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γ-Alumina composite membranes modified with microporous silica for CO_2 separation

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γ-Al_2O_3 composite membranes have been modified with microporous silica layers to improve the separation factor of CO_2 to N_2. From the analysis of micropore volume fraction and CO_2 adsorption behaviour of SiO_2 unsupported membranes, it was found that the SiO_2 membrane layer feasible to separate CO_2 could be obtained from a sol prepared by hydrolysis of tetraethyl orthosilicate in aqueous nitric acid solution (acid concentration of 0.001 M and sol pH of 2.0). The unsupported membrane prepared from this optimum sol had a micropore volume fraction of 0.85 and CO_2 adsorption amount of 27 $cm^3(STP)g^{-1}$ at 0.1 MPa and 25 °C. Defect-free silica modified γ-Al_2O_3 membranes could be synthesized by dipcoating or pressurized coating from outside the support. The CO_2/N_2 separation factor of these membranes varied severely with the separation process parameters, such as transmembrane pressure, stage cut and CO_2 concentration in feed gas. γ-Al_2O_3 membranes modified by dipcoating and pressurized coating had a CO_2/N_2 separation factor of 2.4 and 1.45, respectively, at $\Delta P = 0.3$ MPa, stage cut = 0.1, and 25 °C for a CO_2 feed gas mole fraction of 0.5. The CO_2/N_2 separation factor at 25 °C decreased with increasing heat-treatment temperature. The main mechanisms of CO_2 permeation through silica modified membranes were surface diffusion and Knudsen diffusion. © *1999 Kluwer Academic Publishers*

1. Introduction

Ceramic membranes have received extensive attention in recent years because of their excellent chemical and thermal stabilities, especially in the application of gas separation and catalytic membrane reactor processes [1, 2]. The separation of CO_2, which is the origin for the worldwide greenhouse effect, from flue gases has become one of the most important processes in the environmental field in recent years. Many techniques [3–19] have been used to produce CO_2 permselective ceramic composite membranes, including surface modification of ready-made γ-alumina and glass membranes through which Knudsen diffusion has predominantly occurred.

Based on the modification route, one can roughly distinguish five main types of surface modification methods to obtain high CO_2 separation efficiency: metal oxide impregnation [3–5], chemical vapour deposition (CVD) [7–10] or polymerization [11–13] of organic compounds, silane coupling [14], and sol–gel derived coating [15–19].

Uhlhorn and coworkers [3, 4] modified the γ-alumina membrane with MgO by the reservoir method, similar to the conventional impregnation technique, to enhance the adsorption and surface diffusion of CO_2 as well as to reduce the pore size. However, their membrane showed CO_2/N_2 permselectivity (the ratio of single gas permeabilities) of only unit almost the same as the Knudsen ideal separation factor value, 0.8. It was attributed that strong adsorption of CO_2 occurred on the MgO sites, resulting in a decrease in CO_2 mobility. Other oxides were impregnated into the γ-alumina composite membrane by Ma *et al.* [5] Contrary to the case of the MgO impregnated membrane of Uhlhorn *et al.*, CO_2/N_2 permselectivities of iron and aluminum oxide modified membranes were 1.67 and 1.50, respectively. From a CO_2 equilibrium adsorption study on unmodified and iron oxide modified membranes, they observed that the CO_2 equilibrium adsorption capacity of the modified membrane is higher than that of the pure γ-alumina membrane and this provides an increase in CO_2 permeability by surface diffusion. They also studied the gas permeation and separation characteristics of hollow fibre glass membranes [6]. At 343 K and 2.8 MPa (applied pressure), their glass membrane showed a CO_2/N_2 separation factor of 25 using helium as a purge gas. It is doubtful if their membranes could be used practically, however, because the glass fibre has very low mechanical strength compared with typical ceramic membranes. Also the reported CO_2/N_2 separation factor might be lowered if there was no purging gas in their experimental process, as additional He/CO_2 separation processes would be required when applied in industrial use.

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Okubo and Inoue [7–9] synthesized the surface modified membrane with hydrophilic silanol groups by introducing tetraethylorthosilicate vapour into pores and decomposing the vapour on the pore walls of glass membranes. The permeation mechanism of CO_2 and N_2 through this modified membrane was micropore diffusion, indicating that the resultant pore size is smaller than 2 nm and CO_2/N_2 permselectivity at 333 K is about 1.6. After preparation of stainless steel supported ZrO_2 and SiO_2 membranes, Cot and coworkers [10] treated these ceramic–metal composite membranes with fluorinated polymer films using a plasma enhanced CVD technique. The CO_2/N_2 permselectivities of treated membranes were 1.25–1.61 for the membrane type.

By the *in situ* polymerization technique, Li and Hwang [11, 12] obtained silicon polymer–glass membranes with the CO_2/N_2 permselectivities of 1.5–10.3 depending on the organic silane compound used. The reason for the increase in the permselectivity was ascribed to micropore diffusion of CO_2 through their membranes. Sugawara *et al.* [13] produced the same type of membranes to that of Li and Hwang, except the support membrane was modified. Their siloxane–anodic aluminum oxide membranes showed a CO_2/N_2 permselectivity value of higher than ten.

