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GAS PERMEATION PROPERTIES OF ION-EXCHANGED LTA-TYPE ZEOLITE MEMBRANES

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ABSTRACT

NaA-type zeolite membranes were prepared on a 1.7-mm i.d. porous α-alumina tube by repeating a hydrothermal reaction. The membranes, which were prepared by four repetitions, were ion-exchanged with Ca^{2+} and K^{+}, and the permeation for single-component and mixed gases were investigated at 35°C. The NaA-type membrane showed a hydrogen permeance of $(0.8–2.6) \times 10^{-8}$ mol $\cdot$ m^{-2} s^{-1} Pa^{-1} and a hydrogen/*n*-butane ideal separation factor of 12–15. The permeability properties of the membrane for binary mixtures were dependent on the size of the permeating molecules and their adsorptivity to the zeolite. The KA-type zeolite membrane showed a higher ideal separation factor for a hydrogen/nitrogen system than did the NaA- and CaA-type zeolite membranes. The pores of the CaA-type zeolite membrane were larger than those in the NaA- and KA-type zeolite membranes, and showed

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higher permeances to *n*-butane and *i*-butane. All the zeolite membranes contained non-zeolitic pores, which decreased the selectivity of permeation.

Key Words: Inorganic membrane; LTA-type zeolite; Gas separation; Ion-exchange

INTRODUCTION

A Linde Type A (LTA-type) zeolite with sodium cations (hereafter, referred to as NaA-type zeolite) has a formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$, and contains sodalite cages with apertures of approximately 0.4 nm. When the zeolite is ion exchanged with Ca^{2+} and K^+, the aperture dimension is changed to 0.5 and 0.3 nm, respectively (1). Attempts to prepare LTA-type zeolite membranes by a one-step process (2–7), as well as by multi-step processes (8–14), have been reported with seedings and chemical treatments. Kita (15) reported that NaA zeolite membranes were extremely effective for the dehydration of organic solvents by pervaporation. The separation factors (α) of water to ethanol, methanol, acetone, dioxane and dimethylformamide were 16,000; 2,500; 6,800; 9,300; and 8,700, respectively. However, the membrane prepared by those workers contained pores through which noncondensable gases permeated only at low selectivities. Wang et al. (16) prepared an NaA-type zeolite membrane and showed that gases permeated through the membrane in the following order: ethylene $>$ carbon dioxide $>$ methane $>$ nitrogen $>$ oxygen. Aoki et al. (11,14) fabricated a NaA-type zeolite membrane by repeating a hydrothermal reaction and determined that the ideal separation factor for H_2-N_2 system were 4.5–4.8, which were higher than the value for the Knudsen diffusion mechanism.

In general, gas permeation through porous membranes is explained by mechanisms such as Poiseuille flow, Knudsen diffusion, surface diffusion, and molecular sieving. When the ratio of pore diameter to molecule diameter approaches unity, the permeation is affected by the molecular structure and the affinity between permeating molecules and pore walls. Thus, LTA-type zeolite membranes have a high potential to separate small molecules through pores, which can be controlled by ion exchange with various cations. Jafar and Budd (17) prepared a KA-type membrane by ion exchanging a NaA membrane with an aqueous KCl solution of 0.1 mol/L for 3 h at 20°C. The membrane was then used for removal of water from isopropanol-water mixtures by pervaporation. Both NaA- and KA-type zeolite membranes were found to be highly selective under conditions of low water concentrations. Heink et al. (5) obtained a CaA-type membrane by ion exchanging a NaA-type membrane and determined the diffusivities of ethane and propane through the membrane. To date, however, no studies have been reported

on gas permeation for ion-exchanged LTA-type zeolite membranes. In this report, NaA-type zeolite membranes were ion exchanged with K^+ and Ca^{2+}, and permeation properties of the membranes for single-component gases and binary gas mixtures were determined.

