13X 제올라이트 흡착제 충진에 의한 Na형 Faujasite 제올라이트 분리막의 CO_2/N_2 선택도 및 CO_2 투과도 동시 증가 현상

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A Simultaneous Improvement in CO_2 Flux and CO_2/N_2 Separation Factor of Sodium-type FAU Zeolite Membranes through 13X Zeolite Beads Embedding

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요 약: 분리층 두께가 5 μm이며 Si/Al 몰비가 1.5인 Na형 faujasite 제올라이트 분리막을 이차성장 공정에 의하여 제조하였고, 투과부에 13X 제올라이트 흡착제 충진 전후의 진공모드에서의 CO_2/N_2 분리거동을 CO_2/N_2 몰비가 1인 혼합기체에 대하여 30°C에서 평가하였다. 충진된 13X 제올라이트 흡착제는 CO_2 투과도와 CO_2/N_2 선택도를 동시에 증진시켰다. 이 현상은 13X 제올라이트 흡착제 충진이 다공성 α-알루미나 지지체의 기공채널을 통한 CO_2 탈출을 증진시킴으로써 faujasite 제올라이트/α-알루미나 상계면에서의 CO_2 탈착을 증진시켰기 때문으로 설명되었다. 본 논문으로부터 흡착제와 분리막의 혼성화는 일반적으로 보여지는 선택도와 투과도의 역비례 관계를 획기적으로 개선할 방법임이 확인되었다.

Abstract: Sodium type faujasite (FAU) zeolite membranes with a thickness of 5 μm and a Si/Al molar ratio of 1.5 were prepared by the secondary growth process. The CO_2/N_2 separation in the vacuum mode was investigated at 30°C for an equimolar CO_2-N_2 mixed gas before and after embedding 13X zeolite beads in the permeate side. The embedded 13X zeolite beads improved both CO_2 permeance and CO_2/N_2 separation factor, simultaneously. The phenomenon was explained by an increment in the CO_2 desorption rate at the FAU zeolite/α-Al_2O_3 phase boundary due to an enhanced CO_2 escaping through the pore channels of the α-Al_2O_3 support layer. In the present paper, it will be emphasized that a hybridization of a membrane with an adsorbent can provide a key to break through the trade-off between permeance and separation factor, generally shown in a membrane separation.

1. Introduction

In recent years, a membrane separation process has attracted much attention due to the equipment and processing simplicities, the scale-up feasibility, and the energy efficiency [1]. Separation capacity of a membrane is generally described with two materials charac-teristics. One is permeance (Π) or flux (J), and the other is selectivity. Permeance means how fast a species permeates through it, and selectivity indicates how much faster one species permeates than others. In a view-point of an engineer, permeance and selectivity are related to the amount and purity of recovered species, respectively, even though those are affected by membrane operation conditions and modes. Therefore, a good membrane means one simultaneously showing

both large permeance and high selectivity. Unfortunately, a membrane with a larger permeance shows a lower selectivity and *vice versa*. L. Robeson *et al.* have reported the clear trade-off for polymeric membranes [2]. Therefore, it is meaningful to design a membrane to break through the trade-off.

Nowadays, a sodium-type FAU zeolite membrane with a mean micropore diameter of 7.4 Å becomes one of the most noticed inorganic membranes, since it has high potentials in recovering carbon dioxide [3], dewatering liquid organics [4], and separating organic mixtures [5]. As the authors feared, it isn't free from the trade-off. The trade-off between CO_2 permeance and CO_2/N_2 separation factor was reported by others [6,7].