Hyun *et al.* [14] modified the α-alumina and titania supported γ-alumina membranes by silane coupling with phenyltriethoxysilane, which is known to have a chemical affinity for CO_2. They suggested that the separation efficiency of the γ-alumina membranes modified by silane coupling was strongly dependent on the hydroxylation tendency of the support materials. The separation factor of CO_2 to N_2 through the γ-alumina–titania composite membrane modified with the 10 wt % silane solution was 1.7 at 90 °C given an applied pressure of 0.2 MPa for the binary mixture containing 50 vol % CO_2, while there was no improvement of CO_2/N_2 permselectivities and separation factors in the α-alumina supported case.

Through the polymeric silica sol coating of γ-alumina membranes, Cho *et al.* [15] obtained CO_2 to N_2 permselectivities and separation factors of 1.4 and 1.72 at room temperature, respectively. They described that the CO_2/N_2 separation mechanism of their membranes was such that the more strongly adsorbed and less mobile CO_2 molecules reduced the effective pore size and then N_2 gas molecules could not flow easily because of repulsive forces as well as steric hindrance effects. Micropore diffusion through their membranes, however, did not feature in their report. Although Uhlhorn *et al.* [16, 17] and de Lange *et al.* [18] have modified the supported γ-alumina layer with a polymeric silica gel through which micropore diffusion occurred, CO_2 permeabilities in comparison with that of N_2 were not reported. Okui *et al.* [19] have prepared organic–inorganic hybrid membranes by modification of γ-alumina membranes with composite sol containing tetramethoxysilane or phenyltrimethoxysilane. The pore size of the coated top layer was about 2 nm and the transport mechanism of O_2 as well as CO_2 suggested in their paper was surface diffusion. The CO_2/N_2 permselectivity of the hybrid membrane using a phenyl group was about six at room temperature.

Far from the modification technique, preparation and gas separation characteristics of zeolite membranes, such as ZSM-5, and silicalite having a uniform pore size of about 0.55 nm have been studied considerably in recent years for their prominent molecular sieving abilities [20–23]. In case of separation between CO_2 and N_2, having a very small difference in molecular size, however, reported permselectivities are so far less than 3.7.

In this study, α-alumina supported γ-alumina membrane layers have been modified by the microporous silica layer coating to improve the CO_2/N_2 separation factor using colloidal silica sols. The optimum sol for modification was selected from analysis of micropore volume fraction and CO_2 adsorption amounts for SiO_2 unsupported membranes. Final membranes modified by dipcoating or pressurized coating with the optimum sol were evaluated by the measurement of gas permeability and CO_2/N_2 separation factor in the point of view of separation process parameters, such as transmembrane pressure, stage cut, CO_2 concentration in feed gases and thermal stability of membranes.

2. Experimental procedure

2.1. Preparation of γ-alumina membranes and silica sols

γ-Al_2O_3 membranes were prepared by a dipcoating of tubular α-Al_2O_3 supports (outside diameter, 8 mm; thickness, 0.8 mm; length, 100 mm; and mean pore diameter, 0.1 μm) with a boehmite sol. The preparation methods of supports, boehmite sols and γ-Al_2O_3 composite membranes are given in detail in [14, 24, 25]. The average pore size of the γ-Al_2O_3 layer had already been found to be about 2.2 nm [25].

Synthetic γ-Al_2O_3 membranes were modified with colloidal silica sols to obtain CO_2 permselective layers. Silica sols were prepared from tetraethyl orthosilicate (TEOS, 98%, Aldrich) and deionized water containing nitric acid (60–62%, Junsei Chemical Co.) in the procedure described by Chu *et al.* [26]. TEOS was added to an aqueous nitric acid solution. This mixture was stirred vigorously for 2 h at room temperature. After hydrolysis reaction at the interface between TEOS and aqueous phases, the mixture became a transparent sol. To obtain the optimum silica sols feasible to produce CO_2 permselective layers, the concentration of nitric acid in deionized water was varied from 0.0005 to 0.1 M. The solid content was fixed to 0.5 mol l^{-1} based on SiO_2. A silica sol by the hydrolysis of TEOS in high alkaline water [24] was also synthesized for comparison with the aforementioned acidic one.

Unsupported membranes were prepared by evaporating the sol in polystyrene dishes at room temperature followed by heating to 200–400 °C at a heating rate of 0.5 °C min^{-1}, holding for 2 h. These unsupported membranes were then analysed by CO_2 and N_2 adsorption isotherms, Brunaver–Emmett–Teller (BET) specific surface areas, and micropore volumes using the volumetric surface area analyser (Gemini 2375, Micromeritics).

TABLE I Conditions for surface modification with silica layers

Modification method	Membrane being modified	Modification condition			Reference figure
		Pressure (MPa)	Time		
			First coating (h)	Second coating (h)	
Dipcoating	γ-Al_2O_3/α-Al_2O_3	—	20^a	20^a	Fig. 1a
Pressurized coating from outside the support	γ-Al_2O_3/α-Al_2O_3	0.1–0.2	1	—	Fig. 1b
Pressurized coating from inside the support	α-Al_2O_3	0.1–0.6	1	1	Fig. 1c

[a] Measurements are in seconds.

