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Separation of CO_2-CH_4 and CO_2-N_2 Systems Using Ion-exchanged FAU-type Zeolite Membranes with Different Si/Al Ratios

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Abstract−FAU-type zeolite membranes with different Si/Al ratios were hydrothermally synthesized on the outer surface of a porous α-Al_2O_3 support tube. The permeances of the membranes to CO_2, CH_4 and N_2 were then measured at 308 K for single-component and equimolar binary systems. The separation properties were dependent on both the Si/Al ratio and the ion-exchange treatment. For single-component systems, a lower Si/Al ratio resulted in the incorporation of a larger number of Na^+ ions. For a CO_2-CH_4 mixture, both CO_2 permeances and CO_2/CH_4 selectivities were approximately half the values obtained for a binary CO_2-N_2 mixture. The highest selectivities, obtained using the NaX(1) zeolite membrane, were 28 for CO_2/CH_4 and 78 for CO_2/N_2. The RbY, RbX(1) and RbX(2) zeolite membranes showed larger CO_2 permeances, compared with those of the original Na-type membranes. Ion-exchange with K^+ ions was the most effective for the NaY zeolite membrane in that both the CO_2 permeance and the CO_2/CH_4 selectivity were increased.

Key words: FAU-type Zeolite, Membrane, Ion Exchange, Gas Separation, Selectivity

INTRODUCTION

Zeolite membranes have considerable potential for use in the separation of small-sized molecules, and a number of studies have been reported for MFI [Aoki et al., 2000a; Dong et al., 2000; Gump et al., 2000; Lai et al., 2000; Matsufuji et al., 2000a; Millot et al., 2000; Nelson et al., 2001; Noack et al., 2000; Pan and Lin, 2001; Tuan et al., 2000; Van de Graaf et al., 2000; Xomeritakis et al., 2000], LTA [Aoki et al., 2000b; Okamoto et al., 2001; Xu et al., 2000], FAU [Hasegawa et al., 2001; Kita et al., 2000; Li et al., 2001; Nikolakis et al., 2001], MOR [Bernal et al., 2000; Lin et al., 2000], FER [Matsufuji et al., 2000b], SAPO-34 [Poshusta et al., 2000, 2001] and MCM-48 [Nishiyama et al., 2001] membranes. The FAU-type zeolite has relatively large pores, which are composed of 12-membered oxygen rings of approximately 0.74 nm in diameter. Thus, FAU-type zeolite membranes do not show strict molecular-sieving properties, as do the MFI-types, and separation by FAU-type zeolite membranes is usually achieved by differences in the adsorptivities of permeates. The larger pores of FAU-type zeolite membranes are, however, beneficial for higher permeation rates, compared to the MFI- and LTA-type zeolite membranes.

The FAU-type zeolite includes X- and Y-types, Si/Al ratios of which are 1-1.5 and 1.5-3.0, respectively. Thus, the number of cations, which can be coordinated in the X-type structure, is larger than that in the Y-type structure. Kusakabe et al. [1997, 1998] prepared NaY and NaX zeolite membranes on porous α-Al_2O_3 support tubes and investigated their properties in terms of the separation of CO_2 from N_2. The CO_2/N_2 selectivity reached a maximum of approximately 100 for the NaY-type zeolite membrane at a permeation temperature of 308 K. Permeance to CO_2 decreased with a decrease in the Si/Al ratio. Kusakabe et al. [1998, 1999] further investigated the permeation properties of Y-type zeolite membranes, which had been ion-exchanged with alkali and alkali-earth cations. The Y-type zeolite membranes, ion-exchanged with K^+, Rb^+, Cs^+ and Mg^{2+} ions, showed high CO_2/N_2 selectivities, compared to NaY-type zeolite membranes.

Vapor permeation [Kita et al., 2000; Jeong et al., 2001] and pervaporation [Kita et al., 2000; Li et al., 2001] of organic compounds have also been studied using FAU-type zeolite membranes. Nikolakis et al. [2001] separated a benzene-cyclohexane mixture using an NaX-type zeolite membrane and obtained the maximum benzene/cyclohexane selectivity of 160 at 373 K with a benzene permeation flux of 0.27 $mmol \cdot m^{-2} \cdot s^{-1}$. Similar results were reported by Kita et al. [2000] and Jeong et al. [2001]. Nikolakis et al. [2001] attributed the high permeation selectivity to the adsorption selectivity of the permeates on the feed-side surface of the membrane. However, Jeong et al. [2001] showed that the adsorption selectivity on the feed-side surface of the membrane was not a major factor. Thus, the interactions of pore walls and permeating molecules are important for the permeation selectivities of FAU-type zeolite membranes, but the mechanism is not fully understood.

