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Separation of CO_2 by modified γ-Al_2O_3 membranes at high temperature

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Abstract

The composite membranes of γ-Al_2O_3 were fabricated by sol–gel coating with boehmite (AlOOH) sol. The thickness of the membranes were in the range of 2–5 μm depending on the number of coatings and the concentration of the sol. The permeabilities of He, N_2, and CO_2 were measured at temperatures of 298–673 K and pressures of 101.3–405.2 KPa. The permeability through γ-Al_2O_3 membrane was constant with the pressure difference and decreased with the square root of temperature. The main mechanism of gas transport through γ-Al_2O_3 membrane was thus proved as Knudsen diffusion. CaO was impregnated on the γ-Al_2O_3 membrane to improve separation factor by introducing interactions between CO_2 gas molecules and the pore wall, but high separation factor was not obtained. Silica modified γ-Al_2O_3 membrane was also prepared to increase the separation factor. The separation factor of CO_2 to N_2 was increased to 1.4 at 298 K though it decreased with increasing temperature. The separation experiment of a CO_2/N_2 mixture was also performed. The separation factor was 1.72 at 298 K and 1.5 at 673 K, which were much higher than that of the Knudsen diffusion mechanism, 0.8.

Keywords: Inorganic membranes; Gas separation; Surface diffusion; Sol–gel method; Surface modification

1. Introduction

Inorganic membranes have great potential for the separation of gases at high temperature. There has been extensive investigation on the preparation and characterization of γ-Al_2O_3 membranes for gas separation for the past few years [1–9]. γ-Al_2O_3 membrane which has an average pore diameter of 2.5 nm, a sharp pore size distribution and no defects could be obtained by the sol–gel technique [2]. However, the relationships among membrane synthesis parameters, microstructures, and gas permeation properties are still not well understood.

The transport of pure gases through γ-Al_2O_3 membranes occurs by three mechanisms: Knudsen diffusion, laminar flow, and surface diffusion. The permeability of a membrane, taking into account all three mechanisms, is described by

$$F_o = \frac{\epsilon\mu\bar{r}^2}{8\eta RT}\bar{P} + \left(\frac{2\epsilon\mu\bar{r}}{3RTL}\right)\left(\frac{8RT}{\pi M}\right)^{0.5} + \frac{2\epsilon\mu D_S}{\bar{r}A_0N_{av}}\frac{dx_S}{dP} \quad (1)$$

where ϵ is the porosity, $\bar{r}$ is the mean pore radius, μ is a shape factor, R is the gas constant, T is the temperature, L is the thickness of the membrane, $\bar{P}$ is the mean pressure, η is the viscosity of the gas, M is the molar mass of the gas, A_0 is the surface area occupied by an

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adsorbed molecule, N_{av} is Avogadro's constant and x_S is the percentage of occupied surface compared with a monolayer [4].

Since the pores of the γ-Al_2O_3 membranes are very small (<5 nm), laminar flow (first term on the right hand side) is considered to be negligible if there are no defects. The second term represents Knudsen diffusion, which occurs when the mean free path of the molecule is much larger than the mean pore radius of the medium. Gases can be separated by Knudsen diffusion due to differences in their molecular weights. So, this is valid only for the separation of light gases such as H_2 and He from heavier ones. However, in the case of gases whose molecular weights are nearly equal, another separation mechanism should be employed in order to obtain high separation factors.

Separation factors can be improved by introducing an interaction between one component of the gas mixture and the pore wall by chemical modification. If the adsorbed gas molecules are mobile on the surface of the pore, it will diffuse along the surface concentration gradient [4]. This flow is called the surface diffusion and described by the third term of Eq. (1). Clearly surface diffusion becomes more important when the pore size is decreased.

There have been two kinds of modification methods to obtain high separation factors. One method was to decrease the pore size using CVD or sol–gel reactions and the other was to change the chemical nature of the internal surface by impregnation of catalyst which can activate surface diffusion.

Yamaki et al. narrowed the micropores of the γ-Al_2O_3 membranes by packing with ultrafine ZrO_2 particles formed by a reversed micelles technique. The separation factor of hydrogen to nitrogen was about 4.5 [5].

Uhlhorn et al. modified γ-Al_2O_3 membranes with polymeric silica solution. This modification had the effects not only to give chemical affinity on the membrane surface but also to decrease the pore size. The transports of condensable gases, CO_2, propane, and propylene were largely enhanced at room temperature [3]. A similar permeation result was reported using amorphous silica membrane that was coated on porous alumina support [6]. This membrane showed a high separation factor for CO_2 at temperatures less than 250°C.

MgO was impregnated into the γ-Al_2O_3 membranes to enhance the adsorption and surface diffusion effect. CO_2 permeation rate, however, was decreased by the modification though the amount of CO_2 adsorbed was increased [7,8]. It was attributed to the fact that the introduction of MgO gave more strong basic sites and strongly bonded CO_2 on these sites were less mobile.

On the basis of the adsorption study that most CO_2 molecules adsorbed on the $BaTiO_3$ powders were mobile at 773 K, Kusakabe et al. prepared $BaTiO_3$ membranes by sol–gel methods [9]. The separation factor of CO_2 to N_2 was about 1.12–1.2 at 373–773 K.

In this study, the relationships between the important parameters in the formation of γ-Al_2O_3 membranes and the resulting microstructures are studied. Two kinds of modification methods are then presented. Finally, the gas transport and separation properties of three different membranes over the temperature of 298–673 K are investigated.

