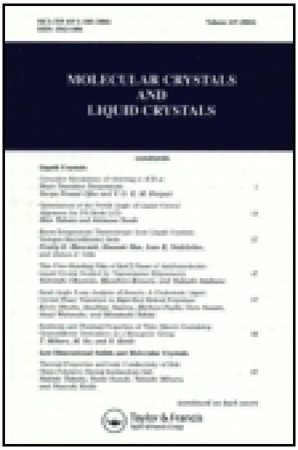

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Preparation and Characterization of Porous Carbons By Defluorination of Ptfe with Alkali Metals - Effect of Alkali Metals on the Porous Structure -

Osamu Tanaike [a], Noriko Yoshizawa [a], Hiroaki Hatori [a], Yoshio Yamada [a], Soshi Shiraishi [b] & Asao Oya [b]

[a] Institute for Energy Utilization, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, 305-8561, Japan

[b] Faculty of Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma, 376-8515, Japan

To cite this article: Osamu Tanaike, Noriko Yoshizawa, Hiroaki Hatori, Yoshio Yamada, Soshi Shiraishi & Asao Oya (2002): Preparation and Characterization of Porous Carbons By Defluorination of Ptfe with Alkali Metals - Effect of Alkali Metals on the Porous Structure -, Molecular Crystals and Liquid Crystals, 388:1, 45-50

To link to this article: http://dx.doi.org/10.1080/10587250215275

Mol. Cryst. Liq. Cryst., Vol. 388, pp. [459]/45–[464]/50
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113844

PREPARATION AND CHARACTERIZATION OF POROUS CARBONS BY DEFLUORINATION OF PTFE WITH ALKALI METALS
– EFFECT OF ALKALI METALS ON THE POROUS STRUCTURE –

Osamu Tanaike, Noriko Yoshizawa, Hiroaki Hatori,
and Yoshio Yamada
Institute for Energy Utilization, National Institute
of Advanced Industrial Science and Technology (AIST),
16-1 Onogawa, Tsukuba, Ibaraki 305-8561, Japan

Soshi Shiraishi and Asao Oya
Faculty of Engineering, Gunma University,
1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

Porous carbons were prepared by defluorination of poly-tetrafluoroethylene (PTFE) with various alkali metals and their porous structures were compared. Using sodium for defluorination resulted in a characteristic mesoporous carbon having a large mesopore volume with the narrow pore-size distribution of 2–3 nm diameter, in contrast to using potassium and rubidium which produced also mesoporous carbons but their pore-size distributions were wide spread. This difference seemed to be caused by the dispersion state of the alkali metal fluoride particles formed during defluorination.

Keywords: porous carbon; mesopore; carbyne; PTFE

INTRODUCTION

Polytetrafluoroethylene (PTFE), a polymer having a polyethylene structure where all the hydrogen atoms are substituted by fluorine, is known to be changed to so-called carbyne-type carbon by its chemical defluorination reaction [1,2]. This carbyne structure consists of one-dimensional molecular chains of carbon with *sp*-hybrid orbital, and it is also known to be

Part of this work is supported by a grant-in aid for "Research for the Future" Program from the Japan Society for the Promotion of Science (JSPS).

unstable structure. For example, the carbyne structure obtained from PTFE defluorinated by potassium metal was reported to be easily converted to stable sp^2 carbon in air [3].

One of recent interesting attempts for carbyne is to utilize it as a raw material for new functional carbon materials because it is supposed that the carbyne structure is too unstable and is transformed to other structures and forms of carbon easily. For example, carbon nanotubes, which are one of carbon materials most attracting attention recently, were reported to be synthesized via the carbyne structure from PTFE [4].

Porous carbon materials are also known to be synthesized from PTFE via a carbyne structure [5–8]. In this case, a carbyne-like structure is formed and cross-linked around fluoride by-product during defluorination of PTFE, and the fluoride particles are removed by acid treatment to leave spaces as pores in the carbon matrix. Defluorination of PTFE is carried out by using various reducing agents, such as lithium amalgam [5,6], lithium metal [7], lithium naphthalenide [7], or potassium metal [8]. The produced porous carbons had both micro- and mesopores with a large surface area, but the porous structure of resultant carbons were often different from each other. We synthesized porous carbons from PTFE using potassium metal vapor for defluorination and reported their porous structures previously [8]. In this paper, various alkali metals were used for defluorination of PTFE and the effect on the porous structure of resulting carbons was investigated.