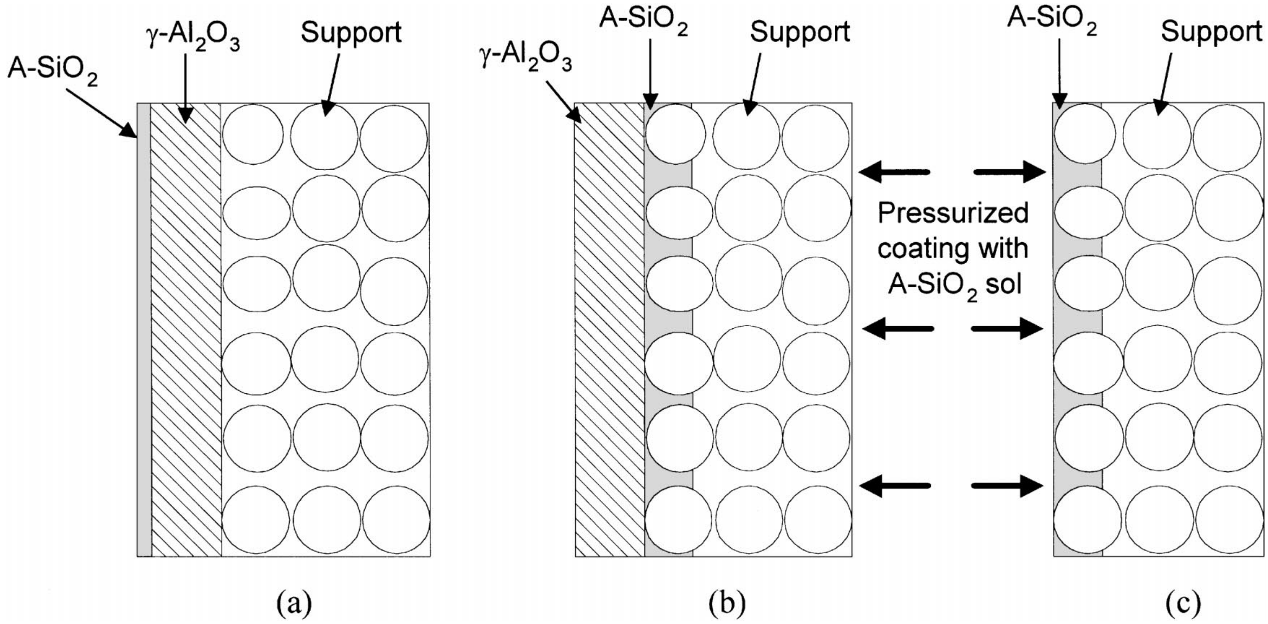


Figure 1 Schematic illustrations of acidic SiO_2 (A-SiO_2) layers: (a) dipcoating and (b) pressurized coating from outside the support of the γ-Al_2O_3 composite membrane, and (c) pressurized coating from inside the bare α-Al_2O_3 support.

2.2. Surface modification by silica layers

Surface modification with silica sols was performed not only to the synthetic γ-Al_2O_3 composite membranes but to the bare α-Al_2O_3 supports, as shown in Fig. 1. The first method (Fig. 1a) is conventional dipcoating on the γ-Al_2O_3 layer with silica sols; the second is silica-layer coating at the interface between the γ-Al_2O_3 layer and the α-Al_2O_3 support by pressurizing the silica sols from the support outside (Fig. 1b). The third method (Fig. 1c) is pressurized coating of the bare α-Al_2O_3 support inside, as already reported elsewhere [24]. The conditions for each modification method are summarized in Table I. In the case of dipcoating (Fig. 1a), the inner surface of the γ-Al_2O_3 layer was brought into contact with the silica sol for 20 s. For pressurized coatings, the outside (Fig. 1b) or the inside (Fig. 1c) of the membrane tube was brought into contact with the sol under the pressure and time periods given in Table I. After every modification (coating) step, membranes were dried for 1 day in air at room temperature followed by heat treatment in the same manner as for the unsupported membranes.

2.3. Membrane characterization and separation factor measurements

The microstructure of the silica modified membranes was observed by scanning electron microscopy (SEM; Akash, SX-30E). From the N_2 permeability measurements, the existence of cracking in the modified layers was examined as described earlier [24]. The CO_2/N_2 permselectivity (ratio of CO_2 permeability to N_2 permeability) and the separation factor, $Y_{CO_2}(1-X_{CO_2})/X_{CO_2}(1-Y_{CO_2})$, were also determined by analysing the composition of feed (X_{CO_2}) and permeate (Y_{CO_2}) gas mixtures with a gas chromatograph (GC-680D, Young-In Scientific Co. Ltd) using the tailored apparatus shown in Fig. 2. Helium was used as the carrier gas in the gas chromatograph measurement, and

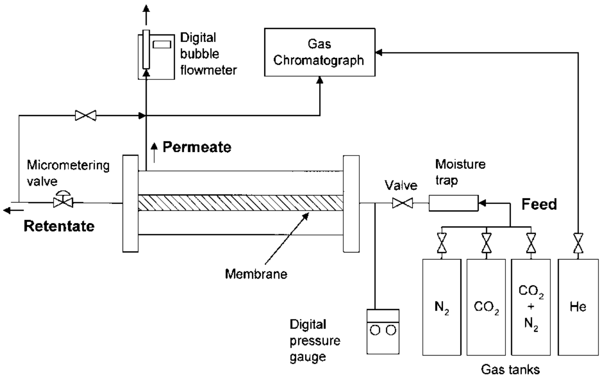


Figure 2 Schematic diagram of the gas permeability and separation factor measurement apparatus.

a sampling loop was installed in the chromatograph for automatic injection of gas samples. A sweep gas was not used in this study. Evolution of the separation factor with separation process parameters, such as the trans-membrane pressure (difference between feed and permeate gas pressures, ΔP), stage cut (ratio of permeate to retentate gas flow rates, θ), and CO_2 concentration in feed gases were evaluated.

