P-1

Effects of permeation test conditions on CO_2/N_2 separations of NaY zeolite membranes

Churl-hee Cho[*,a], Young-soo Ahn[a], Moon-hee Han[a], Sang-hoon Hyun[b]

[a] *Functional Materials Research Center, Korea Institute of Energy Research, Taejon 305-343, Korea*

[b] *Department of Ceramic Engineering, Yonsei University, Seoul 120-749, Korea*

[*] Corresponding author. Tel.: +82-42-860-3505; fax: +82-42-860-3133; e-mail: chcho@kier.re.kr

Since Kyoto protocol in 1997, carbon dioxide recovery using membranes has been attended due to its potential applications to recover high purity carbon dioxide with low processing cost. Because carbon dioxide membrane should operate in chemically and thermally severe conditions and requires high permeance, an inorganic membrane is more favorable than a polymeric membrane. Many inorganic materials have been considered as carbon dioxide membranes. Among them, templated silica [1-2], molecular sieving carbon [3-6], and nanoporous zeolite [7-8] membranes are representative and show promising performances on carbon dioxide separation. In the inorganic membranes, there is an apparent trade-off between separation factor and permeance, and also is an overall trend of decreasing separation factor with increasing permeation temperature. Especially, it is remarkable that NaY zeolite membrane shows not only good CO_2/N_2 separation factor but also excellent CO_2 permeance [7-9]. In a gas separation system using a membrane, its gas recovery rate is directly related to the gas flux through a membrane. Gas permeation flux is dependent on both membrane-intrinsic permeation properties and system-operational variables. Therefore, in the present study, influences of permeation test conditions (permeation temperature, feeding rate, feed composition, feed pressure and He sweeping rate) on CO_2/N_2 separation of NaY zeolite membrane were investigated. From the investigations, CO_2 and N_2 permeation mechanisms and pre-requirements for its real applications to carbon dioxide recovery process in a combustion flue gas will be discussed.

In the present study, a defect-free NaY zeolite membrane was successfully prepared on the outer surface of an α-Al_2O_3 tube which had been hydrothermally treated at 110°C for 24 hours in an aqueous solution of which composition was $Al_2O_3:SiO_2:Na_2O:H_2O = 1:6:14:840$ in a molar basis. CO_2 and N_2 permeation properties of NaY zeolite membrane were evaluated under various permeation test conditions. The optimum synthesis condition for NaY zeolite preparation was so different from ones reported by others [7-13].

Figure 1 represents SEM images for (a) surface and (b) cross-section of NaY zeolite membrane prepared in the present study. Zeolite crystals were uniformly deposited on the α-Al_2O_3 support and its average thickness was around 5μm. From XRD analysis, the grown zeolite crystals were faujasite zeolite phases. Also, in the composition analysis using EDS, the atomic ratio of Si to Al in the faujasite zeolite membrane was around 2. Therefore, it was confirmed that the zeolite crystals grown on the outer surface of α-Al_2O_3 support were NaY zeolite crystals.

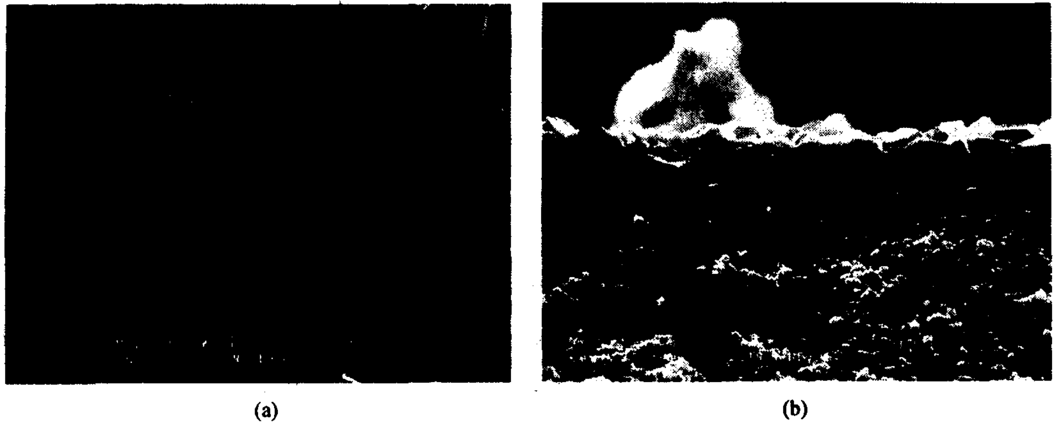
(a) (b)

Fig. 1. SEM images of (a) surface and (b) cross-section of NaY zeolite membrane

Table 1 represents CO_2 and N_2 permeances in single component systems and CO_2/N_2 permselectivity. With increasing permeation temperature, CO_2 permeance showed a maximum at 80°C, N_2 permeance continuously increased, and CO_2/N_2 permeselectivity decreased. It is evident that N_2 permeance was comparable to CO_2 permeance.