In the present study, we report on the preparation of FAU-type zeolite membranes with different Si/Al ratios on the outer surface of α-Al_2O_3 support tubes by means of a hydrothermal synthesis. The membranes were ion-exchanged with Rb^+ and K^+ ions, and their permeation properties were investigated by using equimolar mixtures of CO_2-CH_4 and CO_2-N_2 at 308 K. The role of the interactions between the pore walls and permeating molecules was then discussed.

EXPERIMENTAL

FAU-type zeolite membranes were prepared on the outer sur-

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face of porous α-Al_2O_3 support tubes (NOK Corp., Japan) by the same procedures as were reported previously [Hasegawa et al., 2001; Kusakabe et al., 1999]. The properties of the support tube were: length=200 mm; outside diameter=2.1 mm; inside diameter=1.7 mm; void fraction=0.39; and pore size=120-150 nm. A solution used for synthesis was prepared by mixing water glass, $NaAlO_2$ and NaOH. The composition of the starting solution was Al_2O_3 : SiO_2 : Na_2O : H_2O=1 : x : 17 : 975, where the SiO_2 ratio, x, was 12.8 for NaY-type zeolite [Hasegawa et al., 2001], 6.4 and 4.8 for NaX-type zeolites. Hereafter, the samples, which were prepared using these solutions, are referred to as NaY-, NaX(1)- and NaX(2)-type zeolites, respectively. The solution was stirred for 4 h at room temperature prior to the synthesis. The outer surface of the support tube was rubbed with NaX zeolite particles (Tosoh Corp., #F-9; Si/Al=1.25, crystal size=3-5 μm). The seeded alumina tube was then placed into a tubular autoclave, which was filled with the synthesis solution. This autoclave was then horizontally positioned into an oven, and kept at 363 K for 24 h. The prepared zeolite membranes were ion-exchanged with a 0.10 mol·L^{-1} solution of either KCl or RbCl, rinsed with deionized water, and then air-dried. NaY, NaX(1) and NaX(2) zeolite particles were also prepared under the same conditions as were used for the synthesis of the membranes. The Si/Al ratio and the degree of ion-exchange were determined by energy-dispersive X-ray analysis (EDX, Kevex Delta Class).

Permeation tests [Kusakabe et al., 1997] were carried out using single-component CO_2, CH_4 and N_2, as well as equimolar mixtures of CO_2-CH_4 and CO_2-N_2. Helium was used as a sweep gas. The total pressure of both sides of the membrane was maintained at 101.3 kPa, and the permeation temperature was fixed at 308 K throughout the experiments. Permeance was calculated from the following equation.

$$\text{Permeance} = \frac{(\text{mol of gas transferred per unit time})}{(\text{membrane area})(\text{partial pressure difference})} \qquad (1)$$

The selectivity was defined by the ratio of permeances. The isotherms of single-component CO_2, CH_4 and N_2 were determined using an adsorption unit (Bell Japan, FMS-BG). The micropore size distributions were decided by an adsorption method (Micrometrics, ASAP2001).

RESULTS AND DISCUSSION

The formation of the FAU-type structure was confirmed based on XRD by Kusakabe et al. [1997]. The Si/Al ratios, as determined by EDX, were 1.54 for NaY, 1.26 for NaX(1) and 1.16 for NaX(2) zeolite samples. Each membrane consisted of two zeolite layers [Kusakabe et al., 1997]: an inner layer formed in the voids of the support (ca 5 μm in thickness) and an outer layer formed on the surface (ca 3 μm in thickness). For all membranes, the top surface was smooth.