2. Experimental procedures

2.1. Preparation of γ-Al_2O_3 membrane

A porous α-alumina tube was used as the support. The physical properties of the support are summarized in Table 1. Fig. 1. shows the microstructure of the inner and the outer surfaces of the support. The inner surface is more uniform than the outer one and suitable for coating. The outer surface of the support, except the 10 mm section in the middle, was sealed with a SiO_2-B_2O_3-Na_2O sealant (Nippon Electric Co.) using the procedure given by Yamaki et al. [5].

Boehmite sol was prepared by hydrolyzing aluminum isopropoxide, $Al(OC_3H_7^i)_3$, as proposed by Yol-

Table 1
Physical properties of the support tube

Manufacturer	MKS[a] (Multiporelon TD-1)
Material	α-Al_2O_3 (92%)
Inside diameter	8 mm
Outside diameter	10 mm
Average pore diameter	1.4 μm
Porosity	34%
Heat stability	5–800°C (max: 1000°C)
Pressure stability	inner pressure 49.0×10^4 Pa outer pressure 29.4×10^5 Pa

[a] MKS, Mitsui Grinding Wheel Co., Ltd.

Fig. 1. SEM photographs of the α-Al_2O_3 support tube (× 10 K): (a) outer surface; (b) inner surface.

das [10]. To obtain a stabilized sol, HCl was added and peptization was performed under vigorous stirring at 90°C for 24 h. The initial concentration of the sol was 0.5 Al mol/l. The particle size of the sol changes with the mole ratio of HCl/Al and the aging time. The particle sizes were examined by the dynamic light scattering (DLS, Ar laser, MALVERN 7032CE) method.

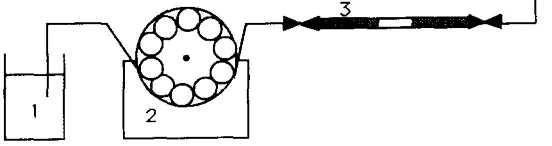

Fig. 2. Schematic diagram of the filtration apparatus: 1, sol; 2, multistaltic pump; 3, glass sealed support; 4, outlet drain.

Coating on the inside surface of the support tubes were performed by the filtration method [11]. A schematic diagram of the coating apparatus is shown in Fig. 2. When the support tube was filled with the sol to the outlet drain part, the pump was off. The pressure inside of the tube was higher than the atmosphere because the outlet drain part was positioned higher than the support and the sol was filtered through porous support. The remaining sol was removed by reversing the direction of rotation of pump after 10 min. After coating, the membrane was dried overnight in atmosphere, and then calcined at 550°C for 2 h after heating at a rate of 1°C/min. The pinhole free γ-Al_2O_3 supported membranes were prepared by repeating the cycle of coating, drying, and calcination.

Unsupported boehmite thin films were obtained by pouring small amount of the sol in the petri dish and drying at 30°C in an oven. They were calcined to γ-Al_2O_3 at the same heat treatment conditions as in the preparation of supported γ-Al_2O_3 membranes. The

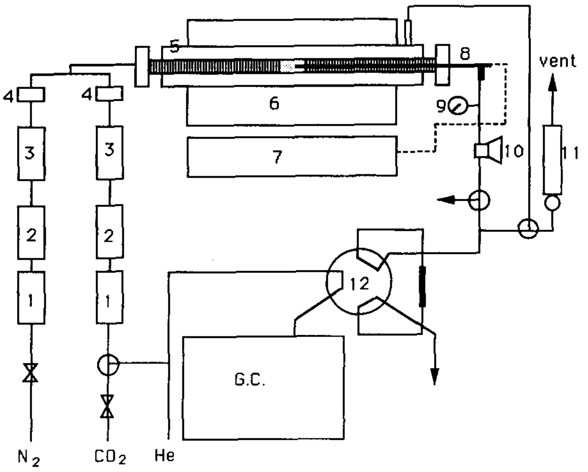

Fig. 3. Schematic diagram of the apparatus for gas separation experiment: 1, water trap; 2, oxygen trap; 3, MFC; 4, check valve; 5, gas cell; 6, furnace; 7, PID controller; 8, thermocouple; 9, pressure gauge; 10, back pressure regulator; 11, digital bubble flowmeter; 12, 6-port switching valve.

microstructure of the membrane was characterized using SEM (FT-SEM Hitachi, S-90, Jeol JSM-840A), XRD (Rigaku DMAX-B, CuK_α), and BET (Micromeritics Co., Accusorb 2100E).

2.2. *Surface modification*

The chemical modifications of γ-Al_2O_3 membranes with CaO or silica were carried out by the same filtration method as used in γ-Al_2O_3 coating. The impregnation of CaO in the pore of γ-Al_2O_3 membranes was performed using 0.1 M solution of $Ca(CH_3COO)_2$. CaO impregnated γ-Al_2O_3 membranes were prepared by repeating impregnation, drying, and heating procedure several times.

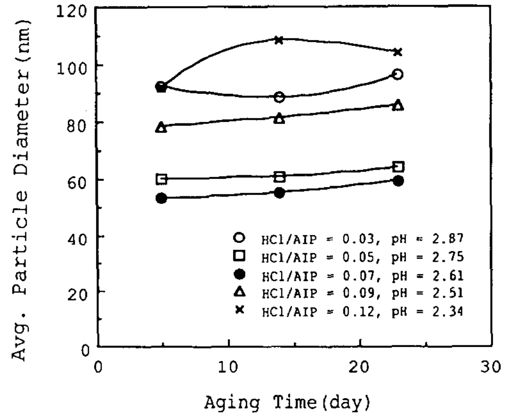

Fig. 4. Effect of the acid concentration of the sol and the aging time on the average particle diameter in the sol.

