Porous Carbons from Octafluoronaphthalene by Chemical Reaction and Heat-treatment

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Porous carbons were obtained from octafluoronaphthalene defluorinated with sodium metal. When the by-product, NaF was removed with acid solution and the product was treated at 1073 K, the carbon gave a high surface area with mesopores as well as micropores. The coexistence of NaF during heat-treatment of the defluorinated product, however, brought about the formation of pores with a squarish shape.

Carbonaceous materials are usually obtained by heat-treating various organic compounds, coal tar pitch, polymers, and so on at high temperatures.[1,2] Texture and structure of the carbons thus prepared depend mainly on the nature and the molecular structure of starting materials and their carbonization process. Since a lot of thermal reactions take place in parallel at the carbonization process, it is difficult to control a reaction scheme by which a desirable product can be selectively obtained, even if a specific raw material could be employed. Kavan et al. have reported the preparation of carbyne-like materials by electrochemical defluorination of perfluorinated compounds.[3,4] We also have prepared porous carbons by direct reduction of poly(tetrafluoroethylene) (PTFE) with alkali metals.[5,6] Since the reaction proceeds at temperatures lower than 473 K, it could be possible to control the reaction conditions and at the same time to obtain more sophisticated carbon materials if the reaction product is used as a precursor of nanocarbons. In fact, Kawase et al.[7] and Hlavaty et al.[8] have reported the transformation of the defluorinated products into carbon nanotubes. In this process, linear carbyne-like carbons are formed at the first step and then partial crosslinking reaction occurs between these linear chains to form aromatic carbon network due to conventional sp^2 carbons. When these carbons are heat-treated at higher temperatures, however, some of the carbon species which are not involved in aromatic structure are subject to pyrolysis. It would result in lowering of the carbonization yield, because the original PTFE polymer contains aliphatic C–C bonding which is thermally unstable.

In this study, we used octafluoronaphthalene ($C_{10}F_8$, OFN) as a starting compound in stead of PTFE in order to enhance carbon yield of the products and also to obtain specific carbons different from conventional ones. The compound, OFN is one of perfluoroaromatic compounds, in which all of hydrogen atoms of naphthalene are substituted by fluorine. It has a melting point of 360–361 K and sublimes at room temperature under vacuum.

OFN is a commercially available reagent and employed without purification. Sodium metal was purified in vacuum in the conventional manner. The reaction of OFN and the sodium metal was performed in a glass tube in the absence of air by contacting the OFN powder to sodium vapor through a breakable seal; after the seal was ruptured by a hammer under vacuum, only the tube containing purified sodium metal was kept at 423 K using a pipe heater until OFN sublimed completely at room temperature. The as-prepared sample was taken out of the sealed tube and separated into two parts; the one was washed with alcohol, 0.1 mol/L HCl solution, and water in order to remove the by-product, NaF. After the sample was dried in a vacuum oven at 383 K (OFN-AT), it was heat-treated under nitrogen stream at 1073 K (OFN-AT-1073). The other containing NaF was treated at 773 K for 1 h under nitrogen gas. Thereafter NaF was removed by acid-washing in the same manner (OFN-773-AT). Also the sample was heat-treated again at 1073 K (OFN-773-AT-1073).

The morphology and the texture of these samples were observed with a Hitachi FE-SEM, Type S-4700 and a JEOL JSM-TEM. The pore structure of the samples was characterized by measuring N_2 adsorption isotherm at 77 K using an apparatus of Nihon Bell BELSORP 28-SA.

The elemental analysis showed that both samples, OFN-AT and OFN-773-AT contain 3.4–1.7% of hydrogen and 16.2–14.1% of oxygen. These atoms are considered to result from surface oxidation occurring on exposure to air and/or in contact with the acid solution, as already confirmed on PTFE defluroination.[5] It is evident that these atoms present as oxygen-containing functional groups such as C–OH, C=O, or COOH. The carbon yield up to 1273 K was found from thermogravimetric analysis to be 67.0% on the basis of OFN-AT defluorinated completely, being much higher than that obtained in case of PTFE defluorination (45%).[5]

The morphology of OFN-AT and OFN-773-AT was observed by SEM. After sublimed OFN molecules were defluorinated with sodium vapor in gas phase and/or on the surface of melted Na in the sealed glass tube, the naphthalene molecules or their aggregates deposit gradually onto the tube. The SEM observation of OFN-AT indicates regular stacking of carbon species. When the defluorinated product containing NaF was firstly heated up to 773 K and then treated with the acid solution, a lot of fibrous bundles appeared. The detailed results on the morphology and the changes of these fibers with heat-treatment are under investigation.