Figs. 1(a) and (b) show the permeation data for CO_2-CH_4 and CO_2-N_2 for the FAU-type zeolite membranes, respectively. For all cases, CO_2 permeated faster than N_2 and CH_4. This can be explained by the fact that CO_2 is adsorbed more strongly than CH_4 and N_2 as shown in Fig. 2, and by the smaller kinetic diameter (CO_2: 0.33 nm, N_2: 0.36 nm, CH_4: 0.38 nm) [Breck, 1974]. The permeances were the highest for the NaY-type zeolite membrane and decreased with a decrease in the Si/Al ratio. However, the adsorptivities of CO_2 and CH_4 were not significantly influenced by the Si/Al ratio. The number of Na$^+$ ions which were originally incorporated in the zeolite

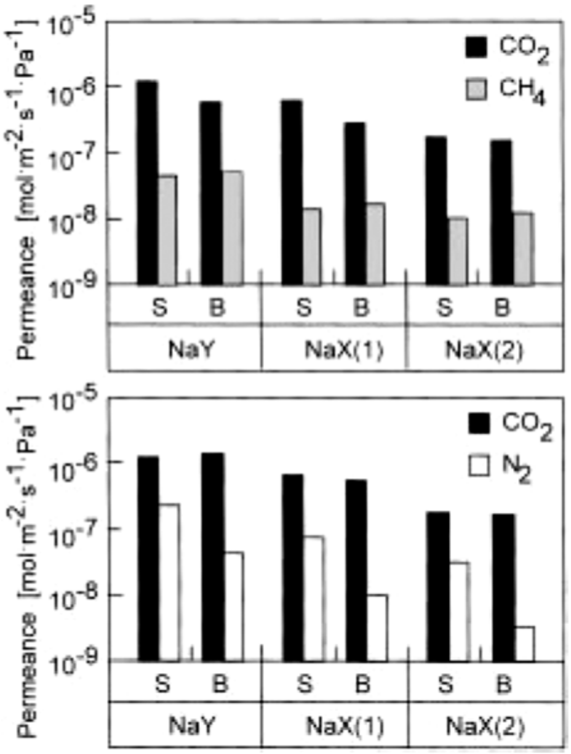

Fig. 1. Permeances through NaY-, NaX(1)- and NaX(2)-type zeolite membranes for (a) CO_2-CH_4 and (b) CO_2-N_2 systems.
S: Single-component; B: equimolar binary mixture

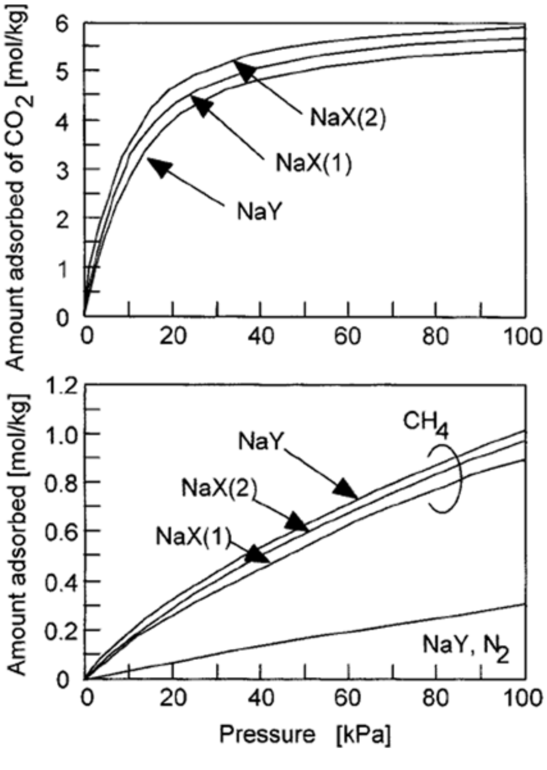

Fig. 2. Adsorption isotherms for single-component CO_2, CH_4 and N_2 on NaY, NaX(1) and NaX(2) zeolite particles.