3. Results and discussion

3.1. Characteristics of unsupported membranes

The membranes used for CO_2 separation should have pores small enough to enhance surface diffusion while restraining Knudsen diffusion of CO_2. Also, it is desirable that the membrane material has higher CO_2 adsorption abilities than that of N_2. Therefore, the micropore volume fraction and CO_2 and N_2 adsorption isotherms of SiO_2 unsupported membranes were measured to select the most feasible SiO_2 sol for modification.

The micropore volume fraction can be defined as the ratio of the micropore volume to the total pore volume [27, 28]. This can be a scale for estimating pore sizes in membranes having Type I isotherms [27] for N_2 at 77 K, i.e. the higher the micropore volume fraction the smaller the membrane pore size. Fig. 3 shows the N_2 adsorption isotherms on SiO_2 unsupported membranes at 77 K. It is clearly observed that all the SiO_2 unsupported membranes, including the basic one, have Type I adsorption isotherms for N_2, which implies that the mean pore diameter in the membranes is smaller than 2 nm [27]. The variation of micropore volume fraction with the concentration of nitric acid in hydrolysing aqueous solutions is given in Fig. 4 for acidic SiO_2 unsupported membranes. As can be seen in Fig. 4, the micropore volume fraction varies severely from 0.35 to 0.85, with its apex at an acid concentration of 0.001 M, though all membranes show a Type I isotherm. This indicates that the membrane synthesized by the sol with an initial acid concentration of 0.001 M can be expected to have the smallest pore size. It can be expected that this membrane has the highest surface diffusivity of CO_2 while restraining Knudsen diffusion, as the surface mobility is inversely proportional to the membrane pore size [29]. Comparing the basic silica sol with the acidic one, the relative pressure, P/P_o, where N_2 adsorption in membrane pores is completed is about 0.35 for the basic SiO_2 membrane while it is below 0.1 for the acidic sol, as shown in Fig. 3. From these N_2 adsorption behaviours, the micropore volume fraction of the basic SiO_2 membrane was 0.3.

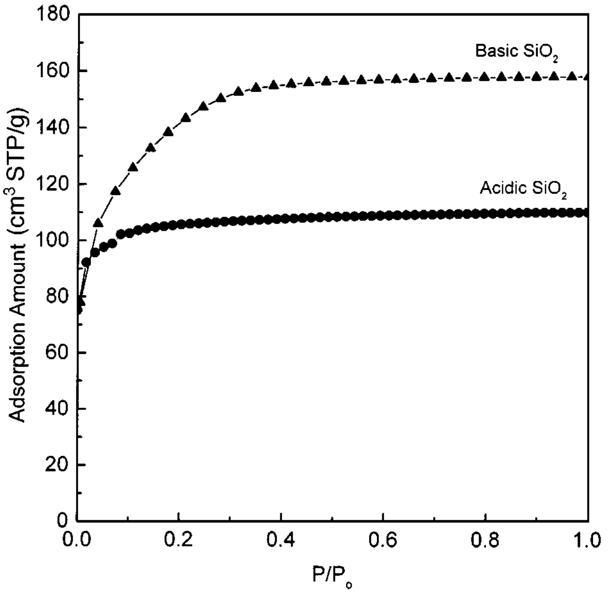


Figure 3 N_2 adsorption isotherms on SiO_2 unsupported membranes heat treated at 200 °C.

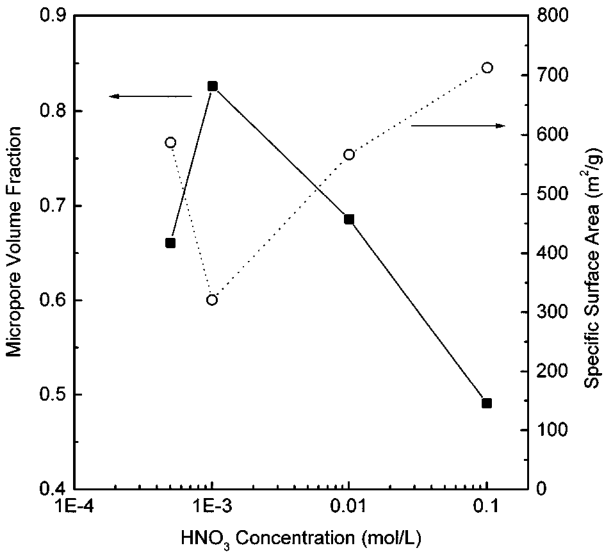


Figure 4 Micropore volume fraction and specific surface area versus concentration of HNO_3 in aqueous solution for acidic SiO_2 unsupported membranes heat treated at 200 °C.

