite framework by acid washing. The porous carbons were examined with elemental analysis, X-ray diffraction, N<sub>2</sub> adsorption at -196 °C and water adsorption at 25 °C. The BET surface area of all the samples was determined using the data in the relative pressure range of 0.01-0.05. The micropore volume was calculated from the Dubinin-Radushkevich (DR) equation. The mesopore volume was determined by subtracting the micropore volume from the volume of N<sub>2</sub> adsorbed at a relative pressure of 0.95.

## Results and discussions

The carbon fraction in each zeolite/carbon composite was calculated from the data of its elemental analysis using the carbon to ash ratio where ash was regarded as zeolite equivalent, and the results are given in Table 1. The carbon fraction of the composites increased with the increase of temperature and time of CVD. The results of the elemental analysis for porous carbons synthesized were summarized in the last part of Table 1. The ash content of all the samples was found to be 0 wt%, indicating complete removal of the template zeolite. Carbon and nitrogen contents increased with the increase of the acetonitrile-CVD temperature and time, especially for nitrogen content.

Table 1. Experimental conditions, carbon fraction in the composites and the results of elemental analysis for the carbons

Notation	Synthesis conditions		Carbon fraction (g/g of zeolite)	Elemental analysis of the carbon (wt%)			
	Tem. (°C)	Time (h)		C	H	N	O (diff.)
A7(1)	700	1	0.21	85	4	2	9
A8(1)	800	1	0.23	86	3	4	7
A9(1)	900	1	0.24	88	1	7	4
A8(2)	800	2	0.25	88	2	6	4
A8(3)	800	3	0.27	89	1	7	3

Fig. 1 shows XRD patterns for the porous carbons obtained. For the A7(1) carbon, no apparent peak was observed, which indicates that the porous carbon fabricated at the lower CVD temperature can not keep a structural regularity. For the A8(1) carbon, its XRD pattern shows a weak and broad peak at about 6°. The presence of such XRD peak indicates that to some extent a structural regularity was transferred from

the crystal structure of zeolite Y. However, in the case of A9(1) carbon, its XRD peak at about 6° is much lower than that of A8(1) carbon. Furthermore, a broad peak at about 25° appeared, which indicated that during this CVD, most of the carbon probably deposited on the external surface of zeolite particles at such higher temperature. These results indicate that 800 °C is an optimum CVD temperature for

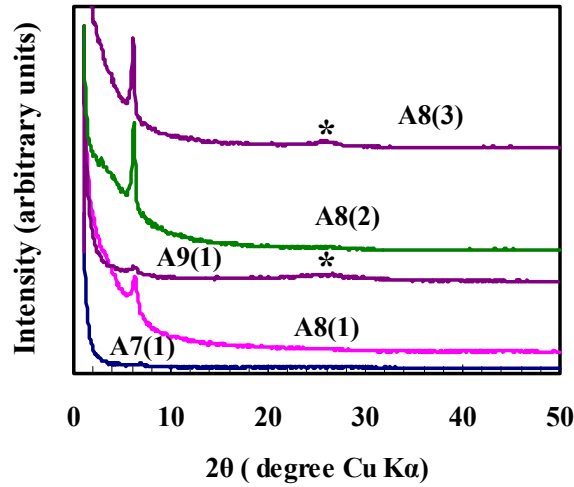


Figure 1. XRD patterns of the porous carbons obtained

the synthesis of microporous carbon with better regularity. To further increase the regularity, the CVD time was increased to 2 h and 3 h. The XRD pattern of the A8(2) carbon gives a strong peak at about 6°. In the case of A8(3), besides the sharp peak appeared at 6°, a broad peak was also observed at around 25°. This broad peak can be ascribed to the carbon layer stacking from the deposition on the external surface of zeolite particles as suggested by Ma et al. [1]. Based on the above results and discussion, it is reasonable to conclude that there is an optimum CVD condition for the fabrication of highly ordered and N-containing microporous carbon. In the present work, the CVD for 2 h at 800°C is the best.