In another paper submitted to this journal [8], the authors prepared sodium type FAU zeolite membranes with diverse materials characteristics such as the Si/Al ratio, the thickness, and the intercrystalline void, and then the CO_2/N_2 separations obtained in the He sweeping mode were reported. The overall CO_2 permeation is a series reaction, which is composed of the CO_2 adsorption in feed side, the CO_2 surface diffusion along the micropore channels, and the CO_2 desorption in permeate side. In the previous paper [8], one of remarkable things was that the CO_2 desorption in permeate side might be the rate-determining (slowest) step of the overall CO_2 permeation. This means that if the CO_2 desorption is enhanced, CO_2 permeance and CO_2/N_2 separation factor might be improved simultaneously. In other words, the trade-off between CO_2 permeance and CO_2/N_2 separation factor could be overwhelmed.

In the present paper, the authors suggest that an adsorbent embedding in the permeate side might be a key to improve CO_2 desorption in permeate side or to increase CO_2 permeance and CO_2/N_2 separation factor simultaneously.

2. Experimental

Sodium type FAU zeolite membranes A, B, C, and D were prepared by the secondary growth process. In the secondary growth process, sodium type FAU zeolite layers were heterogeneously grown in a hydrothermal condition on the outer surface of an α-Al_2O_3 support tube (Ceracomb, Korea). The hydrothermal temperature and time were 80°C and 24 hr, respectively. The hydrothermal solution was $0.75Al_2O_3$-$7.5SiO_2$-$14Na_2O$-$840H_2O$ in a molar basis. The porous α-Al_2O_3 support tube has a porosity of 35 vol% and a mean pore diameter of 120 nm. The outer and inner diameters were 10.5 and 7.5 mm, respectively, and the length was 80 mm. Before the secondary growth process, a lab.-made nanometer-sized (230 nm) seed, which was composed of NaY zeolite and α-Al_2O_3 particulates, was introduced to the outer surface *via* a vacuum-assisted filtration process. The detailed synthesis procedure has been described elsewhere [8].

The crystalline phase and morphology were analyzed by X-ray diffractometer (D/max2000-UltimaPlus Rigaku, Japan) and scanning electron microscopy (XL30, Philips, Holland), respectively. In the SEM morphology observation, the molar ratio of Si to Al in the formed zeolite layer was evaluated by EDS analysis.

Carbon dioxide adsorption and desorption isotherms at 30°C for a commercial NaY zeolite particle (Cat. No. 334448, Aldrich Chemical Co., USA) and a 13X zeolite bead (10 × 20, UOP, USA), will be embedded in the permeate side, were obtained with using a magnetic suspension balance (Rubotherm Präzisionsmebβ technik, De).

The interior (permeate side) of the prepared sodium type FAU zeolite membrane was fully packed with the commercial 13X zeolite beads with a diameter of 1 to 2 mm. The embedding amount was 4.65 g. The amount of the formed FAU zeolite layer was simply calculated to be 0.017 g with using the theoretical density (1.27 g/cm^3), the thickness (5 μm), and the outer diameter of the porous support (10.5 mm). The embedded 13X zeolite beads has around 274 times weight of the formed FAU zeolite layer!

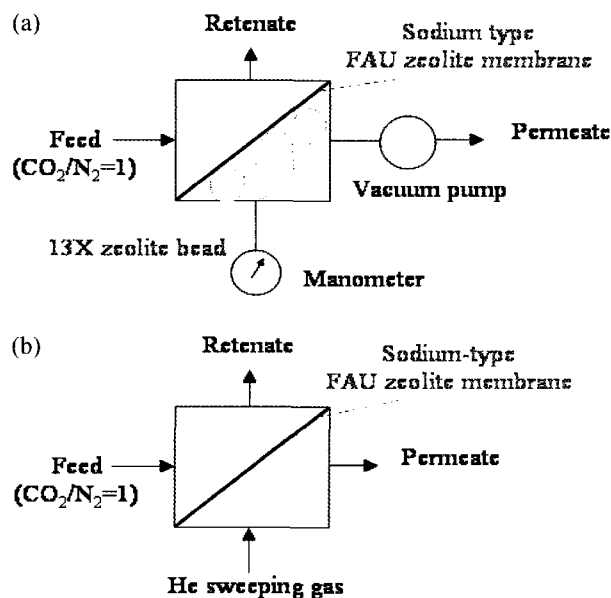CO_2/N_2 separations in vacuum mode were evaluated at 30°C for an equimolar mixture of CO_2 and N_2