EXPERIMENTAL

A porous α-alumina tube (o.d. = 2.8 mm; i.d. = 1.9 mm; average pore size = 150–170 nm), supplied by NOK (Japan), was used as the support of the LTA-type zeolite membrane. The outer surface of the support tube was rubbed with a NaA zeolite powder (75 μm in size) for seeding. After the rubbing treatment, the support tube was cut to a length of 30 mm and subjected to hydrothermal zeolite synthesis (14). The gel was prepared from water glass, $NaAlO_2$, NaOH, and deionized water. The initial composition of the solution was $Na:Si:Al:H_2O$ = 2:1:1:240 on a molar basis. The hydrothermal synthesis was performed at 100°C for 5 h in an autoclave, where the support tube was kept vertical in the solution. The reaction was repeated four times using fresh solution. These conditions were suitable for the preparation of LTA-type zeolite membranes as reported by Aoki et al. (14). After the synthesis, the membranes were thoroughly washed with distilled water and dried in air at 70°C. The cation exchange of the NaA-type zeolite membranes was carried out using aqueous 0.1 mol/L solutions of either $CaCl_2$ or KCl at ambient temperature for 8 h. After the ion-exchange treatment, the membranes were thoroughly washed with deionized water until the pH value of the rinse water became neutral. The resulting membranes were then dried in air at 70°C. The morphology of the membranes was observed by scanning electron microscopy (SEM) (Hitachi S-900). The extent of ion exchange in the membranes was determined by an energy-dispersive X-ray analyzer (EDX) (Kevex Delta Class). The adsorptivity of the LTA-type zeolite was determined using an adsorption unit (Shimadzu Micromeritics ASAP 2010) after drying the sample *in vacuo* at 150°C for 12 h.

Gas permeation tests were carried out in a coaxial cylindrical cell, which was described in detail by Kusakabe et al. (18), with hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), methane (CH_4), *n*-butane (n-C_4H_{10}), and isobutane (i-C_4H_{10}). Water vapor (H_2O), which was generated by bubbling, was added as needed to the feed to a final concentration of 3%. The membrane was connected to a stainless steel tube with epoxy resin, and the permeant-enabling portion of the membrane was 10–15 mm long. Each single-component gas was fed on the outside of the membrane tube. The permeate side (the inside of the membrane tube) was swept with a stream of argon or helium, and the concentration of the permeants was determined by gas chromatography using a thermal conductivity detector (Shimadzu GC-8A). The total flow rates on

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the feed and permeate sides were determined with soap-film flow meters. The partial pressure of permeants on the permeate side was maintained below 1 kPa by varying the flow rate of the sweep gas. The total pressure on both sides of the membrane was maintained at 101.3 kPa throughout the experiment. The permeation cell was placed in an electric furnace at 35°C. The permeance is defined as moles of gas permeated per unit time and unit membrane area, divided by the partial pressure difference between feed and permeate sides.

RESULTS AND DISCUSSION

Figure 1 shows the fractured surface of the NaA-type membrane. The zeolite membrane, which is composed of polycrystals, is 3 μm thick. The NaA-type membrane prepared by Aoki et al. (11) was 2–3 μm thick and was comparable to membranes prepared by four repetitions of the hydrothermal synthesis in the present study. Figure 2 shows the permeances of NaA-type membranes to single-component gases. The molecular dimensions of permeants were based on Lennard-Johnes potentials (1). Figure 3 shows that the permeances decrease and