The variation of micropore volume fraction of acidic SiO_2 unsupported membranes with the pH of precursor sols prepared from an initial acid concentration of 0.001 M is also given in Fig. 5. The maximum value of the micropore volume fraction occurs at a pH of 2.0,

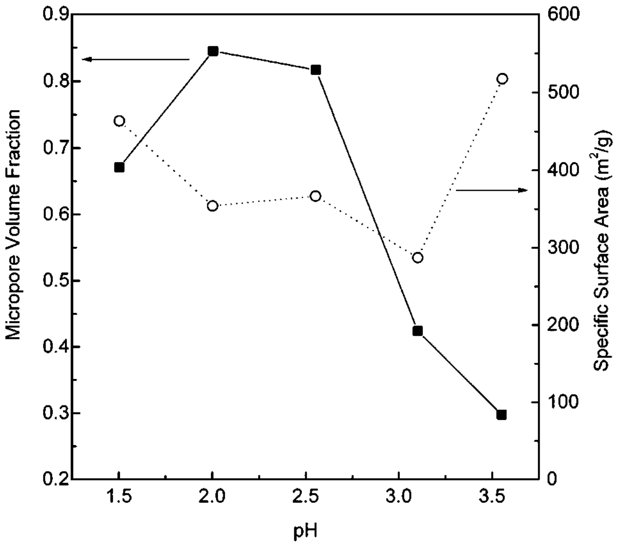


Figure 5 Micropore volume fraction and specific surface area versus pH of precursor sols for acidic SiO_2 unsupported membranes heat treated at 200 °C.

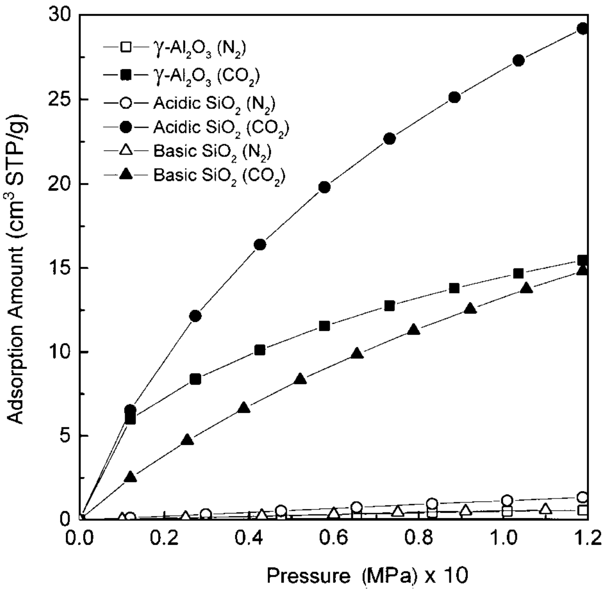


Figure 6 CO_2 and N_2 adsorption isotherms on γ-Al_2O_3 and SiO_2 unsupported membranes at 25 °C.

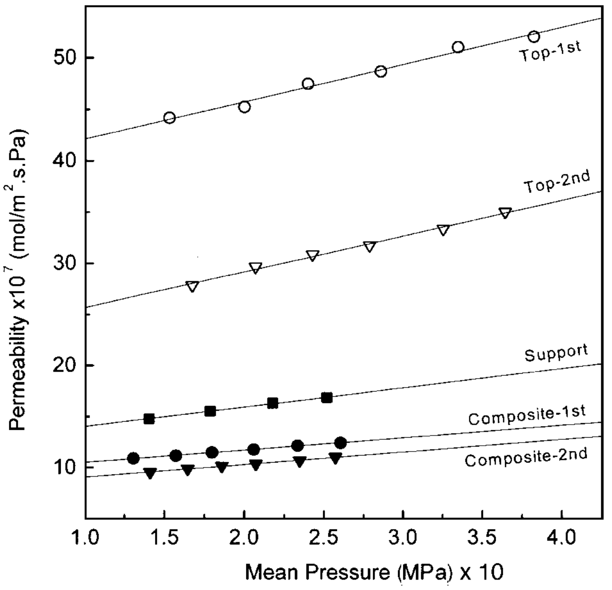


Figure 7 N_2 permeabilities of acidic SiO_2 membranes prepared by pressurized coating of the α-Al_2O_3 support.

which is three times larger than that of pH 3.5. From the micropore volume fraction measurements, it can be concluded that an acidic SiO_2 precursor sol with an initial acid concentration of 0.001 M and a pH of 2.0, was optimum to obtain CO_2 permselective membrane layers, in the range studied.

This optimum SiO_2 unsupported membrane was further analysed by CO_2 and N_2 adsorption amounts at 25 °C in comparison with those of γ-Al_2O_3 and basic SiO_2 membranes as shown in Fig. 6. The amount of CO_2 adsorption on acidic SiO_2 was about 27 $cm^3(STP)g^{-1}$, about two times higher than for other membranes at a pressure of 0.1 MPa. Contrary to the case for CO_2 adsorption trends having Type I isotherms, N_2 isotherms are practically linear and they obey Henry's law over the pressure range studied [29]. Ratios of CO_2 to N_2 adsorption amounts on acidic SiO_2, basic SiO_2 and γ-Al_2O_3 unsupported membranes were about 14.5, 9.2 and 15.7, respectively, and the magnitude of the ratios is independent of the amount of CO_2 adsorption. The ratio of CO_2 to N_2 adsorption amount on the γ-Al_2O_3 membrane showed the highest value, however, it should be noted that CO_2 mobility on the membrane pore wall is linearly dependent on the slope of the pressure to adsorption amount plot (Fig. 6) as well as on the absolute value of the CO_2 adsorption amount, because gas flux by the surface diffusion mechanism is proportional to the surface concentration gradient of adsorbed species [29]. As a consequence, the micropore volume fraction and CO_2 adsorption amount data of unsupported membranes suggest that a CO_2 permselective layer having a maximum CO_2/N_2 separation factor can be synthesized by acidic SiO_2 sols of initial acid concentration of 0.001 M and pH of 2.0 in the range of this study.