EXPERIMENTAL

Commercially available PTFE powder (MP1500J: Dupont-Mitsui Fluorochemical Co. Ltd.) with a polymerization degree of ca. 10^6, average diameter of 20 μm and the specific surface area of 8–12 m^2/g was used as a raw material. Excess amount of lithium, sodium, potassium or rubidium metal and PTFE of 0.6−1 g were sealed together in a glass tube under vacuum, and then heated at 473 K in an oven for several days. In this process, lithium and sodium metal were directly contacted with PTFE powder but potassium and rubidium needed to be separated from PTFE to react as the vapor because the latter metals were more reactive than the former ones and it was dangerous that molten potassium or rubidium strongly reacted with PTFE to ignite easily. Lithium and sodium, on the other hand, contacted with PTFE without ignition in this temperature range of defluorination. The black color products were taken out from the tube slowly and exposed to air for a while, and then washed by water and immersed in 0.1 M HCl aqueous solution for two days to remove alkali metal fluorides. After the product had been dried thoroughly at 383 K in vacuum, nitrogen adsorption/desorption isotherms were measured at 77 K. TEM bright field images were also observed for the same products with the acceleration voltage of 200 kV.

RESULTS AND DISCUSSION

Nitrogen adsorption/desorption isotherms of the products from PTFE defluorinated by sodium (Na-PTFE), potassium (K-PTFE) and rubidium (Rb-PTFE) are shown in Figure 1, and their BET surface areas calculated using the isotherms in Figure 1, are summarized in Table 1. Lithium metal did not react with PTFE at 473 K and the defluorination by lithium was impossible. Since all three isotherms in Figure 1, belong to type IV in the IUPAC, mesoporous carbons [9] were found to be synthesized in all cases. On the other hand, micropores were also developed in the carbons because of a large amount of nitrogen adsorbed at the very low relative pressure. When sodium metal was used for defluorination of PTFE, a remarkable isotherm curve is obtained, having a characteristic steep slope line in the relative pressure range 0.1–0.4 and a large BET surface area, in contrast to the other two. When potassium metal was used instead, a quite similar

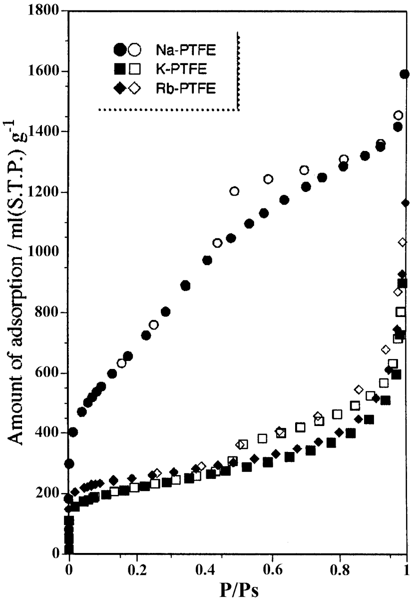

FIGURE 1 Nitrogen adsorption(closed marks) and desorption (opened marks) isotherms of Na-, K- and Rb-PTFE carbons measured at 77 K.

TABLE 1 BET Specific Surface Areas of Resultant Porous Carbons using Various Alkali Metals

Sample	BET specific surface area (m^2/g)
Li-PTFE	(unreacted)
Na-PTFE	2225
K-PTFE	784
Rb-PTFE	898

isotherm and BET surface area which we have already reported [8] were obtained. The reaction with rubidium showed a similar isotherm to that of potassium and the BET surface area slightly increased but it is not much different from potassium compared with sodium. In Figure 2, pore size distribution curves of the three porous carbons defluorinated by Na, K, and Rb calculated from the adsorption branches of each isotherms in Figure 1 by Dollimore-Heal method [10,11], are shown. The curve of Na-PTFE has a clear large peak of pore size in 2–3 nm which is mesopore range quite near to micropore, while those of K- and Rb-PTFE are have no large peak in the mesopore range. These results show that all three carbons, Na-, K- and Rb-PTFE have micropores and mesopores, but only Na-PTFE has a large amount of additional mesopores with the diameter of 2–3 nm which makes it comparable with other mesoporous materials, such as mesoporous silica,

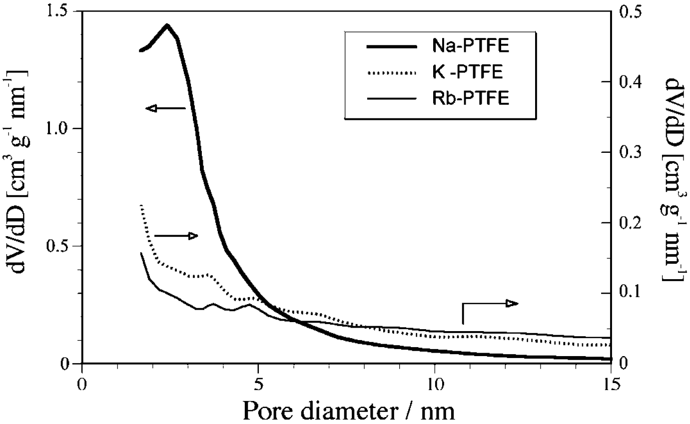

FIGURE 2 Pore size distribution curves of Na, K- and Rb-PTFE carbons calculated from the adsorption branches in Figure 1 by Dollimore-Heal method.