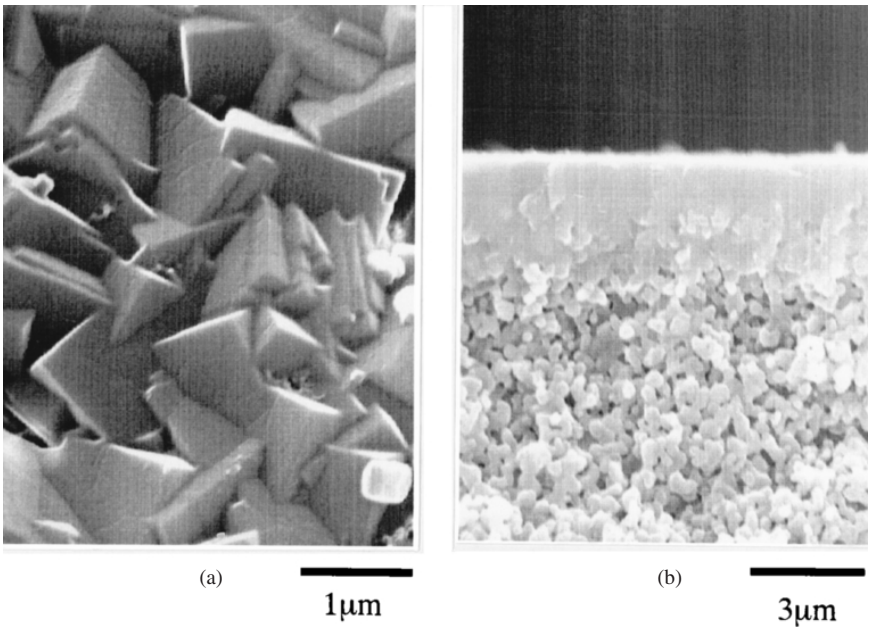

Figure 1. SEM images of an A-type zeolite membrane: (a) surface and (b) fracture surface.

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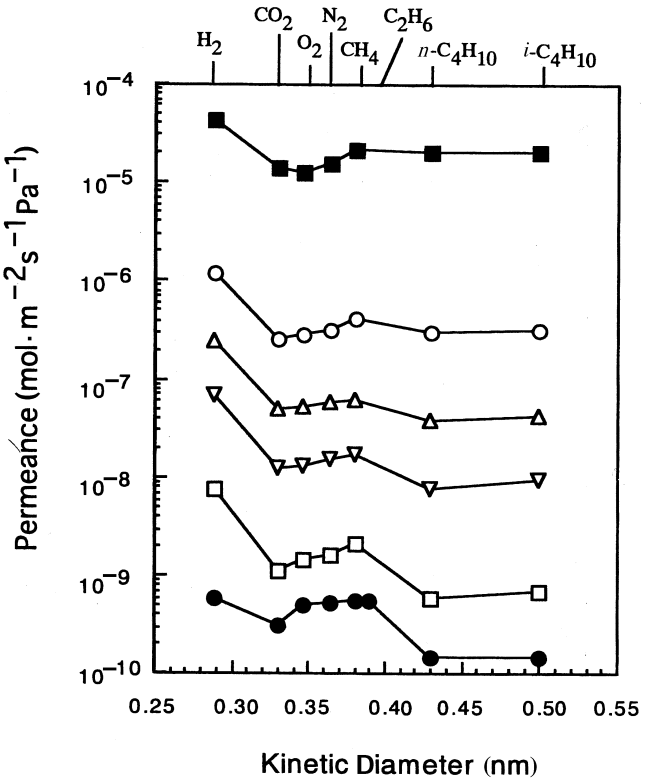

Figure 2. Effect of the repetition of the hydrothermal reaction on permeances at 35°C for NaA-type zeolite membranes. Repetition: 0 time (■), 1 time (○), 2 times (△), 3 times (▽), 4 times (□); data of Aoki et al. (19) (●).

the permeation selectivities increase with number of repetitions of the hydrothermal synthesis. As shown in Fig. 2, the permeances of this membrane were approximately one order of magnitude larger than those of the membrane prepared by Aoki et al. (19). The permeances of the membrane decreased sharply from H_2 to CO_2 and from CH_4 to n-C_4H_{10}. Meanwhile, the permeances of the membrane described by Aoki et al. (19) changed only between C_2H_6 and n-C_4H_{10}. A difference in permeances between CH_4 (or C_2H_6) and n-C_4H_{10} is typical for both type of membranes and can be attributed to the size of the zeolitic pores (0.4 nm). The ideal separation factors between these permeants were the same for both membranes. The ideal separation factor for the Knudsen mechanism for a mixture of H_2 and n-C_4H_{10} was 5.34, and the ideal separation factor of H_2 to n-C_4H_{10} was 13 at 35°C for the membrane prepared by four-time repetitions.