Table 1 Permeance and permselectivity as a function of temperature

Temperature(°C)	Permeance (10^{-7} mol/m^{2}secPa)		Perm-selectivity
	CO_2	N_2	CO_2/N_2
30	4.54	0.75	6.1
50	5.16	1.39	3.7
80	5.26	1.85	2.8
100	5.06	2.23	2.3

Figure 2 represents CO_2 and N_2 fluxes and CO_2/N_2 separation factor at 30 °C as a function of feed pressure. The feeding and He sweeping rates were 350 and 146 ml/min, respectively. As feed pressure increased, CO_2 and N_2 fluxes a little increased. Relatively, N_2 flux showed more gradient increasing behavior than CO_2 flux, so that CO_2/N_2 separation factor decreased as feed pressure increased. In Langmuir adsorption theory, an equilibrium adsorption of a gas on a porous adsorbent increases as gas pressure increases [9]. Therefore, the slight increase of CO_2 flux with feed pressure originated in the slight increase of equilibrium adsorption, because CO_2 partial pressure in feed side increased as feed pressure increased. If N_2 permeation through NaY zeolite membrane was governed by Knudsen flow, N_2 permeance should be independent of feed pressure. In the present study, N_2 permeance rapidly decreased as feed pressure increased. This indicates that N_2 permeation through NaY zeolite membrane might not be governed by Knudsen flow mechanism at the permeation temperature of 30 °C. Kusakabe and coworkers have reported that the high CO_2/N_2 selectivity of NaY zeolite membrane stemmed from the effective obstruction of CO_2 molecules adsorbed in narrow pores to the penetration of nonadsorptive N_2 molecules [7]. The slight increase of equilibrium adsorptions will more effectively prevent N_2 molecules from permeating through nanopores in NaY zeolite membrane. Therefore, the improved driving force due to the increase of N_2 partial pressure difference will be compensated with the decreasing driving force due to the improved obstruction by adsorbed CO_2 molecules. Also, it is remarkable that CO_2 flux was nearly independent of feed pressure. This means that the increment of feed pressure doesn't improve CO_2 recovery rate in a CO_2 separation system with NaY zeolite membrane, so that it is necessary to prepare NaY zeolite membranes with large permeating area for its improvement of CO_2 recovery rate.

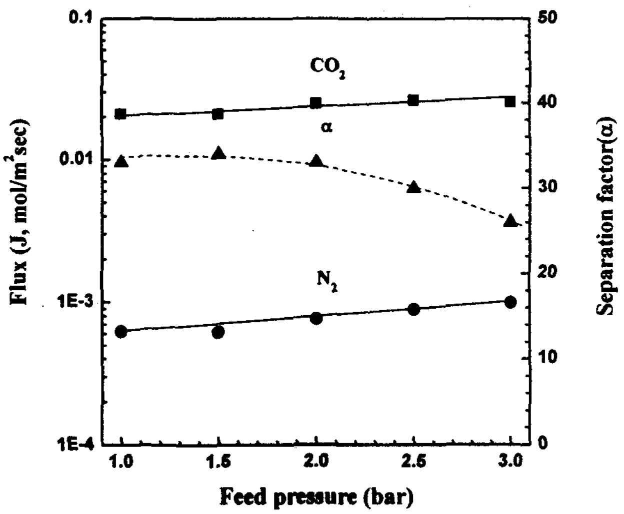

Fig. 2. Flux and Separation factor as a function of feed pressure

Figure 3 represents CO_2 and N_2 fluxes and CO_2/N_2 separation fator as a function of permeation temperature. Feed gas was an equimolar mixture of CO_2 and N_2 gases, and its pressure and feeding rate were 2 bar and 350 ml/min, respectively. He sweeping rate was 146 ml/min. As permeation temperature increased, CO_2 flux increased up to 4.5 x 10^{-2} mol/m^{2}sec at 50 °C and then decreased. On the other hand, N_2 flux continuously increased with permeation temperature increasing. Kusakabe and coworkers have reported similar results and then explained by the degraded CO_2 adsorptive affinity and the improved CO_2 surface diffusivity with permeation temperature increasing [8]. If N_2 permeation through NaY zeolite membrane is governed by Knudsen flow,