(a)

Retentate

Sodium type
FAU zeolite membrane

Feed
(CO_2/N_2=1)

Permeate

Vacuum pump

13X zeolite bead

Manometer

(b)

Retentate

Sodium-type
FAU zeolite membrane

Feed
(CO_2/N_2=1)

Permeate

He sweeping gas

Fig. 1. Schematic diagrams for the permeation experiments in the (a) vacuum and (b) He sweeping modes.

(a)

(b)

Fig. 2. SEM images for the (a) top surface and (b) fractured section of the prepared sodium-type FAU zeolite membrane.

before and after embedding the 13X zeolite beads (Fig. 1(a)). The feeding rate of the equimolar mixed gas was 350 mL/min and the feed pressure was 2 bars. The vacuum in the permeate side was made by an oil-less vacuum pump (DTC-21, Ulvac Kiko Inc., Japan) and the degree of vacuum in the permeate side was measured with a wide range diaphragm manometer (P/N 902074, BESTECH Ind., USA). For comparison, CO_2/N_2 separations were also evaluated at 30°C in He sweeping mode (Fig. 1(b)). The feeding rate was 350 mL/min, the feed pressure was 2 bars, and the He sweeping rate was 146 mL/min. The detailed permeation experiment in the He sweeping mode has been described elsewhere [8].

3. Results and Discussion

Representative SEM images for the top surface and fractured section of a prepared zeolite membrane were shown in Fig. 2(a) and (b), respectively.

The thickness of the formed zeolite layer was around 5 μm and the molar ratio of Si to Al was 1.5. XRD analysis showed that the formed zeolite phase is FAU typed. Therefore, the formed zeolite membrane
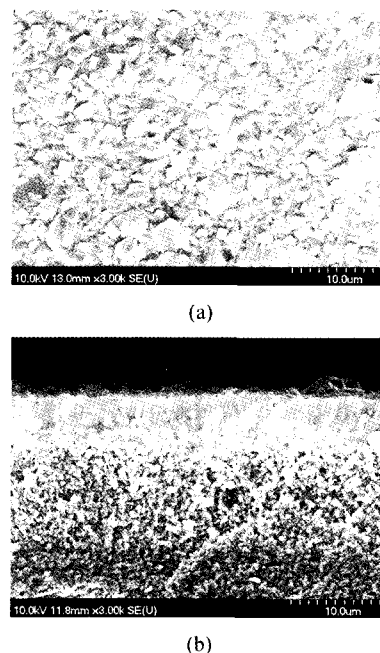
was a FAU zeolite membrane, being at the boundary between NaX and NaY phases.

CO_2/N_2 separations through the membranes A, B, C, and D were evaluated in the He sweeping mode and the results were summarized in Table 1. All the membranes show an excellent CO_2/N_2 separation: the average fluxes of CO_2 and N_2 were 3.5 × 10^{-2} and 6.9 × 10^{-4} mol/m²sec, respectively. The average CO_2 permeance (Π_{CO2}) was 6.0 × 10^{-7} mol/m²secPa and the average CO_2/N_2 separation factor (α) was 33.5. The separation factor is the selectivity obtained in mixed gas mode [8]. Considering that the CO_2 partial pressure in the feed side is 760 torr, the difference in the CO_2 partial pressure between the feed and permeate sides was around 440 torr. It was so interesting that the small driving force (440 torr) made such a high CO_2 flux (3.5 × 10^{-2} mol/m²sec). The CO_2/N_2 separation obtained in the He sweeping mode informs us an upper limit of separation through it. Nonetheless, it has little engineering meaning, because the He sweeping mode can't be applied to a real membrane system due to the low effectiveness in cost and processing.