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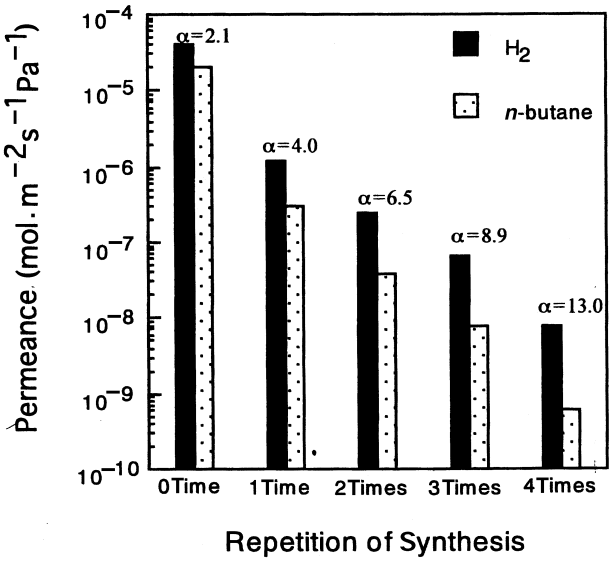

Figure 3. Ideal separation factors of H_2 to n-C_4H_{10} at 35°C for NaA-type zeolite membranes shown in Figure 2.

Figure 4 shows the permeances to single-component gases for the ion-exchanged LTA-type zeolite membranes. This membrane was prepared separately under the same conditions as the membrane for which data are shown in Figs. 2 and 3. The permeances through the CaA-type membrane were high, and those through the KA-type zeolite membrane were low compared to those of the NaA-type zeolite membrane. As determined by EDX, 96% and 97% of Na^+ in the NaA-type zeolite membrane were exchanged to Ca^{2+} and K^+, respectively. In the CaA-type zeolite, Ca^{2+} species are located at sites distant from the 8-ring openings. However, in the NaA-type zeolite, the 8-ring openings are partially narrowed by the presence of Na^+. Thus, the exchange of Na^+ with Ca^{2+} increases the pore diameter to 0.5 nm. As shown in Fig. 4, the ideal separation factor of an equimolar mixture of CH_4 and n-C_4H_{10} decreases to 1.86 from 2.50 for the NaA-type zeolite membrane. The permeances to n-C_4H_{10} and i-C_4H_{10}, the sizes of which are smaller and equivalent to the pore size of the NaA- and CaA-type zeolite membranes, increase respectively to 3.84×10^{-9} and 3.43×10^{-9}, from 1.72×10^{-9} and 1.76×10^{-9}, as the result of ion exchange from Na^+ to Ca^{2+}. Because the non-zeolitic pores in the CaA- and KA-type zeolite membranes are the same as those of the NaA-type zeolite membrane, the increases in permeances of the CaA-type zeolite membrane over those of the KA-type zeolite membrane should be attributed to the expansion of the zeolitic pores by the ion exchange to Ca^{2+}. The permeances to

C_4H_{10} gases through the NaA- and KA-type zeolite membranes can be attributed to the non-zeolitic pores. The bold line in Fig. 4 shows the calculated permeances for the NaA-type zeolite membrane. The data were determined under the assumption that all *i*-C_4H_{10} molecules permeate through the non-zeolitic pores, where the Knudsen diffusion mechanism prevails. The calculated data suggests that a substantial fraction of H_2 molecules permeates through the zeolitic pores.

Figure 5 shows that the permeances to H_2 and N_2 for the ion-exchanged membranes can be summarized as CaA > NaA > KA for single-component systems. The ideal separation factors of H_2 to N_2 by membrane are KA > NaA > CaA. With the exception of the KA-type zeolite membrane, in which H_2/N_2 separation factor for the binary system was greater than the ideal separation factor for single-component systems, the H_2/N_2 separation factor of CaA- and NaA-type zeolite membranes was not changed by the coexisting component. Figure 6 shows the effect of gas composition on permeances for H_2-CO_2 and N_2-CO_2 systems. The permeance to CO_2 in the presence of H_2 and N_2 is approximately equal to that for the single-component CO_2. This is contrary to the findings for the Y-type zeolite membranes, reported by Kusakabe et al. (20,21). The analysis of the permeation through the Y-type zeolite membranes shows that a permeant that adsorbs to the pore walls permeates at a slower rate than a coexisting non-ad-