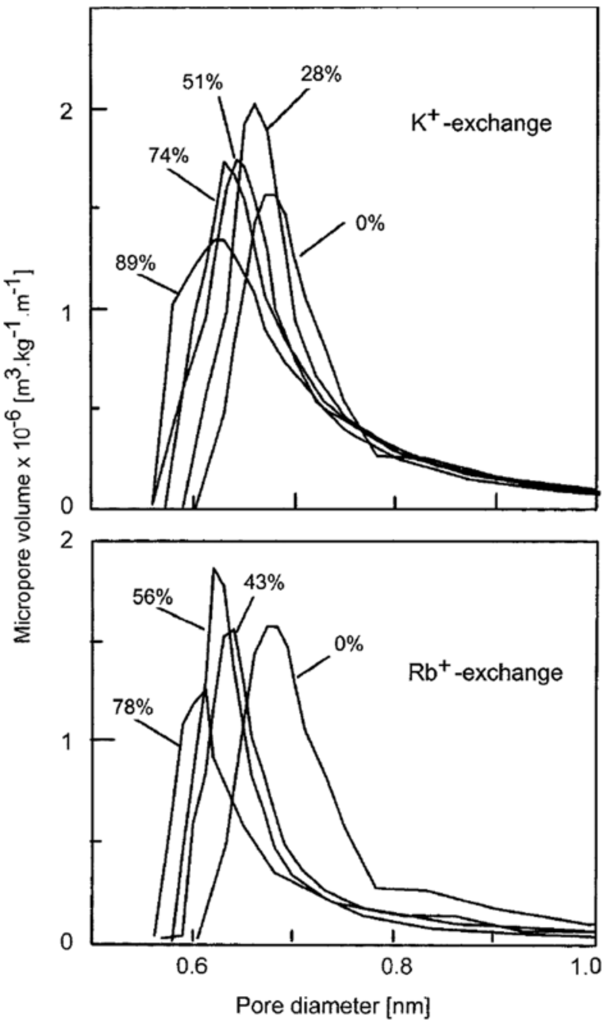

Fig. 3. Size distributions of micropores for K and Rb and ion-exchanged zeolites. Numbers refer to the degree of ion-exchange.

structure was dependent on the Si/Al ratio, and was of the order of NaX(2)>NaX(1)>NaY. These results suggest that the permeation rates are related to the size of zeolitic pores, although the pores are larger than the permeating molecules as shown in Fig. 3.

The CO_2 permeance of the NaY-type zeolite membrane for the binary CO_2-N_2 system was larger, and the N_2 permeance was much smaller than those for single-component systems. However, the reverse tendencies were observed for the CO_2-CH_4 system; namely, the CO_2 permeance for the binary system was smaller than that for the single component system. As a result, the CO_2/CH_4 selectivity for the binary system was significantly low, compared to the ideal CO_2/CH_4 selectivity (ie., selectivity calculated from permeances for single-component systems), as indicated in Table 1. Kusakabe et al. [1997, 1998, 1999] reported that these results could be attributed to the preferential adsorption of CO_2 from the binary mixture of CO_2 and N_2. Similar permeation behaviors were obtained in the present study for the NaX(1)- and NaX(2)-type zeolite membranes. Furthermore, they explained the permeation properties using a sorption-diffusion model, and diffusion coefficients of CO_2 and N_2 were calculated. The diffusion coefficient of CO_2 was one order of magnitude smaller than that of N_2, because CO_2 was the strongly adsorbed component on zeolites. The reverse tendency of the CO_2/CH_4 selectivity was caused by diffusion coefficients.

Table 1. CO_2 selectivities of FAU-type zeolite membranes with different Si/Al ratios

Membrane	Si/Al molar ratio	System	Selectivity	
			CO_2/CH_4	CO_2/N_2
NaY	1.54	Single	28	6
		Binary	12	30
NaX(1)	1.26	Single	51	9
		Binary	18	60
NaX(2)	1.16	Single	18	5
		Binary	13	53

Figs. 4(a) and (b) show the relationship between CO_2 permeances and CO_2 selectivities for the binary systems of CO_2-CH_4 and CO_2-N_2, respectively. The permeances and selectivities of CO_2 for the CO_2-CH_4 system were half the values found for the CO_2-N_2 system. When the NaX(1)-type zeolite membrane was used, the maximum selectivity was determined to be 28 for the CO_2-CH_4 system and 78 for the CO_2-N_2 system. The high CO_2/CH_4 selectivities of these FAU-type zeolite membranes (pore size=0.74 nm) were largely the result of the preferential adsorption of CO_2. Poshusta et al. [2000,