To reduce the pore size and to facilitate surface diffusion simultaneously, the γ-Al_2O_3 layer was coated by silica polymeric solution using the same coating method. The composition of the silica polymeric sol (TEOS: 10.9 mol%, H_2O: 55.7 mol%, *n*-propanol: 32.8 mol%, HCl: 0.632 mol%) was taken from the literature [12]. The loads and distributions of silica or calcium oxide in the support layer and the top layer were determined by EPMA (Jeol JXA-8600L) and EDAX (PV9100).

2.3. *Gas permeation experiments*

Gas permeation experiments were performed at 298–673 K using H_2, N_2, CO_2. The schematic diagram of the gas permeation apparatus appears in Fig. 3. The outside of the membrane was kept at atmospheric pressure and the pressure of inside was controlled in the range of 98–392 KPa using a back pressure regulaltor. Carrier gas was not used and the permeation flow rate was measured by digital bubble flow meter (Spelco 2-2910). The gas compositions were analyzed by gas chromatography (Young-In GC 680A) with a TCD detector and activated carbon packed column.

3. Results and discussion

3.1. *γ-Al_2O_3 membranes*

According to Leenaars and Burggraaf [1], the important parameters in the formation of gel layer were the sol concentration, the coating time, the pore size of the support and the type and amount of the acid used to peptize the sol.

In this study, the influences of the amount of acid used to peptize the sol on the particle size in the sol and the microstructures of the calcined γ-Al_2O_3 membranes were studied. Fig. 4 shows the changes of the particle diameter in the sols containing 0.03–0.12 mol HCl per mol AlOOH with aging. The particle diameters measured by DLS were expressed in terms of Stokes diameter assuming spherical particles. The sol of 0.07 HCl/Al mole ratio was most transparent and had the smallest

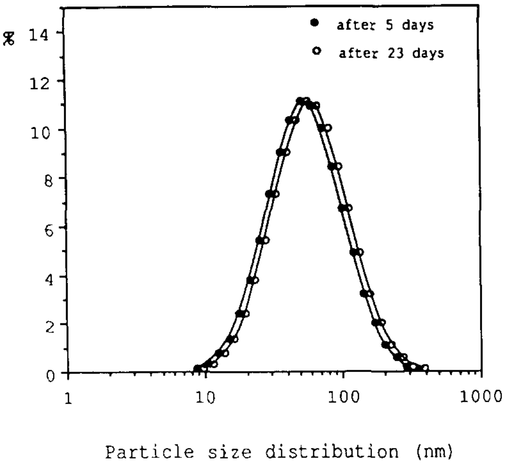

Fig. 5. Particle size distribution of AlOOH sol (HCl/Al = 0.07). Z average: Mean, 53.1 nm (after 5 days); 59.1 nm (after 23 days).

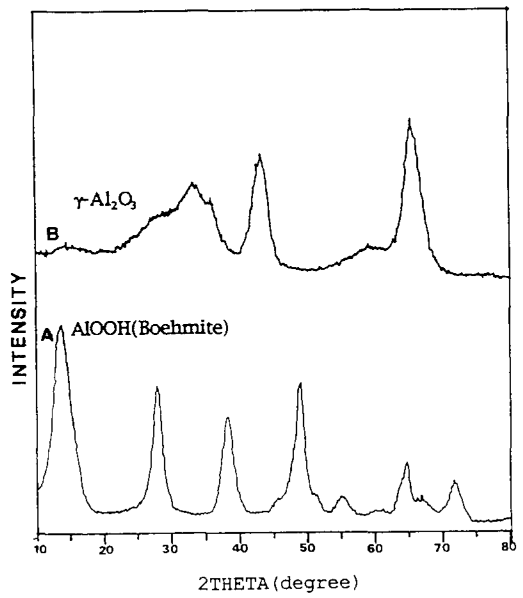

Fig. 6. X-ray diffraction patterns of unsupported membranes (HCl/Al = 0.07): (A) after drying at 30°C; (B) after calcination at 550°C for 2 h.

mean particle diameter; about 50 nm. The particle size distribution was presented in Fig. 5. There was no significant increase in the particle diameter after aging, so the sol was very stable. This optimum value, 0.07 HCl/AlOOH, is in accordance with the results of Yoldas [13], where the gelling volume was minimum when the acid concentration was about 0.07 mol HCl/AlOOH.

To show the influences of the particle size of the sol on the pore size of the membrane, unsupported γ-Al_2O_3 membranes were prepared. It is very difficult to characterize the microstructure of thin γ-Al_2O_3 layer of supported membrane. It is believed that the microstructural characteristics of thin unsupported films are similar to those of supported thin films [2].

Fig. 6 shows the X-ray diffraction patterns of AlOOH xerogel and γ-Al_2O_3 membrane which were prepared from the sol containing 0.07 mol HCl per mol AlOOH.

Fig. 7 presents typical N_2 adsorption–desorption isotherms of γ-Al_2O_3 membranes. The isotherms are almost equal in shape and all of them are classified as type IV isotherms. The pore diameters calculated from the desorption branch were less than 5 nm and had narrow size distributions as shown in Fig. 8.

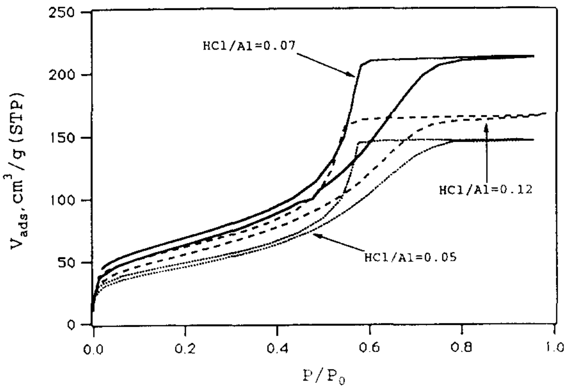

Fig. 7. Nitrogen adsorption–desorption isotherms of γ-Al_2O_3 membranes at 77 K.