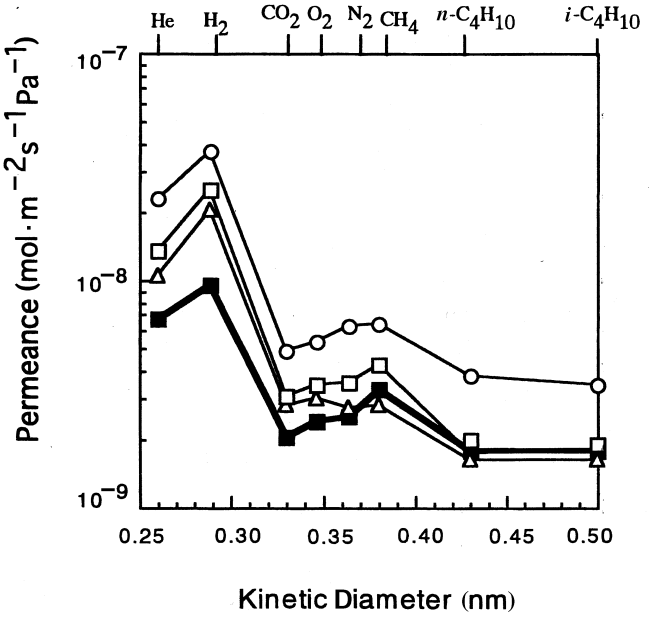

Figure 4. Permeances at 35°C for ion-exchanged LTA-type zeolite membranes. The bold line shows the values calculated based on the Knudsen diffusion mechanism.

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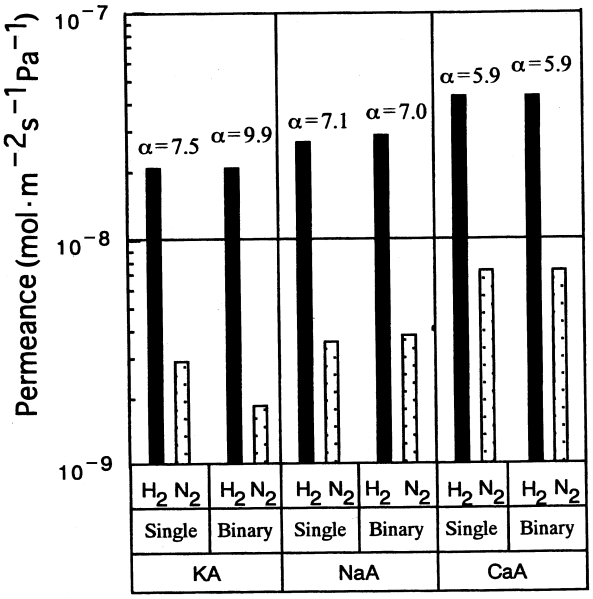

Figure 5. Effect of ion exchange on permeances and selectivities at 35°C.

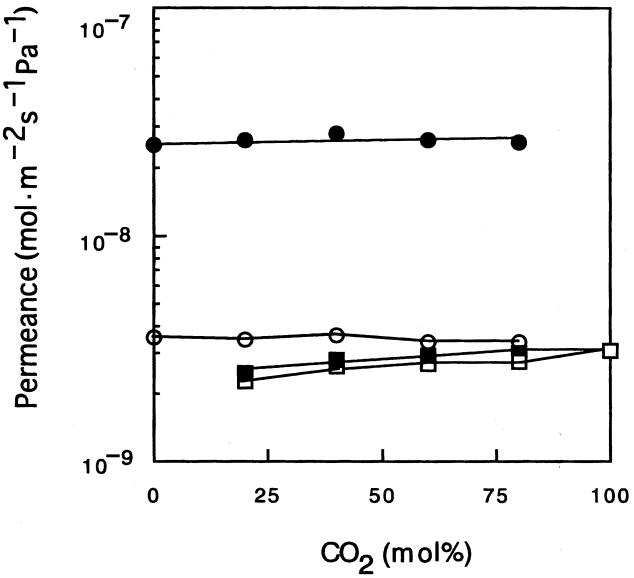

Figure 6. Permeances at 35°C for binary mixtures for an NaA-type zeolite membrane formed by four repetitions. H_2-CO_2 systems: ●, H_2; ■, CO_2: N_2-CO_2 system: ○, N_2; □, CO_2.