Table 1. CO_2/N_2 Separation Evaluated in the He Sweeping Mode for the Membranes A, B, C, and D

Membrane	J (mol/m^2sec)		α	*p (torr)		Π_{CO2} (mol/m^2secPa)
	CO_2	N_2		CO_2	N_2	
A	3.7×10^{-2}	8.3×10^{-4}	28.1	315	11	6.3×10^{-7}
B	4.0×10^{-2}	6.3×10^{-4}	39.1	315	8	6.8×10^{-7}
C	4.1×10^{-2}	7.1×10^{-4}	34.5	322	9	7.1×10^{-7}
D	2.2×10^{-2}	6.0×10^{-4}	32.0	326	12	3.9×10^{-7}
Average	$\mathbf{3.5 \times 10^{-2}}$	$\mathbf{6.9 \times 10^{-4}}$	**33.5**	**320**	**10**	$\mathbf{6.0 \times 10^{-7}}$

* partial pressure in the permeate side

Table 2. CO_2/N_2 Separation Evaluated in the Vacuum Mode for the Membranes A, B, C, and D without the 13X Zeolite Beads Embedding

Membrane	J (mol/m^2sec)		α	*p (torr)		Π_{CO2} (mol/m^2secPa)
	CO_2	N_2		CO_2	N_2	
A	1.6×10^{-2}	2.2×10^{-3}	7.0	42	6	3.6×10^{-7}
B	1.3×10^{-2}	1.4×10^{-3}	9.0	38	4	2.9×10^{-7}
C	2.2×10^{-2}	3.8×10^{-3}	5.4	35	6	4.8×10^{-7}
D	1.8×10^{-2}	4.1×10^{-3}	6.4	41	10	4.0×10^{-7}
Average	$\mathbf{1.7 \times 10^{-2}}$	$\mathbf{2.9 \times 10^{-3}}$	**6.9**	**39**	**6.5**	$\mathbf{3.8 \times 10^{-7}}$

* partial pressure in the permeate side

In the present study, CO_2/N_2 separations through the membranes A, B, C, and D were evaluated in the vacuum mode and the results were summarized in Table 2. As the authors know, this is the first report announcing the CO_2/N_2 separation data in the vacuum mode. The average fluxes of CO_2 and N_2 were 1.7 × 10^{-2} and 2.9 × 10^{-3} mol/m^{2}sec, respectively, and the average CO_2/N_2 separation factor was 6.9. The difference in the CO_2 partial pressure between the feed and permeate sides was 721 torr. Compared with the results obtained in the He sweeping mode (Table 1), the CO_2 flux decreased to be a half and the N_2 flux increased to be four-fold, so that the CO_2/N_2 separation factor decreased to be a fifth. In the permeation experiment in the vacuum mode, it was consistently shown that the CO_2/N_2 separation factor increases and then approaches up to that obtained in the He sweeping mode, as the degree of vacuum in the permeate side increases. This is another evidence announcing that the CO_2 desorption in the permeate side is the rate-limiting step in the overall CO_2 permeation.

Also, it is interesting that the CO_2 flux obtained in the vacuum mode was a half of that obtained in the He sweeping mode, even though the driving force (721 torr) was much larger than that (440 torr) in the He sweeping mode. This means that the He sweeping not only makes a gradient in the chemical potential by reducing the partial pressure in the permeate side but also makes a positive effect on the CO_2 permeation. One reasonable explanation is that the He sweeping increases the CO_2 desorption at the FAU zeolite/α-Al_2O_3 phase boundary due to an enhanced CO_2 escaping from the pore channel of the α-Al_2O_3 support layer with a thickness of 1,500 μm. The thickness of the α-Al_2O_3 support layer is 300 times larger than that of the formed FAU zeolite layer!

Table 3 represents CO_2/N_2 separations evaluated in the vacuum mode for the membranes A, B, C, and D after embedding the 13X zeolite beads in the permeate side.

