

Molecular Sieving Effect of Carbonized Kapton Polyimide Membrane

Hiroyuki Suda* and Kenji Haraya

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba 305, Japan

Microstructural investigation implies that the extremely high gas permselectivity (molecular sieving effect) of a carbonized polyimide membrane results from the decrease of the interplanar spacing and voids.

Recently, much attention has been paid to the synthesis of novel inorganic membranes for gas separation due to their high chemical and thermal stability. One of the candidates is a carbon membrane which is obtained by the pyrolysis of polyimide film.¹ The carbon membrane has been studied extensively and shown to have high gas permselectivities, namely, a molecular sieving effect.²⁻⁵ However, the measured gas permselectivities of 1 to 22 for the He/N₂ gas pair,^{2,4} sometimes lower than those of the original polymer films, have made the keyword 'molecular sieving effect' practically meaningless. Moreover, no structural investigation at the microscopic level related to the effect has yet been reported. We have already reported⁶ that a carbon membrane prepared by carbonization of a Kapton polyimide film under controlled conditions had the highest gas permselectivities yet found. Here, we report the relationship between the gas permselectivity and microstructure of the carbon molecular sieve membrane through permeation measurements and X-ray powder diffraction.

Carbon membranes were fabricated by the pyrolysis of Kapton polyimide film (Toray-Du Pont Inc.) between graphite blocks at 773–1273 K for 2 h with heating and cooling rates of 10 K min⁻¹ under a vacuum of 10⁻⁵ Torr. With increasing pyrolysis temperature, the masses and dimensions decreased abruptly at 873 K, and then gradually due to carbonization as previously reported.^{1,7} The carbon membrane thus obtained at 1273 K contained small amounts of oxygen, nitrogen, and a trace of hydrogen as well as a large amount of carbon. X-Ray diffraction profiles revealed that the carbon membranes were essentially X-ray amorphous and that the crystallinity became higher with increasing pyrolysis temperature (Fig. 1).

The gas permeabilities were measured at 373 K with a high-vacuum time-lag method⁸ under a pressure difference of 1 atm.

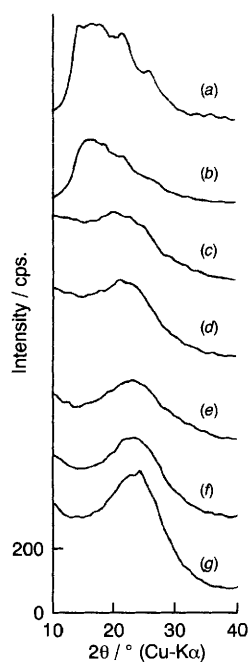


Fig. 1 X-Ray powder diffraction profiles of (a) the original Kapton polyimide film, and the carbonized polyimide membranes pyrolysed at (b) 773 K, (c) 873 K, (d) 973 K, (e) 1073 K, (f) 1173 K and (g) 1273 K

The permeabilities of selected gases were shown to be in the order H₂ > He > CO₂ > O₂ > N₂ for the membranes pyrolysed at 1073 and 1273 K (Fig. 2). The order was in good accordance with the order of kinetic gas diameters.⁹ The permeabilities of the selected gases became lower with increasing pyrolysis temperature. The decrease of an amorphous portion, where these gases preferentially diffuse rather than through a crystalline portion, may be one of the causes of this.

The gas permselectivities (the ratio of permeabilities for chosen gas pairs) became higher with increasing pyrolysis temperature (Fig. 2). For He/N₂ and H₂/N₂ gas pairs, the value reached up to 498 and 900, respectively, for the membrane pyrolysed at 1273 K, the values of which were much higher than those reported^{2,4} by one or two orders of magnitude. The extremely high gas permselectivities imply that in fact the carbon membrane has a molecular sieving effect, by which the membrane can discriminate between small and larger molecules. One of the reasons that we obtained the highest permselectivity is that we pyrolysed the film at a rather higher temperature, and the other is that we selected the polymer film suitable for the pyrolysis. Pyrolysis at lower temperature and/or pyrolysis of other films than Kapton polyimide might bring about the presence of a large amount of an amorphous portion and pores, resulting in the preference for permeation of any gases through these voids. A similar trend was seen on the carbon membrane pyrolysed below 1273 K (Fig. 2). The highest permeability of CO₂ gas observed on the membrane pyrolysed at 873 K suggests a surface diffusion mechanism⁵ caused by the adsorbed CO₂ gas at the wall of these voids.