When OFN-AT was heat-treated at 1073 K for 1 h, round pores with a few nanometers to several tens can be seen in the amorphous carbon. In case of OFN-773-AT the similar pore texture was observed, but comprised of a squarish shape, as can be seen in Figure 1. Taking into account that NaF forms a cubic crystal, the generation of such a characteristic pore shape

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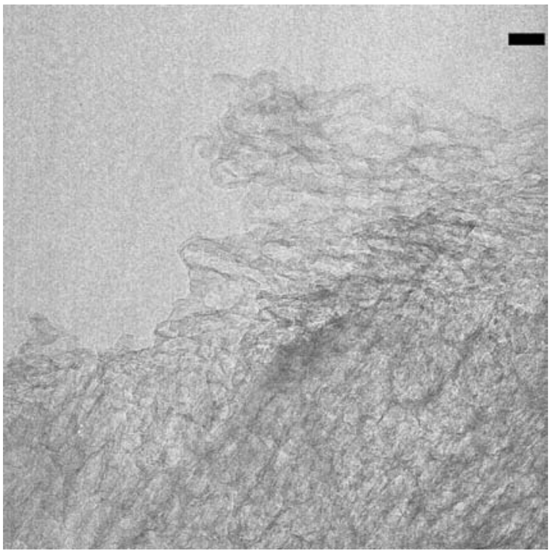

Figure 1. TEM image of OFN-773-AT. Scale bar: 100 nm.

in the carbon is considered to relate to the crystal growth of coexisting NaF during the heat-treatment. The average crystallite size estimated from the X-ray diffraction peaks due to NaF in OFN-773 without the ash treatment was ca. 50 nm, being roughly comparable to the pore size of the carbon.

Adsorption isotherm curves were obtained for OFN-AT and OFN-773-AT. Obviously, both carbons are very porous and OFN-AT is composed mainly of micropore structure, while OFN-773-AT contains considerable mesopores as well as a larger number of micropores. The pore parameters calculated by using α_s plots[9,10] and DH method,[11,12] were summarized in Table 1, together with those of OFN-AT-1073 and OFN-773-AT-1073. When the product containing NaF was heated at 773 K (OFN-773-AT), BET surface area, micro- and mesopore volumes increased as shown in Table 1. In particular, enhancement of the mesopore volume was three times higher than that of OFN-AT. In addition, the pore size of OFN-773-AT increased from 0.53 to 0.78 nm. The crystal growth of coexisting NaF during the heat-treatment may spread the pore size. When the acid-treated sample, OFN-773-AT was again heat-treated at 1073 K for 1 h, the pore shape was very similar to that of the original OFN-773-AT. Since the pores were somewhat contracted, however, micro- and mesopore volumes were decreased as well as the pore size. But the pore distribution between these two samples did not change so much even after further heat-treatment.

As described above, so much difference in morphology between the two kinds of the samples, OFN-AT and OFN-773-AT could not be observed from SEM and TEM micrographs, except for the pore shape. When PTFE was defluorinated with sodium metal in the same manner, the product formed a large amount of mesopores as well as micropores.[6] It is reasonable to consider that the removal of NaF leaves pores in the matrix carbon for both cases. A big difference is that at the first step of the PTFE defluorination, the carbyne-like structure is formed and then gradually transformed to sp^2 carbon network due to partial cross-linking reactions of the carbon chains. On the other hand, it is considered that the defluorinated naphthalene radicals polymerize with the neighboring ones and immediately form oligomers because peripheral carbons on naphthalene possess very high reactivity. Such a disordered polymerization of naphthalene molecules may contribute to the formation of additional micropores.

Table 1. Pore characteristics of the carbons derived from OFNs

Sample	BET surface area/m^2·g^{-1}	Micropore volume[a] /mm^3·g^{-1}	Mesopore volume[b] /mm^3·g^{-1}	Mean pore diameter[a] /nm
OFN-AT	1670	428	181	0.53
OFN-773-AT	2270	731	599	0.78
OFN-AT-1073	1570	499	294	0.71
OFN-773-AT-1073	2180	713	487	0.73

[a]The values were calculated by α_s plot. [b]The values were calculated by DH method.

In summary, defluorination of OFN with sodium metal and subsequent acid treatment produced micro- and mesoporous carbons. It was found that the coexistence of the by-product, NaF during heat-treatment of the defluorinated carbon enhanced the porosity and changed the pores into a squarish shape owing to the crystal growth of NaF during the heat-treatment.

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