The average fluxes of CO_2 and N_2 were 3.5 × 10^{-2} and 2.8 × 10^{-3} mol/m^{2}sec, respectively, and the average

Table 3. CO_2/N_2 Separation Evaluated in the Vacuum Mode for the Membranes A, B, C, and D with the 13X Zeolite Beads Embedding

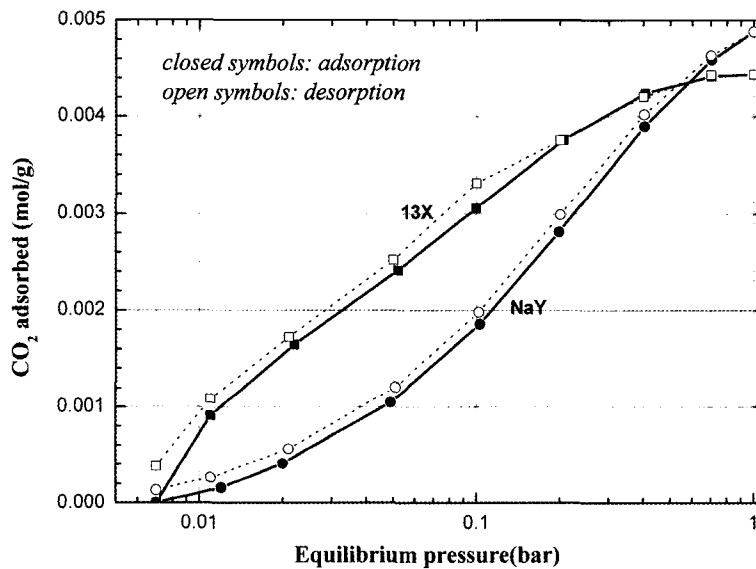| Membrane	J (mol/m²sec)		α	*p (torr)		Π_{CO2} (mol/m²secPa)
	CO_2	N_2		CO_2	N_2	
A	2.9×10^{-2}	2.2×10^{-3}	12.0	61	5	6.9×10^{-7}
B	3.5×10^{-2}	1.9×10^{-3}	17.0	68	4	8.5×10^{-7}
C	4.4×10^{-2}	3.6×10^{-3}	10.8	53	5	1.0×10^{-7}
D	3.1×10^{-2}	3.3×10^{-3}	9.9	64	6	7.5×10^{-7}
Average	3.5×10^{-2}	2.8×10^{-3}	12.4	61.5	5	6.0×10^{-7}

* partial pressure in the permeate side

Fig. 3. CO_2 adsorption-desorption isotherms of NaY zeolite particle and 13X zeolite bead.

CO_2/N_2 separation factor was 12.4. The difference in the CO_2 partial pressure between the feed and permeate sides was 699 torr. Compared with the results obtained before embedding the 13X zeolite beads (Table 2), the CO_2 flux increased to be two-fold, while the N_2 flux didn't change. As a consequence, the CO_2/N_2 separation factor increased to be two-fold by embedding the 13X zeolite beads in the permeate side.

In another paper submitted in the present conference [8], the authors reported that the CO_2 desorption in the permeate side is the rate-limiting step in the overall CO_2 permeation. It is certain that the embedded 13X zeolite beads made a positive effect on the CO_2 desorption in the permeate side. Generally, it is known that 13X zeolite phase shows larger CO_2 adsorption

than FAU zeolite phase [9]. To confirm this, CO_2 adsorption-desorption isotherms at 30°C for a commercial NaY zeolite powder and the 13X zeolite beads were obtained and then represented in Fig. 3.