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sorptive permeant. In addition, a higher concentration of the adsorptive component in the Y-type zeolitic pores results in a higher permeance than that of the nonadsorptive component (20,21). The permeance to N_2 through the Y-type zeolite membranes is only 3–5 times lower than that of CO_2 for single-component systems, but is further decreased by one-order of magnitude for the mixed feed, since the concentration of N_2 in pores is decreased by the presence of the adsorptive component, i.e. CO_2. This can occur if molecules, which are adsorbed on the outer surface of the membrane, enter the zeolitic pores with no migration resistance and is realized for the Y-type zeolite membranes with zeolitic pores of 0.7–0.8 nm. For the A-type zeolite membranes, the permeance to CO_2 was lower than that of O_2, N_2, and CH_4 for single-component systems and remained unchanged for the mixed feed. As shown in Fig. 7, the CO_2 adsorptivity of the NaA-type zeolite prepared in the present study was smaller than that of the Y-type zeolite (20,21). Aoki et al. (19) reported that permeances to permeants, including CO_2 and H_2O, for the NaA-type zeolite membrane showed the following properties:

1. The permeances were not greatly dependent on permeation temperatures over the rage of 308–473 K.
2. For a mixed feed of H_2 and n-C_4H_{10}, permeances were not affected by the presence of the coexisting gas.

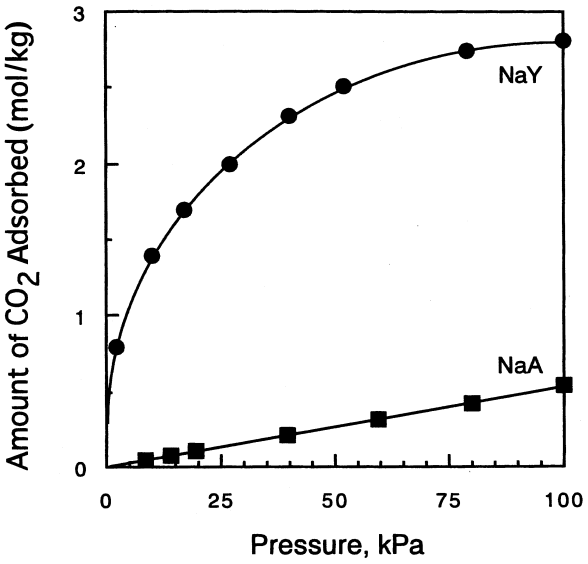

Figure 7. Adsorption isotherms of CO_2 at 35°C for NaA- and NaY-type zeolites.

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3. For a mixed feed of O_2 and n-C_4H_{10}, as well as C_2H_6 and n-C_4H_{10}, the permeance to C_2H_6 was higher and that to n-C_4H_{10} was lower than that for single component systems.

These results suggest that the LTA-type zeolite membranes, which were developed in the present study as well those described by Aoki et al. (11,14,19), possessed zeolitic pores and non-zeolitic pores. Thus, the permeation of gas through the LTA-type membranes is controlled by the configuration of permeants diffused through zeolitic pores, Knudsen diffusion through non-zeolitic pores, and surface diffusion through both types of pores. In a dynamic state of permeation, there might be a substantial barrier for CO_2 molecules, which are absorbed on the outside surface, to migrate into the pores with diameters of 0.4–0.6 nm. In the case of the LTA-type zeolite membrane, therefore, CO_2 molecules, which are rather weakly adsorbed on the surface, tend to enter the non-zeolitic pores, where the permeance is not strongly dependent on adsorptivity. Figure 8 shows the permeance of H_2 and i-C_4H_{10} for single-component feeds and an equimolar mixed feed through the NaA-type zeolite membrane. Compared to the permeance for the single-component systems, the H_2 permeance decreased to some extent, while that to i-C_4H_{10} remained unchanged. The kinetic diameter of i-C_4H_{10} is greater than the diameter of the zeolitic pores; therefore, it permeates through the non-zeolitic pores.