In order to gain further insight into the structural changes of the carbon membranes, we estimated the interplanar spacing (d_{002}) from the 002 peak shift in the X-ray diffraction profiles (Fig. 1) using the Bragg equation, $\lambda = 2d\sin\theta$. Here, λ = wavelength of X-rays (1.5405 Å for Cu-K α radiation), d = interplanar spacing of 002 plane (Å), and θ = diffraction angle (°). The d_{002} values decreased from 4.00 Å for the carbon pyrolysed at 873 K to 3.85 Å for the carbon at 1073 K and to

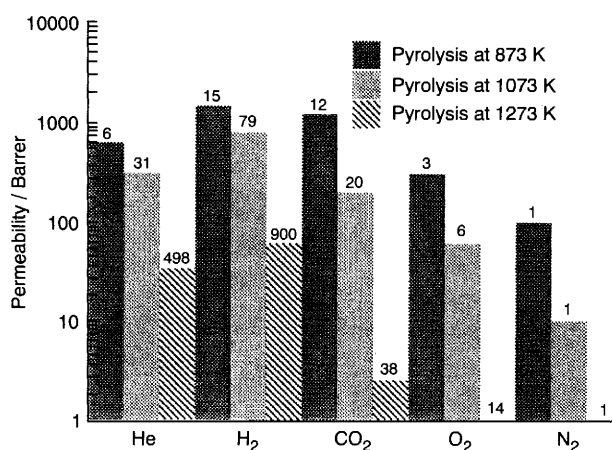


Fig. 2 Gas permeabilities and permselectivities measured at 373 K for the carbonized polyimide membranes pyrolysed at 873, 1073 and 1273 K. Permeabilities are given in Barrer, where 1 Barrer equals 1×10^{-10} cm³ (STP) cm cm⁻² s cmHg. Numerical values are permselectivities, defined as the ratio of permeabilities of chosen gases relative to that of N₂.

3.74 Å for the carbon at 1273 K. The obtained d_{002} values correspond to the interplanar spacings, which should play a crucial role for molecular sieving. We should note here that the free spacing between the graphitised layers is a little narrower than the estimated interplanar spacing. Thus, the larger molecules such as N₂ are more restricted than the smaller ones such as H₂, He, CO₂ and O₂ to permeate through the narrower free spacing close to or smaller than their kinetic gas diameters. Consequently, the high gas permselectivity is considered to come from the decrease of the interplanar spacing.

Additionally, the decrease of an amorphous portion with increasing pyrolysis temperature seems to contribute to the high gas permselectivity. As previously reported,^{7,10} the carbon prepared by the pyrolysis of organic materials has a turbostratic structure, in which layer-planes of graphite-like structure are dispersed in non-crystalline carbon. Several types of pores with diameters of a few tens of Å may also exist¹⁰ at the surface and in the structure into which molecules can penetrate. Thence almost all the molecules may penetrate and diffuse into the membrane *via* these voids. Since the membranes pyrolysed at lower temperatures than 1273 K have more of these voids, it is not difficult for the bigger molecules, even N₂, to permeate the membrane. Instead, as the crystallization proceeds at elevated temperatures, the N₂ molecules are restricted to permeate through the smaller and narrower cross-linked voids, and also through the narrower free spacing. These factors, *i.e.* the

decrease of the interplanar spacing, amorphous portion, and/or pores upon heating might be the origin of the 'molecular sieving effect'.

We would like to express our thanks to Dr S. Mizuta of National Institute of Materials and Chemical Research for use of X-ray diffraction apparatus.

Received, 27th March 1995; Com. 5/01935D

References

- 1 M. Inagaki, S. Harada, T. Sato, T. Nakajima, Y. Horino and K. Morita, *Carbon*, 1989, **27**, 253.
- 2 J. E. Koresh and A. Sofer, *Sep. Sci. Tech.*, 1983, **18**, 723.
- 3 J. E. Koresh and A. Sofer, *J. Chem. Soc. Faraday Trans. 1*, 1986, **82**, 2057.
- 4 H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata and S. Yoshitomi, *Carbon*, 1992, **30**, 305.
- 5 M. B. Rao and S. Sicar, *J. Membr. Sci.*, 1993, **85**, 253.
- 6 K. Haraya and N. Itoh, *Proc. ICOM'93, Int. Congr. Membrane Processes*, Heidelberg, Germany, 1993, pp. 2.5.
- 7 C. Bourgerette, A. Oberline and M. Inagaki, *J. Mater. Res.*, 1992, **7**, 1158.
- 8 R. M. Barrer, *Trans. Faraday Soc.*, 1964, **35**, 628.
- 9 D. W. Breck, in *Zeolite Molecular Sieves—Structure, Chemistry, and Use*, Wiley, New York, 1974, p. 636.
- 10 R. E. Franklin, *Proc. Roy. Soc. (A)*, 1951, **209**, 196.