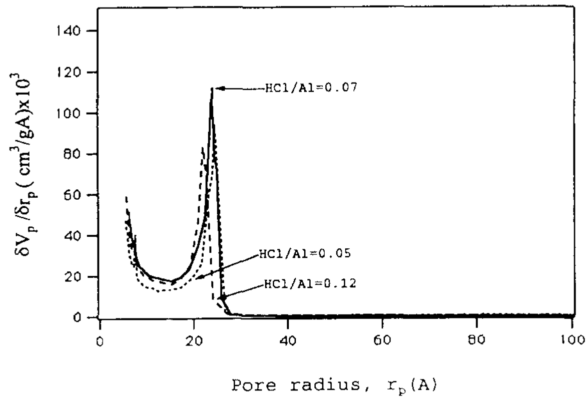

Fig. 8. Pore size distributions of γ-Al_2O_3 membranes calcined at 550°C for 2 h.

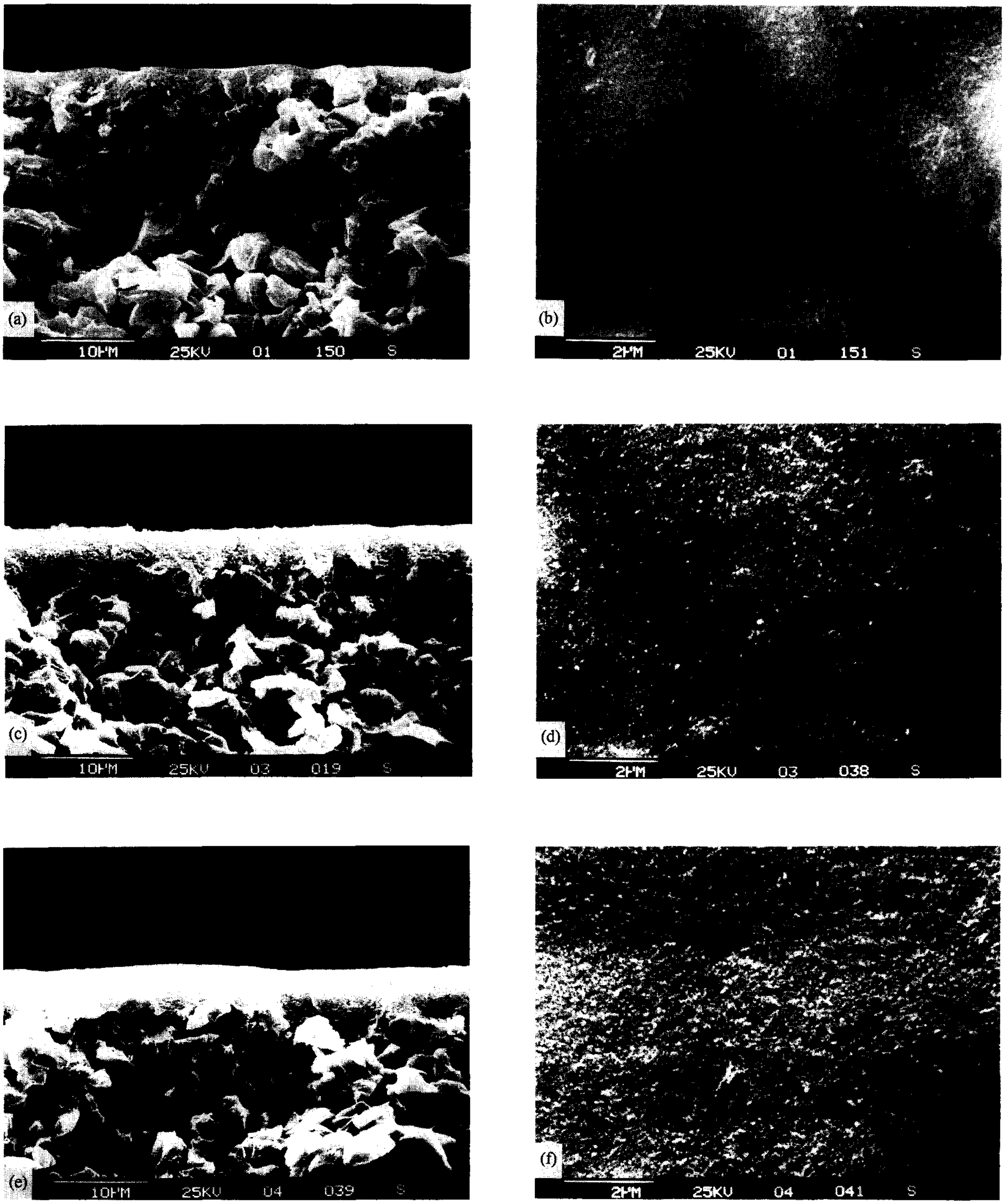

Fig. 9. SEM photographs of γ-Al_2O_3 membranes showing the effect of the number of coating cycles. After 1st coating: (a) fracture surface; (b) top surface after 3rd coating; (c) fracture surface; (d) top surface after 5th coating; (e) fracture surface; (f) top surface.