3.2. Modification of composite membranes with silica layers

Surface modification of the acidic SiO_2 layer was performed by dipcoating, pressurized coating of the γ-Al_2O_3 composite membrane or the bare α-Al_2O_3 support as shown in Fig. 1. N_2 permeabilities of surface modified membranes were measured to examine the presence of cracking in coated SiO_2 layers as described by Hyun and Kang [24]. Fig. 7 shows N_2 permeability data of the SiO_2 composite membrane prepared by pressurized coating from inside the α-Al_2O_3 support as illustrated in Fig. 1c. It is clearly observed from Fig. 7 that the N_2 permeabilities through the SiO_2 top-layers coated once and twice are dependent on the mean pressure. This indicates the existence of defects in the top layers. Such a situation can be explained by the fact that the pores of the support were not filled completely with SiO_2 gels. Considering that the particle size of the SiO_2 sol could not be measured by dynamic light scattering analysis, of which the lower measuring limit is 4 nm, the sol particle size was too small to gel in the support pore (pore diameter of support = 100 nm) during pressurized coating. Since CO_2/N_2 permselectivity of this membrane was merely 0.94, almost the same value as that of the γ-Al_2O_3 composite membranes, it can be concluded that the synthesis of defect-free SiO_2/α-Al_2O_3 composite membranes by pressurized coating failed in all the conditions used in this study. Therefore, SiO_2 sol coatings were performed only on the γ-Al_2O_3 composite membranes.

Fig. 8 shows the fracture surface of the silica modified membrane prepared by dipcoating of the inner surface of the γ-Al_2O_3 membrane, as illustrated in Fig. 1a. The side with the γ-Al_2O_3 layer was brought into contact with the silica sol for 20 s, and then dried at 25 °C and calcined at 200 °C. This procedure was repeated once more. As shown in Fig. 8, the thickness of the silica layer formed was, at most, 150 nm. Silica modified γ-Al_2O_3 membranes were also prepared by pressurizing the silica sols from the support outside (Fig. 1b), thereby allowing the formation of silica layers at the interface between the γ-Al_2O_3 mesoporous layer and the α-Al_2O_3 support, as given in Fig. 9. From the fracture

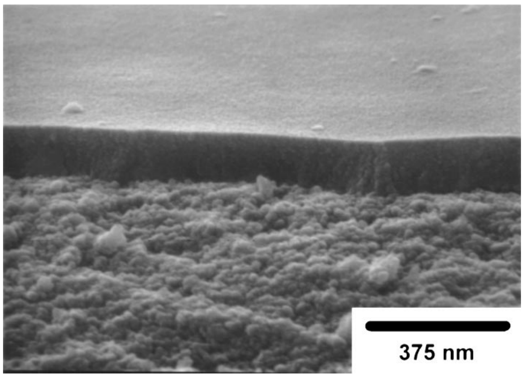


Figure 8 SEM micrograph of the fracture surface of the acidic SiO_2 modified γ-Al_2O_3 membrane prepared by dipcoating.

surfaces in Fig. 9, it can be seen that the thickness of the support pore-filled silica layer was about 7–8 μm. This silica layer covered the α-Al_2O_3 support particles (particle size = 0.4 μm) to the extent that the particles can no longer observed (Fig. 9b). Unlike the case of Fig. 7 for pressurized coating with bare α-Al_2O_3 supports, N_2 permeabilities through silica layers modified on γ-Al_2O_3 composite membranes are independent of pressure in nature, which indicates that the modified SiO_2 layers are crack-free.

3.3. Separation of CO_2/N_2 gas mixtures

The silica modified γ-Al_2O_3 membranes were further evaluated by CO_2/N_2 permselectivity and separation factor measurement at 25 °C. To examine the effect of separation process parameters on CO_2/N_2 separation efficiencies, variations of CO_2/N_2 separation factors with transmembrane pressure, ΔP, and stage cut, θ, were measured. Fig. 10 shows the representative results of the effect of transmembrane pressure. The CO_2/N_2 separation factor increased with increasing transmembrane pressure. This phenomenon can be explained by two mechanisms: (i) the CO_2 adsorption amount in the membrane pore could be increased with increasing pressure; (ii) back diffusion, caused by collision between gases having different molecular weights in gas mixtures, could be reduced by increasing the transmembrane pressure [3].

