Zeolitic Membrane Synthesized on a Porous Alumina Support

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A thin zeolitic membrane on porous alumina support has been synthesized; the permeability of the film to N_2 and O_2 indicated that the membrane was formed in a compact form.

Increasing attention has been paid to zeolites for developing a novel inorganic membrane which is expected to make it possible to separate gases at molecular levels. Few reports have appeared on the preparation of compact and thin zeolitic membranes with reasonable mechanical strength. The occurrence of pinholes and cracks between zeolite crystals was inevitable in the traditional hydrothermal synthesis of zeolite on the surface of a support.[1,2] We report the synthesis of a compact, thin zeolitic membrane on a porous alumina support.

An aluminosilicate gel was prepared by mixing an aqueous solution of sodium silicate (33–35 % SiO_2 and 17–19 % Na_2O by mass), $Al_2(SO_4)_3$ and H_2SO_4. The $SiO_2:Al_2O_3$ ratio of the gel was 25. The gel was buffered at pH 11.5. A porous alumina plate with an average pore diameter of 0.1 μm (Nihon Gaishi Co.) was dipped into the gel and thereby the surface of the plate was covered by a thin layer of the gel. The plate was then dried at 368 K overnight and treated in the presence of triethylamine, ethylenediamine and steam at 448 K for 3 days. Such crystallization of a dry gel to zeolites under a vapour of organic templates has been found by Xu *et al.*,[3] who synthesized ZSM-5 from a dry aluminosilicate gel. Various structural types of zeolites can be synthesized in this synthetic procedure.[4,5] Fig. 1 shows the XRD pattern of the zeolitic membrane, indicating that the zeolitic layer was composed of a mixture of ferrierite and ZSM-5. SEM observations revealed that a thin zeolitic layer (*ca.* 20 μm thick) was formed on the surface of the porous alumina plate (Fig. 2).

The rates of permeation of N_2 and O_2 through a zeolitic membrane with an effective membrane area of 2.2 cm^2 were measured at 298 K. Fig. 3 shows schematically the experimental apparatus used in this study. The zeolitic membrane was stuck on a glass tube with epoxy resin. The flow rate of N_2 or O_2 permeating through the membrane was measured. The permeabilities of N_2 and O_2 were found to be 1.7×10^{-12} and 1.2×10^{-12} mol m N^{-1} s^{-1}, respectively. The ratio of permeabilities, $O_2:N_2$, was 0.69. This value was lower than 0.93 which indicates that gas permeates by the Knudsen diffusion mechanism. The most zeolitic membranes which have been reported in the literature[1] gave an $O_2:N_2$ ratio of 0.93, indicating that permeation occurred preferentially through the holes where gas permeated in the Knudsen diffusion mechanism. On the contrary, formation of a compact zeolitic layer was strongly suggested in the present study because the selectivity to N_2 was higher than that in the region of Knudsen diffusion. Since N_2 adsorbed in zeolite crystals in preference to O_2, the higher selectivity to N_2 is considered to occur when N_2 and O_2 diffuse through the interiors of the zeolite crystals. In spite of the formation of a compact zeolitic membrane, the permeability of N_2 measured were comparable to that reported by Geus *et al.*,[1] 2.7×10^{-12} mol m N^{-1} s^{-1}. We consider that this result was due to the

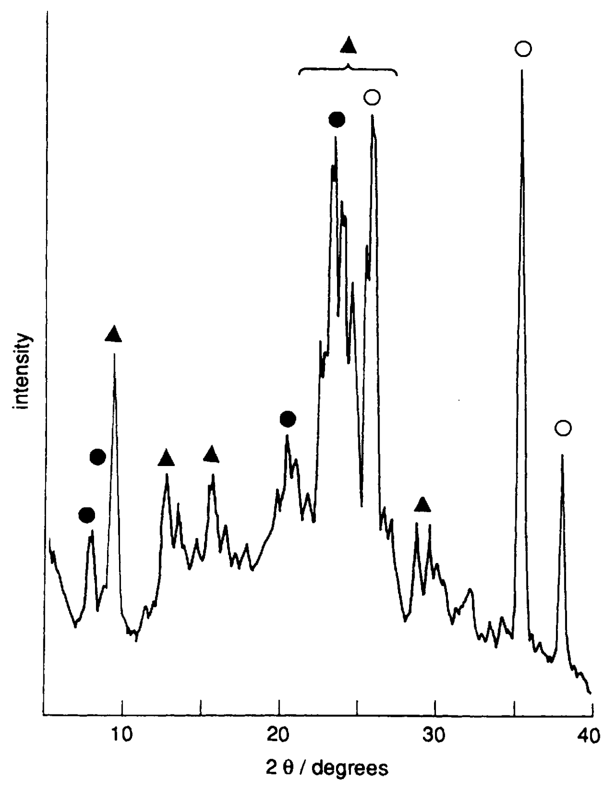

Fig. 1 XRD pattern of the zeolitic membrane: ○, Al_2O_3 substrate; ●, ZSM-5; ▲, ferrierite