Table 2
Membrane thicknesses with coating conditions

Concentration of the sol (M)	No. of coatings	Membrane Thickness (μm)
0.5	7	pinhole
0.8	3	2.0
	4	3.2
	5	4.8
1.2	1	3.3
	2	5.1

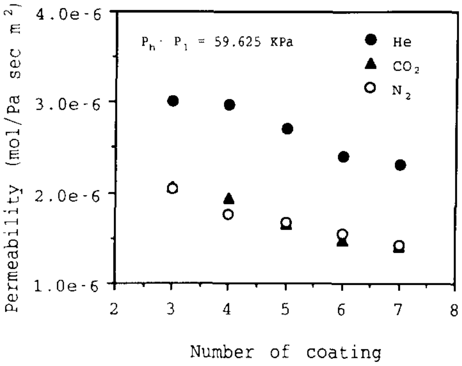

Fig. 10. Effect of the number of coating cycles on gas permeabilities (permeation temperature, 298 K).

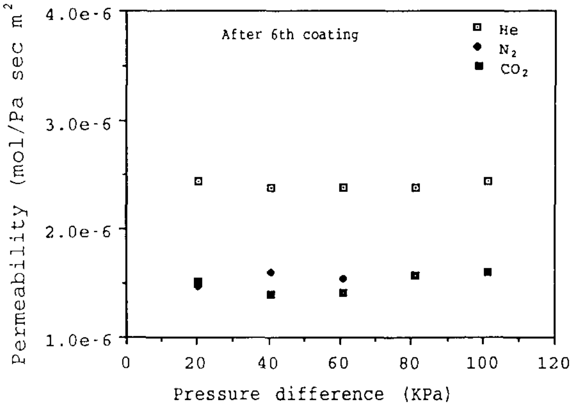

Fig. 11. Gas permeabilities as a function of pressure differences across the γ-Al_2O_3 membrane.

It was expected that the membranes having smaller pore diameter and narrower pore size distribution can be prepared from the sol whose particle size is smaller. However, it can be concluded from above results that the pore size of the γ-Al_2O_3 membranes is not significantly affected by the amount of acid used for peptization in the range of 0.05–0.12, though the sol containing 0.07 mol HCl per AlOOH has the minimum particle size and is the most transparent one. The acid concentration was thus fixed at 0.07 mol HCl/AlOOH for all subsequent experiments.

The gel formation process can be considered as a filtration process. If the concentration of the sol is low, the pore clogging precedes cake formation. Due to this pore clogging, the pore size of the support is reduced and at a certain stage cake formation starts. In the case of very dilute sol, no gel layer is formed because the support is saturated with the dispersion and therefore the capillary pressure drop disappears before cake filtration is obtained. If the sol concentration is high, cake filtration starts immediately and thick gel layer results in cracking or peeling-off during drying. Therefore, a certain minimum concentration is necessary to obtain

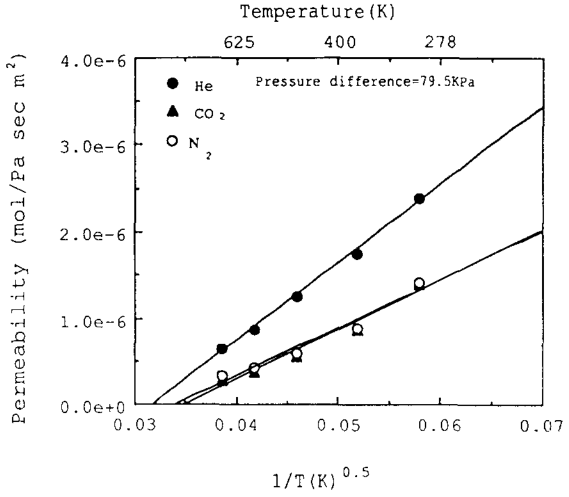

Fig. 12. Gas permeabilities as a function of the square root of the temperature.

Table 3
Effect of the number of impregnation cycles on the load of CaO in γ-Al_2O_3 membrane

Impregnation cycles	Load			
	Atom%		Oxide%	
	Ca	Al	CaO	Al_2O_3
2	1.929	38.457	5.228	94.773
4	3.008	37.109	8.092	90.749
6	3.286	36.787	8.822	89.782

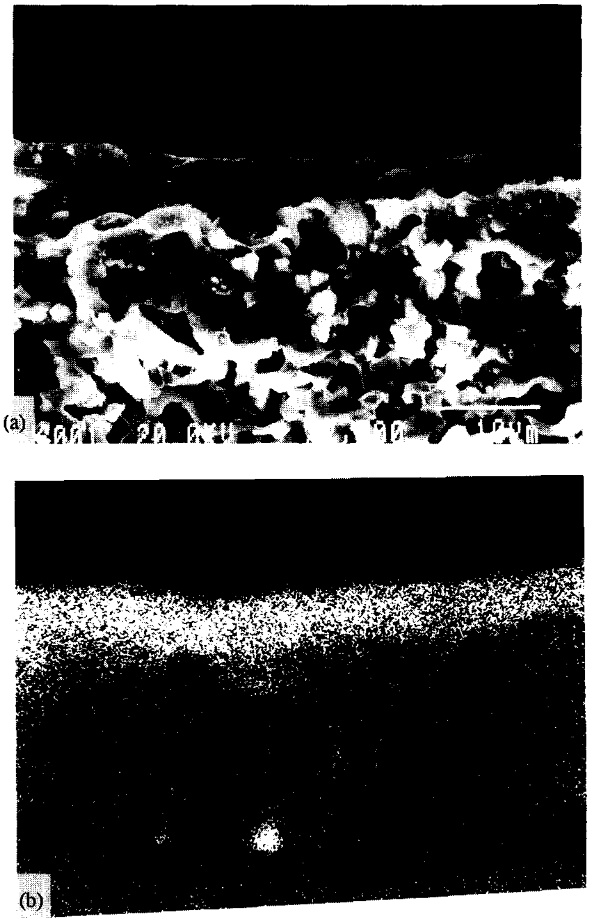

Fig. 13. X-ray map of the fracture surface of CaO impregnated γ-Al_2O_3 membrane prepared after 6 impregnation cycles: (A) SEM photograph; (B) Ca map.

a gel layer at a given pore size of the support [1]. Moreover, Okubo et al. found the repetition of the dipping, drying, and firing procedures is very effective to get the uniform surface without pinholes and cracks [14].