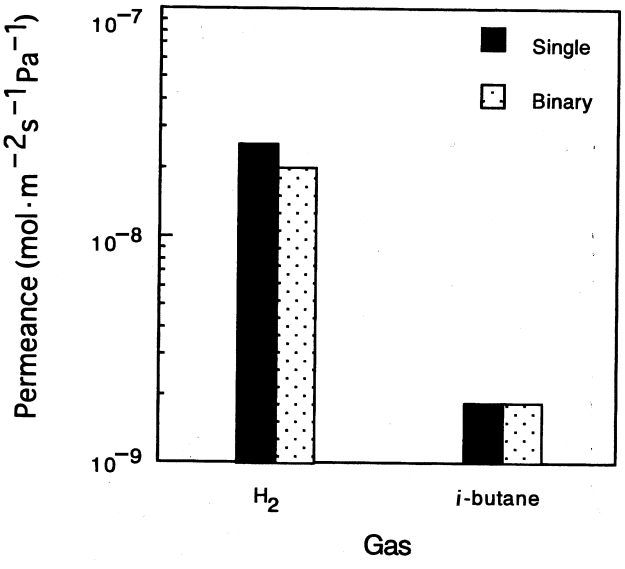

Figure 8. Permeances at 35°C for single-component and equimolar binary systems for NaA-type zeolite membrane formed by four repetitions.

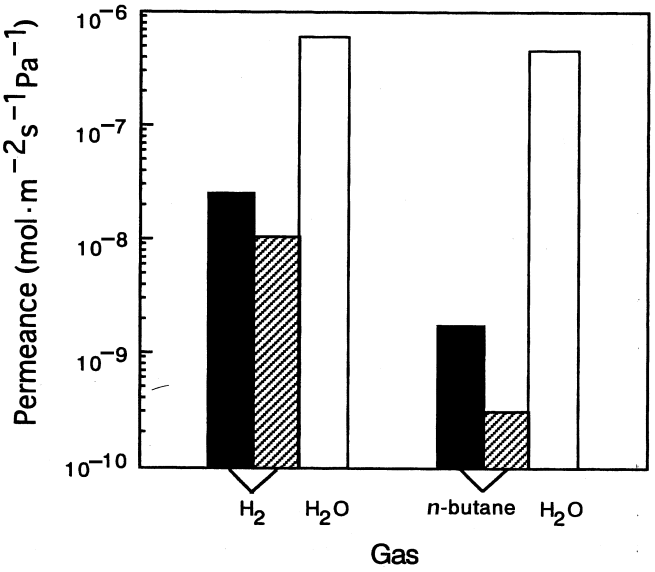

Figure 9. Permeances at 35°C for single-component systems and for moistened systems for NaA-type zeolite membrane formed by four repetitions. ■, single-component system; ▨, moistened system.

Figure 9 shows the permeation of H_2 and n-C_4H_{10} in the single- and moistened-feed systems through the NaA-type zeolite membrane at 35°C. Because the LTA-type zeolite membranes are highly selective for permeating H_2O, the permeance to H_2 decreases in the presence of H_2O. As reported by Aoki et al. (19), the permeance to n-C_4H_{10} in the presence of H_2O decreased sharply. Thus, the separation factor for the H_2/n-C_4H_{10} system was 53.2. If H_2O preferentially blocked zeolitic pores, the permeance to H_2 should have been decreased more than that to n-C_4H_{10}. The result suggests that H_2O blocked both zeolitic and non-zeolitic pores.

CONCLUSIONS

NaA-type zeolite membranes were fabricated on the outer surface of a porous α-alumina support tube by a repetitive short-term hydrothermal procedure. The permeances of single component gases through the membrane with different repeating times were determined. The permeance to H_2 and the ideal separation factor of H_2 to n-C_4H_{10} were in the ranges of (0.8–2.6) $\times 10^{-8}$ mol · m^{-2} s^{-1} Pa^{-1} and 12–15, respectively. Ca^{2+} and K^+ were exchanged on the NaA-zeolite mem-

branes, and the permeation rates of single gases through the membranes were investigated at 30°C. Based on the EDX analysis, the more than 96% of the Na^+ were exchanged by Ca^{2+} and K^+. The membranes showed the permeances in the order of CaA > NaA > KA, which was consistent with the order of aperture size of the zeolite membranes. The permeation properties for binary systems including H_2/CO_2, CO_2/N_2, $H_2/i\text{-}C_4H_{10}$, H_2/H_2O, and $n\text{-}C_4H_{10}/H_2O$, were dependent on molecule size and adsorptivity. Permeants such as $n\text{-}C_4H_{10}$ and $i\text{-}C_4H_{10}$ were only able to pass through the non-zeolitic pores, while H_2 permeated through both zeolitic and non-zeolitic pores.

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