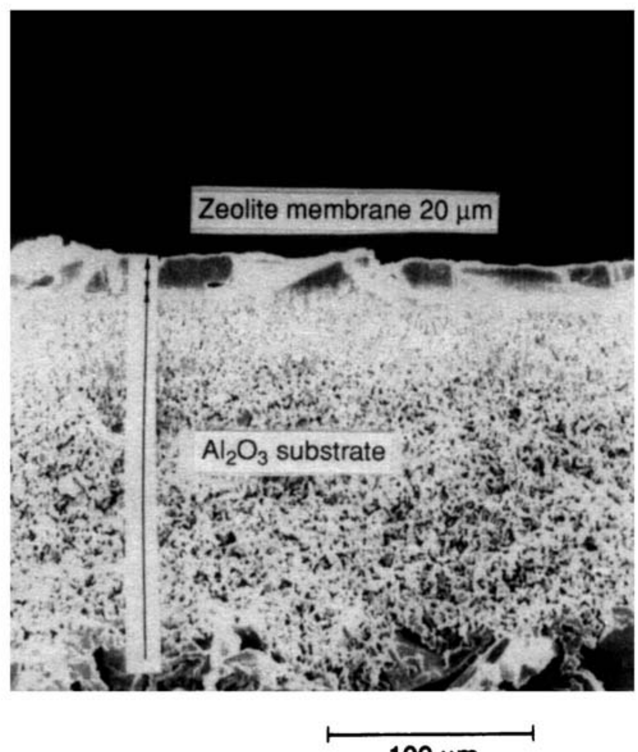

Fig. 2 SEM image of a cross-section of the zeolitic membrane

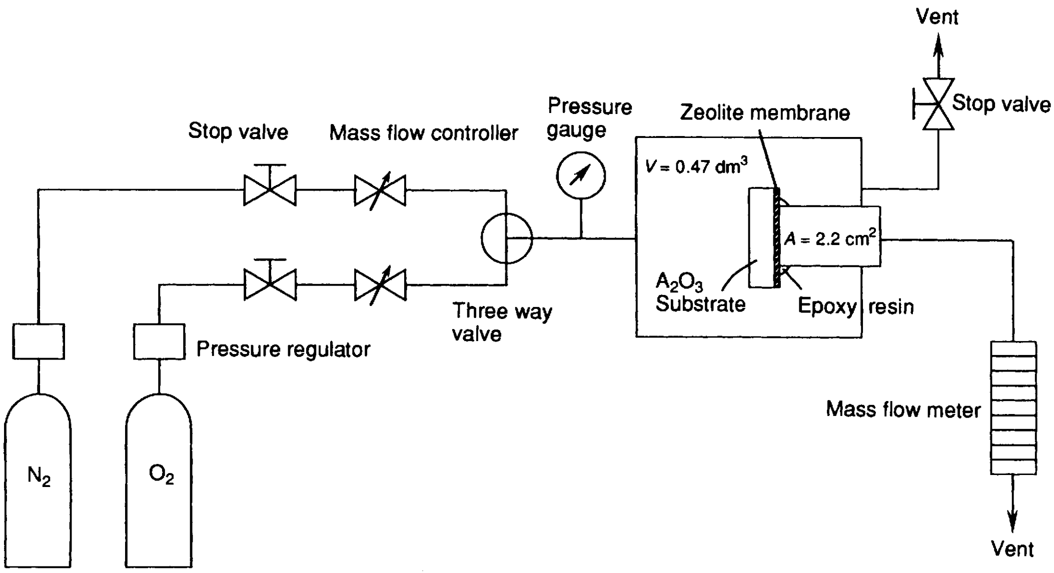

Fig. 3 Experimental apparatus for gas permeation

thickness of the membrane (20 μm): the membrane synthesized in this study was thinner than their membrane for which the thickness was reported to be *ca.* 100 μm.

In conclusion, we proposed and established a new preparation method for a compact zeolitic membrane which would enable separation at molecular levels.

Received, 13th September, 1993; Com. 3/05495K

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