In this study, the mean pore diameter of the support is quite large, 1.4 μm. When the concentration of the sol was 0.5 mol/l, no gel layer was formed even after 7 coating cycles, while 3 μm of gel layer was formed after the 3rd coating in the case of the support whose mean pore diameter is 0.15 μm. Fig. 9 illustrates the changes of membrane thickness with repeated coating, drying, and calcination procedures when the sol concentration was 0.8 mol/l. The thickness of the membrane was in the range of 2–5 μm depending on the number of coating cycles. The effect of the concentration of the sol on the membrane thickness is given in Table 2.

The permeabilities of He, N_2, and CO_2 through the γ-Al_2O_3 membranes with the number of coatings are shown in Fig. 10. The permeabilities were decreased with the number of coating cycles. Gas permeabilities were independent of the mean pressure (Fig. 11) and decreased with the square root of temperature (Fig. 12). Therefore, the main mechanism of gas transport through γ-Al_2O_3 membrane was the Knudsen diffusion and pinhole free γ-Al_2O_3 membranes were prepared.

3.2. CaO impregnated γ-Al_2O_3 membranes

CaO was impregnated on the γ-Al_2O_3 membrane to increase separation factor by introducing an interaction between CO_2 gas molecules and the pore wall. The CaO loads with the number of impregnations analyzed by EDAX are presented in Table 3. After 6 impregnation cycles, the loads of CaO were 8.8%. Fig. 13 shows an X-ray map of the fracture surface of the membrane observed by EPMA. CaO was indeed concentrated on the top layer. It is because impregnation occurs on the surface of the pore and the surface area of the top layer is larger than that of the support.

The results of the gas permeation experiments with CaO impregnated γ-Al_2O_3 membranes are given in Table 4. The separation factor of CO_2 to N_2 was less than 1. This means that the permeability of CO_2 was less than N_2 and the surface diffusion of CO_2 disappeared.

A similar result has been reported by Uhlhorn et al. [7,8]. MgO impregnated γ-Al_2O_3 membranes have

Table 4
Permeability and separation factor of CaO impregnated γ-Al_2O_3 membrane

Temperature (K)	Permeability ($\times 10^7$ mol/Pa s m^2)		Separation factor CO_2/N_2
	CO_2	N_2	
298.15	21.5	21.9	0.98
323.15	17.6	18.4	0.95
373.15	12.9	13.6	0.95
473.15	7.59	8.51	0.89
573.15	5.57	6.59	0.85
673.15	4.69	5.5	0.85

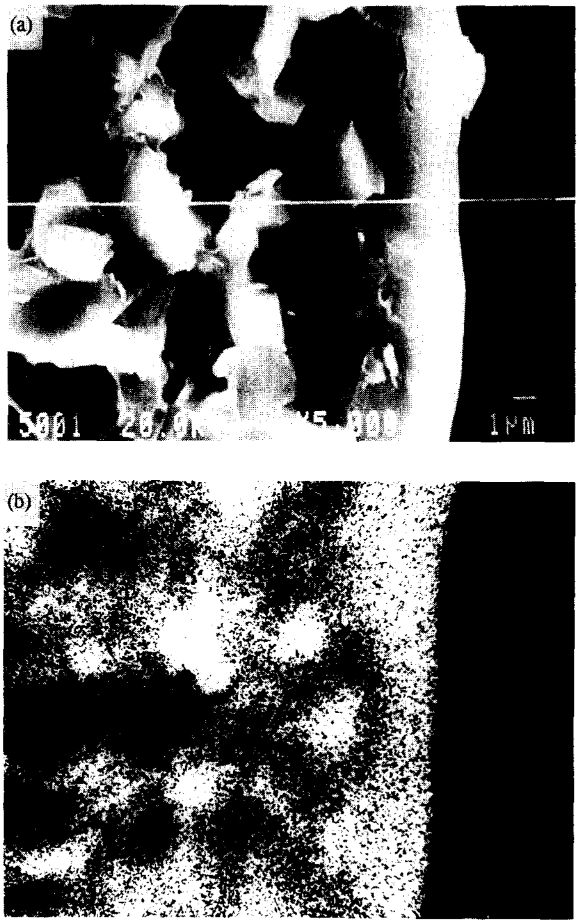

Fig. 14. X-ray map of the fracture surface of silica modified γ-Al_2O_3 membrane prepared after second coating cycles: (A) SEM photograph; (B) Si Map.

been prepared to improve the separation factor by surface diffusion of CO_2. The CO_2 permeability was rather decreased with modification although more adsorption occurred. It was claimed that the introduction of MgO gave strong basic sites and the more strongly bonded CO_2 was less mobile.

According to an adsorption study of Auroux and Gervasini [15], larger amount of CO_2 was adsorbed on CaO surfaces (4 μmol/m^2) than MgO (1 μmol/m^2) and the differential heat of adsorption of CO_2 on CaO surfaces was also higher (160 kJ/mol) than that on MgO (110 kJ/mol). Thus, it is believed that surface diffusion effect nearly disappeared with CaO modification due to high heat of adsorption and low mobility as pointed by out Uhlhorn et al. [7,8].