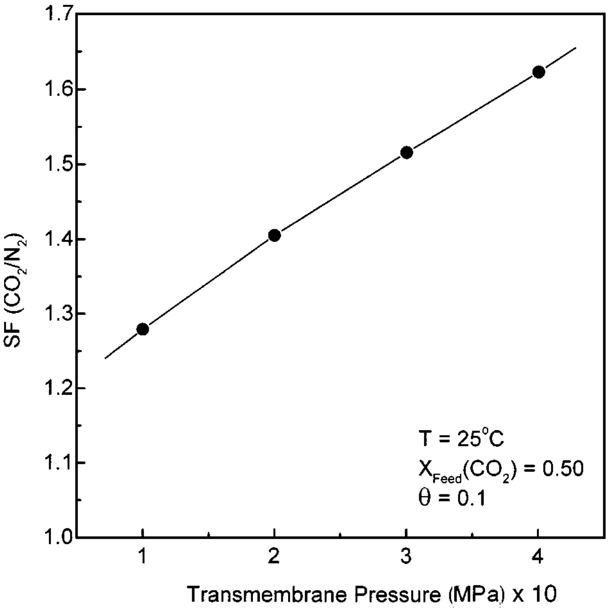
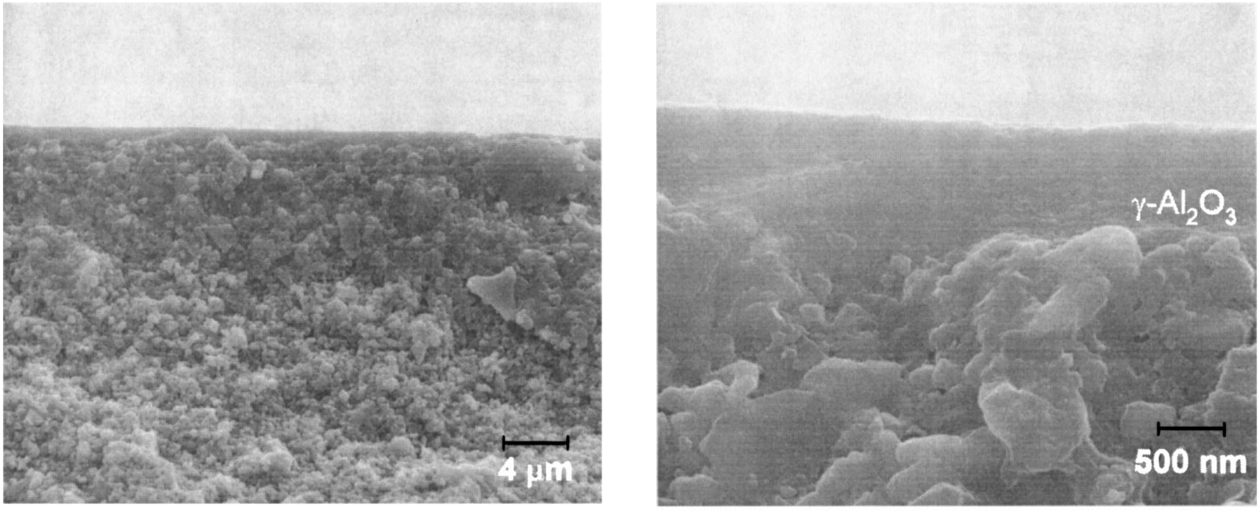


Figure 10 CO_2/N_2 separation factor versus transmembrane pressure, ΔP, of the acidic SiO_2 modified γ-Al_2O_3 membrane prepared by pressurized coating from outside the support.

After faster permeation of CO_2 gas by preferential adsorption and surface diffusion, N_2 gas remains in the feed gas stream. Therefore, the concentration polarization phenomenon, an increase in N_2 concentration on the membrane surface, could appear. This can be reduced by flowing the feed gas (retentate) with or without a sweep gas. In this study sweep gas was not used. The stage cut, i.e. the ratio of the permeate flow rate to the retentate one, could then be a scale of the reduction of this concentration phenomenon. In Fig. 11, variation of the CO_2/N_2 separation factor with stage cut is given



(a) (b)

Figure 9 SEM micrographs of fracture surfaces of the acidic SiO_2 modified γ-Al_2O_3 membrane prepared by pressurized coating from outside the support: (a) ×2500 and (b) ×20 000.

TABLE II CO_2 and N_2 permeabilities, CO_2/N_2 permselectivities and separation factors through γ-Al_2O_3 and acidic SiO_2 modified γ-Al_2O_3 composite membranes prepared by dipcoating ($\Delta P = 0.3$ MPa, $\theta = 0.1$, measurement temprature = 25 °C)

Membrane	Heat-treatment temprature (°C)	N_2 permeability ($\times 10^{-7}$mol m^{-2} s^{-1} Pa^{-1})	CO_2 permeability ($\times 10^{-7}$mol m^{-2} s^{-1} Pa^{-1})	CO_2/N_2 permeability	CO_2/N_2 separation factor $X_{CO_2}{}^a = 0.28$	$X_{CO_2}{}^a = 0.50$
γ-Al_2O_3	500	10.7	10.6	0.99	—	1.05
SiO_2 modified						
First coating	200	2.9	4.9	1.69	1.84	2.03
Second coating	200	1.6	3.4	2.13	2.05	2.38
	300	3.6	5.3	1.47	1.58	—
	400	4.8	6.4	1.33	1.52	—

[a] X_{CO_2}, mole fraction of CO_2 in feed gas.