Table 2. The BET surface area and pore volume of the carbons

Carbons	A7(1)	A8(1)	A9(1)	A8(2)	A8(3)	P7(1)
$S_{\text{BET}}$ (m <sup>2</sup> /g)	2400	2900	2700	3300	2300	4100
$V_{\text{micro}}$ (cm <sup>3</sup> /g)	1.05	1.39	1.32	1.52	1.35	1.93
$V_{\text{meso}}$ (cm <sup>3</sup> /g)	0.13	0.17	0.10	0.07	0.04	0.08

N<sub>2</sub> adsorption isotherms of these carbons are plotted in Fig. 2 and the results of the BET specific surface area and the pore volumes are summarized in Table 2. The N<sub>2</sub> adsorption isotherm for all the carbons is that of Type-I, suggesting the development

of microporosity. All of the carbons possess the BET surface areas over 2000 m<sup>2</sup>/g, micropore volume over 1.0 cm<sup>3</sup>/g, and mesopore volume less than 0.2 cm<sup>3</sup>/g. The A8(2) carbon possess the highest BET surface area and micropore volume in all the carbons investigated.

In order to investigate the effect of N on the affinity to water, A8(2) carbon was characterized by water adsorption and the resultant isotherm is plotted in Figure 3. For comparison, the isotherm of a similar type of N-free microporous carbon is also plotted. This carbon (P7(1)) was prepared by the two step method, but it used propylene as carbon source in CVD process (at 700 °C for 1 h) and its surface area and pore volume are shown in the last column of Table 2. It can be seen from Fig. 3 that the uptake relative pressure of the N-containing porous carbon is smaller than

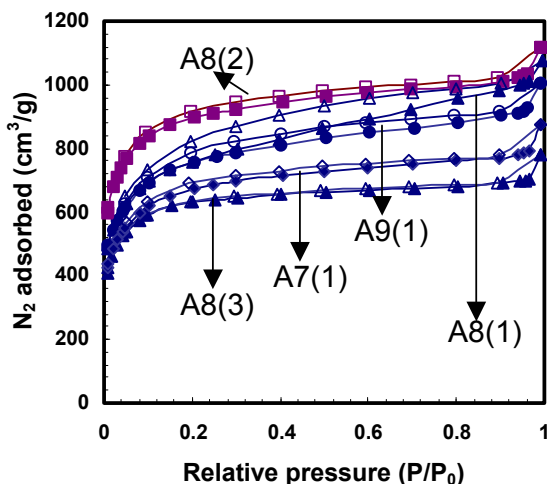


Figure 2. N<sub>2</sub> adsorption isotherms

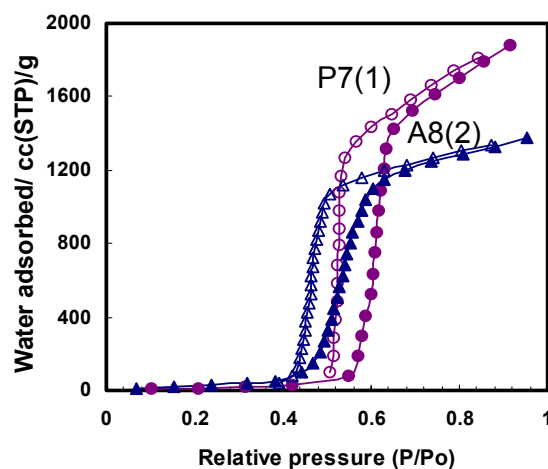


Figure 3. Water vapor adsorption isotherms

that of the N-free porous carbon, which suggests the improvement of wet ability toward water by the N introduction.

## Conclusion

Nitrogen-containing microporous carbon with a three-dimensional nano-array structure was first synthesized by using zeolite Y as template. The resultant microporous carbon possesses a very high surface area (3300 m<sup>2</sup>/g), large micropore volume (1.52 cm<sup>3</sup>/g) and almost no mesopore volume (0.07 cm<sup>3</sup>/g). The results of water vapor adsorption indicate that the introduction of N increases the affinity to water.

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**Reference**

- [1] Ma ZX, Kyotani T, Tomita A. Synthesis methods for preparing microporous carbons with a structural regularity of zeolite Y. *Carbon* 2002; 40:2367–2374.
- [2] Guo YP, Qi JR, Jiang YQ, Yang SF, Wang ZC, Xu HD. Performance of electrical double layer capacitors with porous carbons derived from rice husk. *Materials Chemistry and Physics* 2003; 80:704–709.