There has been an attempt to improve the separation factor by increasing the mobility of adsorbed gas molecules at high temperature. Kusakabe et al. synthesized $BaTiO_3$ membranes on the basis of the adsorption study that most of the adsorbed CO_2 molecules on the $BaTiO_3$ powder were mobile at 773 K. However, the separation factor of CO_2 to N_2 was only 1.12–1.20 [9].

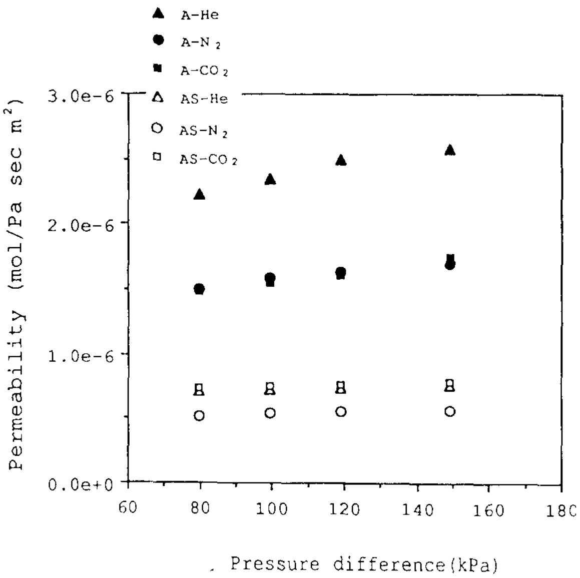

Fig. 15. Permeabilities in a function of pressure differences across the membrane at 298 K: A, γ-Al_2O_3 membrane; AS, silica modified γ-Al_2O_3 membrane.

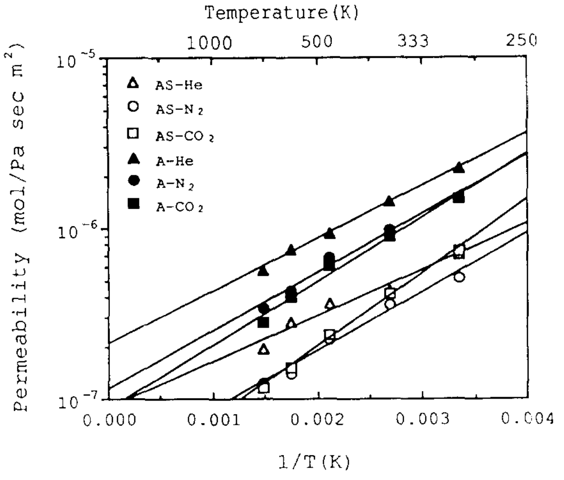

Fig. 16. Arrhenius plots for permeabilities of He, N_2, and CO_2 at 25–400°C: A, γ-Al_2O_3 membrane; AS, silica modified γ-Al_2O_3 membrane.

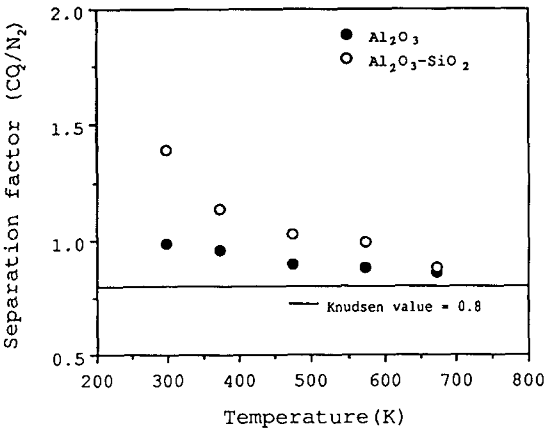

Fig. 17. Effect of the temperature on the gas separation factors of γ-Al_2O_3 and silica modified γ-Al_2O_3 membranes.

Table 5
Effect of silica modification on gas permeability and separation factor[a]

Temperature (K)	Permeability ($\times 10^7$ mol/Pa s m^2)			Separation factor		
	He	N_2	CO_2	He/N_2	He/CO_2	CO_2/N_2
Support	140	110	110	1.33	1.27	1.00
A4	25.0	16.4	16.1	1.52	1.55	0.98
A7	23.1	14.2	14.0	1.63	1.65	0.99
A4-S2	7.40	5.48	7.63	1.35	0.97	1.39

[a] Temperature = 298 K, pressure difference = 119.25 kPa. Ideal separation factors: He/N_2 = 2.65; He/CO_2 = 3.32; CO_2/N_2 = 0.8. A4: γ-Al_2O_3 membrane after 4th AlOOH coating, A7: γ-Al_2O_3 membrane after 7th AlOOH coating, A4-S2: Silica modified γ-Al_2O_3 membrane after 2nd SiO_2 coating on A4.

Therefore, it can be concluded that the separation factor of CO_2 to N_2 cannot be increased sharply by the modification with metal oxide. If the metal oxide gives weak basic sites, surface diffusion occurs but the contribution to total transport is very small. When the membrane surface is modified by the metal oxide that provides strong basic sites, the surface diffusion does not occur because strongly adsorbed gas molecules are less mobile. On the other hand, if the pore size is very small, it seems possible that the separation factor can be increased because more stongly adsorbed and less mobile gas molecules reduce the effective pore size and the gas molecules cannot flow easily because of repulsive forces.

3.3. Silica modified γ-Al_2O_3 membranes

γ-Al_2O_3 membranes were modified using a polymeric solution of silica by the procedure presented in the Experimental section and characterized by SEM/EDX. The synthesis parameters were controlled carefully to give reproducible data. The X-ray map in Fig. 14 indicates silica is uniformly distributed throughout the γ-Al_2O_3 top layer and the support. It reveals that filtered silica sol was gelled in the pore of the membrane by drying.