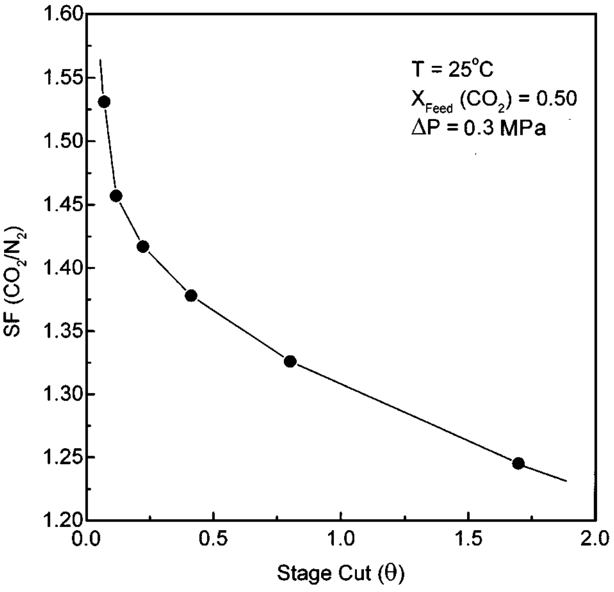


Figure 11 CO_2/N_2 separation factor versus stage cut, θ, for the acidic SiO_2 modified γ-Al_2O_3 membrane prepared by pressurized coating from outside the support.

for the same membrane as in Fig. 10. It can be clearly observed from Fig. 11 that the smaller the stage cut the higher the CO_2/N_2 separation factor. As the stage cut is decreased from 1.7 to 0.05, the CO_2/N_2 separation factor increases from 1.25 to 1.53. It is undesirable that the stage cut is small, as in practical application the amount of non-permeating (not separated) gas (retentate) should be increased. Therefore, transmembrane pressure and stage cut were fixed to 0.3 MPa and 0.1, respectively, to compare the separation efficiency of each silica modified membrane.

Table II shows the variations of CO_2 and N_2 permeabilities, CO_2/N_2 permselectivities and separation factors through the silica modified γ-Al_2O_3 composite membranes prepared by dipcoating. After the second modification, N_2 permeabilities were largely reduced to a value of 1.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} from 10.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} of unmodified γ-Al_2O_3 membrane. This implies that the N_2 permeation rate through the membrane was ruled by the modified silica layer, considering that the thickness of silica layer was only about 150 nm. When the CO_2 mole fraction in the feed gas was 0.5, the CO_2/N_2 separation factor reached as high as 2.4, which is much larger than that of 2.0 for the case of a CO_2 mole fraction of 0.28. As mentioned above, these results can be explained by the fact that surface mobility of CO_2 can be linearly increased by increasing the amount of CO_2 adsorption.

3.4. Thermal stability of modified silica layers

The thermal stability of ceramic membranes is one of the most important factors in their application for gas separation. To evaluate the thermal stabilities of silica modified membranes, CO_2/N_2 separation factor and permselectivity were examined for heat-treatment temperature ranges from 200 to 400 °C. As shown in Table II, CO_2/N_2 separation factors as well as permselectivities were decreased with an increase in heat-treatment temperature, while both CO_2 and N_2 single gas permeabilities were increased. In consequence, the thermal stability of modified silica layers investigated in this study is poorer than that of the basic silica membrane for which N_2 permeability is constant in the heat-treatment temperature range 200–500 °C [24].

It is clearly observed from Table II that the difference between CO_2 and N_2 gas permeability is nearly constant in the firing temperature range 200–400 °C. Providing that the CO_2/N_2 permselectivity of γ-Al_2O_3 composite membranes is near unity, it could be considered that the origin of this difference is surface diffusion of CO_2 through the modified silica layer. Therefore, the decrease in separation efficiency with the increase of heat-treatment temperature is ascribed to the fact that Knudsen permeability is increased by pore growth, although CO_2 permeability by surface diffusion is constant.

4. Conclusions

γ-Al_2O_3 composite membranes were modified with a microporous silica layer using acidic silica sol to improve the separation efficiency of CO_2 to N_2. The main findings of this research are:

1. The optimum sol for modification can be prepared by hydrolysing tetraethyl orthosilicate in a nitric acid aqueous solution of acid concentration 0.001 M. The unsupported membrane prepared from this sol (pH 2.0) had a micropore volume fraction of 0.85 and CO_2 adsorption amount of 27 cm^3(STP)g^{-1} at 0.1 MPa and 25 °C.
2. A defect-free silica modified γ-Al_2O_3 membrane could be synthesized by dipcoating or pressurized coating from outside the support. The CO_2/N_2 separation

factor varied severely with the separation process parameters, such as transmembrane pressure, stage cut and CO_2 concentration in the feed gases.

3. CO_2/N_2 separation factors through the silica modified γ-Al_2O_3 membranes by dipcoating and pressurized coating from outside the support were about 2.4 and 1.45, respectively, at $\Delta P = 0.3$ MPa, stage cut $= 0.1$, and 25 °C for the feed gas of CO_2 with a mole fraction of 0.5.

4. The CO_2/N_2 separation factor of silica modified γ-Al_2O_3 membranes decreased with increasing heat-treatment temperature. The mechanisms of CO_2 permeation through these membranes were surface diffusion as well as Knudsen diffusion.

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