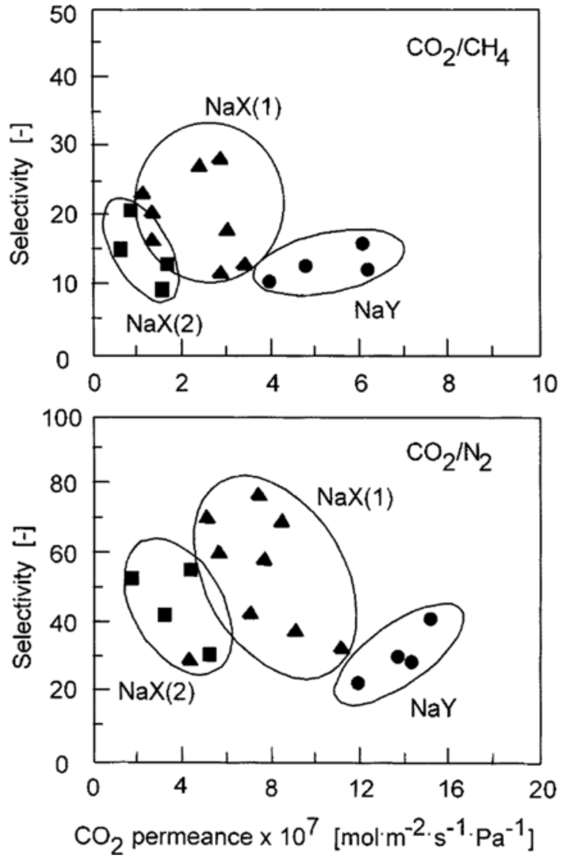

Fig. 4. Relationship between permeance and selectivity of CO_2 for NaY-, NaX(1)- and NaX(2)-type zeolite membranes for (a) CO_2-CH_4 and (b) CO_2-N_2 systems.

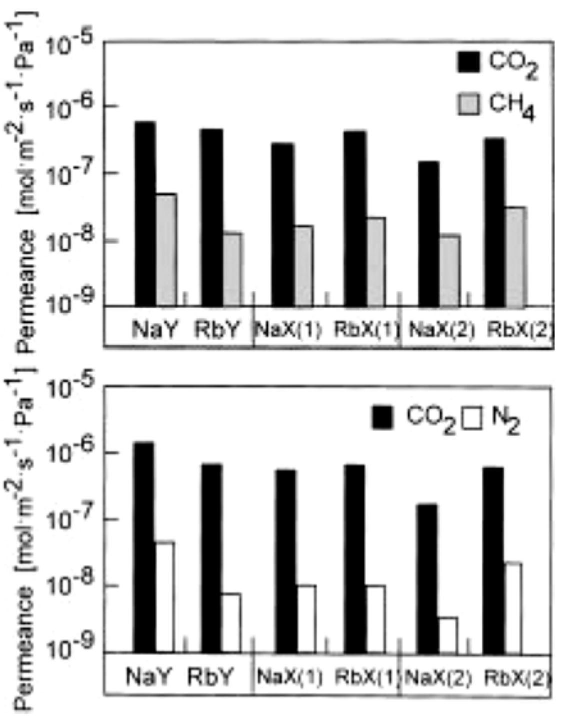

Fig. 5. Permeances through NaY-, RbY-, NaX(1)-, RbX(1)-, NaX(2)- and RbX(2)-type zeolite membranes for (a) CO$_2$-CH$_4$ and (b) CO$_2$-N$_2$ systems.

2001] synthesized an SAPO-34 zeolite membrane (pore size=0.4 nm), which was able to separate CO$_2$ from CH$_4$. The highest selectivity was 36 for an equimolar mixture of CO$_2$-CH$_4$ at 300 K. The single-component CO$_2$ permeance was 2.0×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} under the same conditions. Amorphous silica, which has smaller pores than the Y-type zeolite, is often used as the material for membranes. Silica membranes [De Vos and Verweij, 1998; Tsai et al., 2000] can recognize small gaseous molecules on the basis of their size, and H$_2$ and CO$_2$ permeate at higher rates than CH$_4$ and N$_2$. Tsai et al. [2000] prepared dual-layer microporous silica membranes using a sol-gel method. The CO$_2$/CH$_4$ selectivity was 200 for an equimolar binary mixture at 299 K. However, the CO$_2$ permeance was relatively low (10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}), compared to that of Y-type zeolite membranes.