The permeabilities of the He, N_2, and CO_2 were decreased by a factor of about 3 with modification as shown in Fig. 15. Permeabilities are constant with pressure differences and thus lamina flow is negligible. The permeabilities of He, N_2, and CO_2 through an unmodified and a silica modified γ-Al_2O_3 membranes at temperatures of 298–673 K are presented in Fig. 16. The permeability of CO_2 increased with decreasing temperature. It is considered that this phenomenon is due to surface diffusion and is in accordance with the literature [6]. The separation factor of CO_2 to N_2 was 1.4 at 298 K as shown in Fig. 17, but it decreased with increased temperatures. The surface diffusion nearly disappeared above 673 K because physical adsorption did not occur at high temperature. Therefore, it can be concluded that a high separation factor cannot be obtained by surface diffusion at high temperature. The permeabilities and separation factors of unmodified and

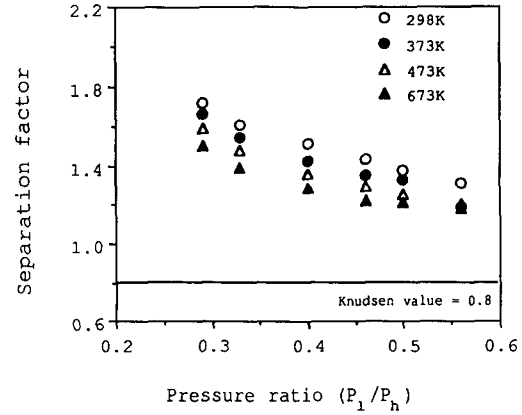

Fig. 18. The separation factor of a CO_2/N_2 mixture (CO_2:N_2 = 1:9) as a fuction of pressure ratio across the membrane (separation factor = $[y/(1-y)]/[x/(1-x)]$ where x and y are the mole fractions of CO_2 at the permeate and the feed side, respectively).

Table 6
Comparison of permeabilities of CO_2 and N_2 through several membrane systems

Reference	Membrane	Pore radius (nm)	T (K)	P (kPa)	Gas	Permeability ($\times 10^7$ mol/Pa s m^2)	Separation factor CO_2/N_2
Uhlhorn et al. [7,8]	MgO–γ-Al_2O_3	2.5–4	293	80–200	N_2	40	
			293	80–200	CO_2	41.7	1.04
MA et al. [16]	γ-Al_2O_3	4	293	150	N2	103	
			293	150	CO_2	72	0.7
	Iron oxide–γ-Al_2O_3		293	150	N_2	28	
			293	150	CO_2	47	1.68
Jia et al. [17]	Zeolite composite	0.3–1.2	293	100	N_2	4.8	
			293	100	CO_2	3.6	1.23
Kusakabe et al. [9]	$BaTiO_3$		373	100	N_2	2.13	1.2
			373	100	CO_2	2.5	
			773	100	N_2	3.13	1.12
			773	100	CO_2	3.5	
Cho et al. [this work]	CaO–γ-Al_2O_3	<2.5	298	140–175	N_2	21.9	0.98
			298	140–175	CO_2	21.5	
			673	140–175	N_2	5.5	0.85
			673	140–175	CO_2	4.69	
	Silica–γ-Al_2O_3	<2.5	298	140–175	N_2	5.2--6.1	1.4
			298	140–175	CO_2	7.4--8.4	
			673	140–175	N_2	1.2--1.3	0.9
			673	140–175	CO_2	1.2--1.2	

silica modified γ-Al_2O_3 membranes are summarized in Table 5.

Separation experiments of a CO_2/N_2 mixture with silica modified γ-Al_2O_3 membrane were also performed over the temperature range of 298–673 K. The effects of the pressure ratio and temperature on the separation factor are shown in Fig. 18. The separation factor was decreased with increasing temperature. By decreasing the pressure ratio over the membrane which is the ratio of the pressure on the permeate side to that on the feed side, back diffusion decreased and thus the separation factor increased. This back diffusion effect was also reported in a H_2/N_2 mixture separation experiment [7]. When the pressure ratio was 0.26, the separation factor was 1.72 at 298 K and 1.50 at 673 K. These permeabilities and separation factors are one of the highest values as shown in Table 6.

4. Conclusions

Pinhole free γ-Al_2O_3 membranes were synthesized by filtration method on the supports which have relatively large pore size and a rough surface. The main mechanism of gas transport through γ-Al_2O_3 membrane was by Knudsen diffusion. γ-Al_2O_3 membranes were impregnated with CaO as an attempt to obtain high separation factors by introducing chemical affinity to the pore wall. However, the seprartion factor of CO_2 to N_2 was not higher than that of the Knudsen diffusion mechanism. Silica modified γ-Al_2O_3 membranes were also prepared to improve the separation factor. The separation factor of CO_2 to N_2 was increased to 1.4 at 298 K while it decreased with increasing temperature. In summary, surface diffusion can be applied as a separation mechanism when the pore size is very small and the temperature is low. However, high separation factors could not be obtained at high temperatures.

5. List of symbols

A_0	surface area occupied by an adsorbed molecule (m^2)
D_s	surface diffusion coefficient ($m^2\ s^{-1}$)
F_0	permeability (mol/Pa s m^2)
L	membrane thickness (m)
M	molar mass (Kg mol^{-1})
N_{av}	Avogadro's constant (6×10^{23})

$\bar{P}$	mean pressure (N m^{-2})
$\bar{r}$	mean pore radius (m)
R	gas constant (8.314 J mol^{-1} K^{-1})
T	temperature (K)
x_S	percentage of occupied surface compared with a monolayer
ϵ	porosity
η	viscosity (N s m^{-2})
μ	shape factor

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