At the CO_2 pressure of 62 torr (0.08 bar), the 13X zeolite bead has two-fold CO_2 adsorption of FAU zeolite phase. Considering that the amount of 13X zeolite beads embedded in the permeate side (4.65 g) is 274 times larger than the formed FAU zeolite layer (0.017 g), the embedded 13X zeolite beads showed 547-fold larger CO_2 adsorption capacity than the formed FAU zeolite layer. Evidently, the embedded 13X zeolite beads will strongly drag the CO_2 molecules entrapped in the pore channels of the α-Al_2O_3 support, so that those will improve the CO_2 desorption rate at the FAU
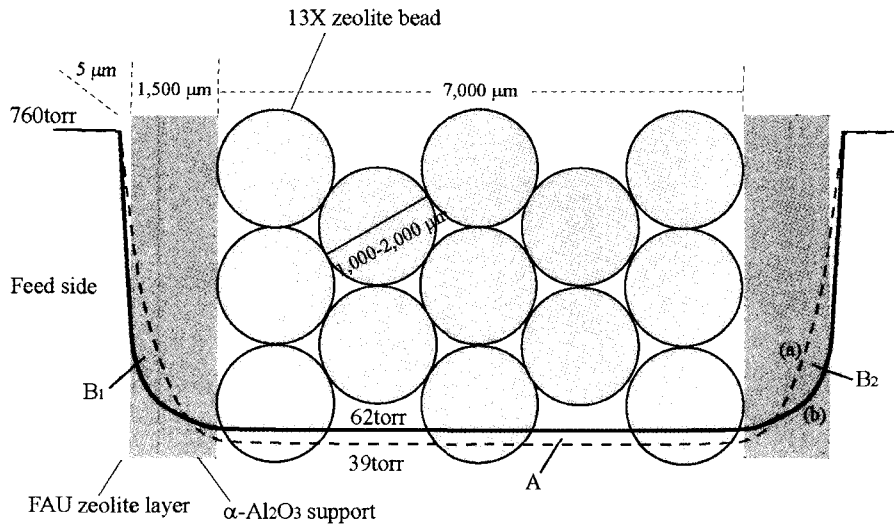
Fig. 4. Supposed CO_2 partial pressure profiles across a sodium-type FAU zeolite membrane (a) before and (b) after embedding the 13X zeolite beads.

zeolite/ α-Al_2O_3 phase boundary. As a result, the embedded 13X zeolite beads increases the CO_2 flux because it increases a gradient in the CO_2 partial pressure between the feed and permeate sides. On the other hand, the embedded 13X zeolite beads makes little effect on a gradient in the N_2 partial pressure, because FAU and 13X zeolite phases show little N_2 adsorption.

Also, it is interesting that the CO_2 partial pressure in the permeate side (62 torr) was larger than that before embedding the 13X zeolite beads (39 torr). The larger CO_2 partial pressure after embedding the 13X zeolite beads was due to the larger CO_2 flux.

Fig. 4 represents supposed CO_2 partial pressure profiles across the membrane before and after embedding the 13X zeolite beads. Considering that the same vacuum pump was used at the similar time, the area A should be consistent with a sum of the areas B_1 and B_2, since the vacuum pump was operated with the same power. Therefore, only one reasonable explanation for the simultaneous improvement of CO_2 permeance and CO_2/N_2 separation factor is an increment in the CO_2 desorption rate at the FAU zeolite/ α-Al_2O_3 phase boundary due to an enhanced CO_2 escaping through the pore channels of the α-Al_2O_3 support layer.

Also, the anomaly induced by embedding the 13X

zeolite beads in the permeate side is an indirect evidence showing that the CO_2 desorption in permeate side is the rate-determining step in the overall CO_2 permeation through a sodium-type FAU zeolite membrane, reported elsewhere [8].

4. Conclusions

The 13X zeolite beads embedding in the permeate side of the FAU zeolite membranes simultaneously improved the CO_2 flux and CO_2/N_2 separation factor, since it made the gradient in the CO_2 partial pressure across the membrane become more steep. The larger gradient in the CO_2 partial pressure was formed by improving the CO_2 desorption rate at the FAU zeolite/ α-alumina phase boundary. Therefore, it was concluded that a hybridization of a membrane and an adsorbent might give an important key to break through the trade-off between flux and separation factor, generally shown in a membrane separation.

Acknowledgements

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