Figs. 5(a) and (b) show the effect of Rb$^+$ ions on permeation properties for equimolar CO$_2$-CH$_4$ and CO$_2$-N$_2$ systems, respectively. For the Y-type zeolite membrane, the permeances to CH$_4$ and N$_2$ greatly decreased by the ion-exchange treatment, and as a result, both CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivities increased. For the X(1)- and X(2)-type zeolite membranes, however, the permeance to all permeants increased. Thus, CO$_2$/CH$_4$ and CO$_2$/N$_2$ selectivities were not improved. Based on these results, the NaY-type zeolite membrane was ion-exchanged with K$^+$, in an attempt to further increase the CO$_2$ selectivities. As shown in Figs. 6(a) and (b), both the CO$_2$ permeance and the CO$_2$ selectivity were improved. This suggests that the incorporation of K$^+$ ions caused a slight decrease in the zeolitic pores, and increased the adsorption of CO$_2$. The CO$_2$ permeance and CO$_2$/CH$_4$ selectivity of the KY-type zeolite membrane was in the range of $(7.5\text{-}9.0)\times10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1} and 25-40, respectively. These values can be assumed to be suitable for CO$_2$ removal in commercial processes [Watanabe, 1999].

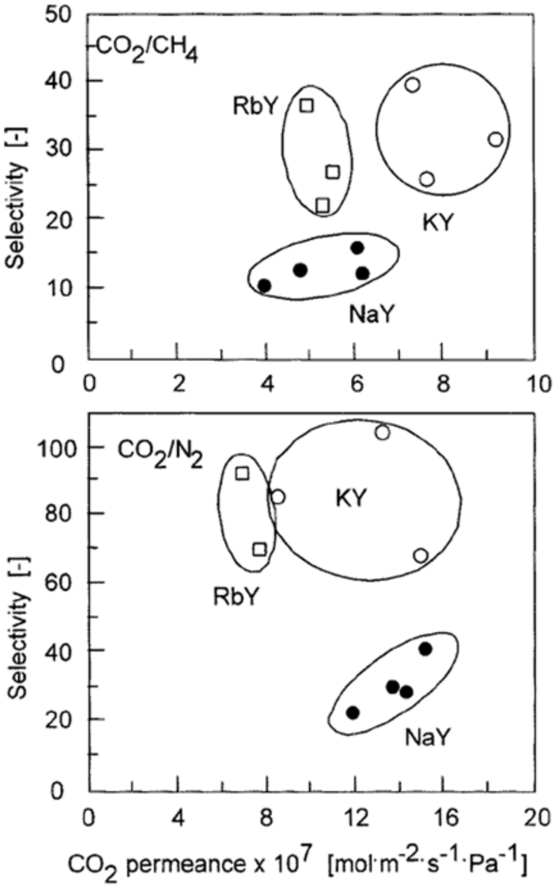

Fig. 6. Relationship between permeance and selectivity of CO$_2$ for NaY-, KY- and RbY-type zeolite membranes for (a) CO$_2$-CH$_4$ and (b) CO$_2$-N$_2$ systems.

CONCLUSIONS

FAU-type zeolite membranes with different Si/Al ratios were prepared by means of a hydrothermal synthesis. Permeances for single-component systems at a temperature of 308 K were in the order of CO$_2$>N$_2$>CH$_4$, and decreased with decreasing Si/Al ratio. Permeances and selectivities of CO$_2$ for the CO$_2$-CH$_4$ system were approximately half the values obtained for the CO$_2$-N$_2$ system. The NaX(1)-type zeolite membrane showed the maximum CO$_2$ selectivities, which were 28 for the CO$_2$-CH$_4$ system and 78 for the CO$_2$-N$_2$ system, respectively. In an attempt to increase the CO$_2$ selectivity, the incorporated Na$^+$ ions were exchanged with Rb$^+$. The effect of the ion-exchange was the highest for the NaY-type zeolite membrane. The CO$_2$ separation ability of the NaY-type zeolite membrane was further improved by ion-exchange with K$^+$. The CO$_2$/CH$_4$ selectivity of the KY-type zeolite membrane was in the range of 25-40, and the CO$_2$ permeance was in the range of $(7.5\text{-}9.0)\times10^{-7}$ mol·m^{-2}·s^{-1}·Pa^{-1}.

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