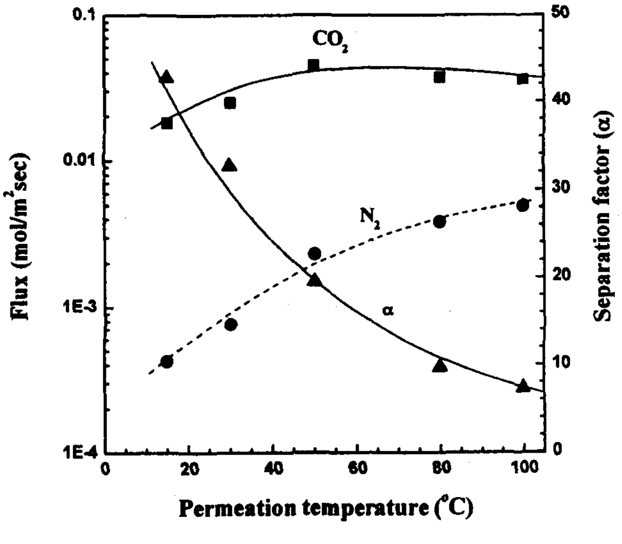

Fig. 3. Flux and Separation factor as a function of temperature

N_2 flux must decrease with permeation temperature [14]. But in the present study, N_2 flux continuously increased as permeation temperature increased. This again indicates that N_2 permation through NaY zeolite membrane is governed by micropore diffusion rather than Knudsen flow, at permeation temperatures of less than 100 °C. Therefore, to improve CO_2/N_2 separation factor, it is necessary to effectively retard N_2 permeation through NaY zeolite membrane.

From the results, as-followings were known: (i) carbon dioxide and nitrogen permeations through NaY zeolite membrane were governed by surface diffusion and micropore diffusion mechanisms, respectively at permeation temperature of less than 100°C, (ii) the feed pressure made little effect on CO_2 flux, so that it is the most important factor to reliably prepare NaY zeolite membrane with a large permeating area in its real applications to separation processes, and (iii) the CO_2/N_2 separation factor decreased as permeation temperature increased, so that to improve separation property at high temperature, it is necessary to develop a technique to retard N_2 permeation at high temperature.

Acknowledgements

This research paper was performed for the Carbon Dioxide Reduction & Sequestration Center, one of 21st Century Frontier R&D Programs funded by the Ministry of Science and Technology of Korea.

References

1. R. M. de Vos and H. Verweji, *J. Membr. Sci.* **143** (1998) 37.
2. R. M. de Vos, W. F. Maier and H. Verweji, *J. Membr. Sci.* **158** (1999) 277.
3. T. A. Centeno and A. B. Fuertes, *J. Membr. Sci.* **160** (1999) 201.
4. T. A. Centeno and A. B. Fuertes, *Sep. Purif. Technol.* **25** (2001) 379.
5. H. B. Park and Y. M. Lee, *J. Membr. Sci.* **213** (2003) 263.
6. H. B. Park, Y. K. Kim, J. M. Lee, S. Y. Lee and Y. M. Lee, *J. Membr. Sci.* in press (2004).
7. K. Kusakabe, T. Kuroda, A. Murate and S. Morooka, *Ind. Eng. Chem. Res.* **36(3)** (1997) 649.
8. Y. Hasegawa, K. Kusakabe and S. Morooka, *Chem. Eng. Sci.* **56** (2001) 4273.
9. K. Kusakabe, T. Kuroda, K. Uchino, Y. Hasegawa and S. Morooka, *AIChE J.* **45[6]** (1999) 1220.
10. H. Kita, T. Inoue, H. Asamura, K. Tanaka and K. Okamoto, *Chem. Commun.* (1997) 45.
11. H. Kita, K. Fuchida, T. Horita, H. Asamura and K. Okamoto, *Sep. Purif. Technol.* **25** (2001) 261.
12. M. Lassinantti, J. Hedlund and J. Sterte, *Micropor. Mesopor. Mater.* **38** (2000) 25.
13. K. Weh, M. Moack, I. Sieber and J. Caro, *Micropor. Mesopor. Mater.* **54** (2002) 27.
14. S. V. Sotrichos and V. N. Burganos, *MRS Bulletin* **24(3)** (1999) 41.