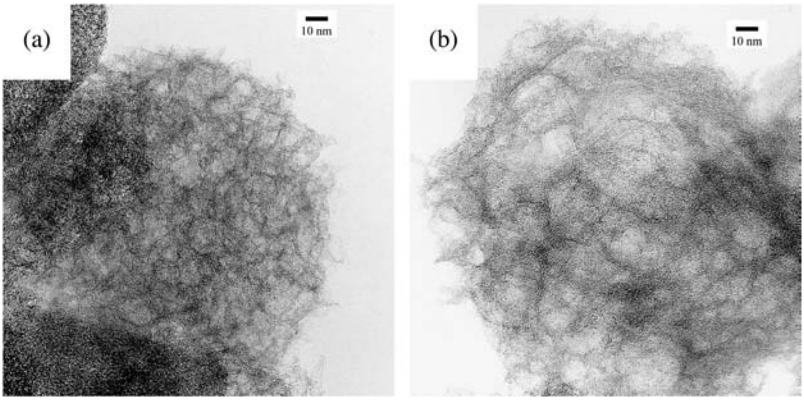

FIGURE 3 TEM images of (a) Na-PTFE and (b) K-PTFE carbons.

and some of them have been often given similar N_2 adsorption results to Na-PTFE [12,13].

TEM images of Na- and K-PTFE carbons are compared in Figure 3. Both images show particles like "foam" containing many circular pore images with diameters of less than 10 nm. Since these pores are imaged like round pore entrances, these carbons from PTFE seem to have a three-dimensional network of spherical mesopores which are the spaces left after fluoride particles were removed. However, there was a tendency that the size of the pores was smaller and the walls of pores were thinner for Na-PTFE than for K-PTFE. Since the walls of the pores were carbon made from PTFE via carbyne, it is supposed that sodium fluoride particles formed during defluorination of PTFE were dispersed better in PTFE than potassium fluoride. Such small particles of sodium fluoride well dispersed in the carbon matrix seem to cause the formation of large amounts of pores with 2–3 nm diameter and thinner pore walls which develop the porosity of Na-PTFE with a large surface area.

CONCLUSION

The pore structure of carbons obtained from PTFE via a carbyne structure was found to be strongly governed by alkali metal species used for defluorination of PTFE. This seems to be caused by the dispersion state of alkali metal fluoride particles in PTFE during defluorination due to the different reactivity of each alkali metals with PTFE. Using sodium, which is less reactive with PTFE than potassium and rubidium, resulted in the formation of well developed mesopores with the size range of 2–3 nm, which is near to micropores. These characteristic porous carbons using alkali metals for defluorination of PTFE, particularly using sodium, are expected to excel in some applications which particularly using sodium, are expected to excel in some applications which need mesopores, such as electric double layer capacitance.

REFERENCES

[1] Heimann, R. B., Evsyukov, S. E., & Kavan, L. (Ed.), (1999). Carbyne and carbynoid structure, *Physics and Chemistry of Materials with Low-dimensional Structures*, Kluwer Academic Publ: Dordrecht.

[2] Kavan, L. (1997). *Chem. Rev.*, *97*, 3061.

[3] Soneda, Y., Maruoka, K., Nakano, M., Akuzawa, N., & Yamada, Y. (1999). *Proc. ADC/FCT '99*, 571.

[4] Yasuda, A., Kawase, N., Matsui, T., Shimidzu, T., Yamaguchi, C., & Matui, H. (1999). *Reactive Funct. Polymers*, *41*, 13.

[5] Jansta, J., Dousek, F. P., & Patzelova, V. (1975). *Carbon*, *13*, 377.

[6] Dousek, F. P., Jansta, J., & Baldrian, J. (1980). *Carbon*, *18*, 13.

[7] Shiraishi, S., Kurihara, H., Tsdubota, H., Oya, A., Soneda, S., & Yamada, Y. (2001). *Electrochem. Solid-state Lett.*, *4*, A5.

[8] Liang, T. T., Yamada, Y., Yoshizawa, N., Shiraishi, S., & Oya, A. (2001). *Chem. Mater.*, *13*, 1933.

[9] Sing, K. S. W., Everett, D. H. W., Haul, R. A. W., Moscou, L., Pierotti, R. A., Rouquerol, J., & Siemieniewska, T. (1985). *Pure and Appl. Chem.*, *57*, 603.

[10] Dollimore, D. & Heal, G. R. (1964). *J. Applied Chem.*, *14*, 109.

[11] Dollimore, D. & Heal, G. R. (1970). *J. Colloid Interface Sci.*, *33*, 508.

[12] Setoguchi, Y. M., Teraoka, Y., Moriguchi, I., Kagawa, S., Tomonaga, N., Yasutake, A., & Izumi, J. (1997). *J. Porous Mat.*, *4*, 129.

[13] Sierra, L. & Guth, J. L. (1999). *Microporous and Mesoporous Mat.*, *27*, 243.