Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Organic-Templating Approach to Synthesis of Nanoporous Silica Composite Membranes (II): MTES-Templating and CO_2 Separation

Y. E. Lee[a]; B. S. Kang[a]; S. H. Hyun[a]; C. H. Lee[b]
[a] Department of Ceramic Engineering, College of Engineering, Yonsei University, Seoul, South Korea [b] Department of Chemical Engineering, College of Engineering, Yonsei University, Seoul, South Korea

To cite this Article Lee, Y. E. , Kang, B. S. , Hyun, S. H. and Lee, C. H.(2005) 'Organic-Templating Approach to Synthesis of Nanoporous Silica Composite Membranes (II): MTES-Templating and CO_2 Separation', Separation Science and Technology, 39: 15, 3541 — 3557
To link to this Article: DOI: 10.1081/SS-200036750
URL: http://dx.doi.org/10.1081/SS-200036750

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 15, pp. 3541–3557, 2004

Organic-Templating Approach to Synthesis of Nanoporous Silica Composite Membranes (II): MTES-Templating and CO_2 Separation

Y. E. Lee,[1] B. S. Kang,[1] S. H. Hyun,[1,*] and C. H. Lee[2]

[1]Department of Ceramic Engineering and [2]Department of Chemical Engineering, College of Engineering, Yonsei University, Seoul, South Korea

ABSTRACT

Nanoporous silica composite membranes for gas separation have been synthesized by the organic-templating sol-gel technique and their CO_2/N_2 separation efficiency has been investigated. Stable organic-templating silica sols capable of coating nanoporous amorphous silica layers on $SiO_2/\alpha\text{-}Al_2O_3$ composite supports were prepared by the two-step acid-catalytic process using the mixture of TEOS and template such as MTES (methyltriethoxysilane) being covalently bonded with TEOS or TPABr (tetrapropylammonium bromide) non-reacted. The $SiO_2/\alpha\text{-}Al_2O_3$ composite supports (pore size 1.6 nm) prepared by pressurized coating of the

---

*Correspondence: S. H. Hyun, Department of Ceramic Engineering, College of Engineering, Yonsei University, 134 Sinchon-dong, Seodaemun-gu, Seoul 120-749, South Korea; Fax: +82-2-365-5882; E-mail: prohsh@yonsei.ac.kr.

DOI: 10.1081/SS-200036750
0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

porous α-alumina tube with a nanoparticulate silica sol were found to be more suitable than pure α-Al_2O_3 composite supports for synthesizing crack-free membranes which have the high CO_2/N_2 separation efficiency. The N_2 permeability of organic-templated silica composite membranes synthesized was about $10^{-8}\,mol/m^2 \cdot s \cdot Pa$ and the CO_2/N_2 separation factor of the MTES-templated silica composite membranes was enhanced up to 19 at room temperature by surface-modifying the templated silica membrane with the TEOS-EtOH solution.

Key Words: Sol-gel technique; Organic-templating; SiO_2/α-Al_2O_3 composite supports; Nanoporous silica membranes; CO_2/N_2 permeability and separation factors.

INTRODUCTION

Gas separation using ceramic membranes has evolved into a commercial technology for industrially important gas separations such as CO_2/CH_4, CO_2/N_2, and O_2/N_2 in recent years. The separation/recovery process of CO_2 has been evaluated as a particularly high value-added process from the point of view of preventing environmental pollution such as the greenhouse effect. Membrane separation technology has been used extensively in various fields of separation processes because it is a simple and low-energy method compared to other processes, such as extraction, distillation, adsorption, and cryogenic processes.[1] In particular, ceramic composite membranes have higher thermal, chemical, and mechanical stabilities than those of polymeric membranes and thus have been expected to be more suitable for gas separation such as CO_2 at high temperatures under severe conditions.

Special attention has been concentrated on reducing the pore size of ceramic membranes to less than 10 Å, and also modifying their surfaces in order to enhance the CO_2/N_2 separation factor by gas transport mechanisms such as molecular sieving, activated micro-pore diffusion, and adsorption-surface diffusion. A number of research group have reported the preparation of zeolite membranes with useful selectivities for gas separation.[1–4] Despite considerable advances in synthetic procedures, the challenge of synthesizing defect free and practical zeolite membranes has not yet been achieved. On the other hand, there are several groups active in studying amorphous silica composite membranes with pore sizes comparable to those in zeolites, which could be easily fabricated.[5–8] In general, these membranes were superior to all previously reported membranes for the separation of gas mixtures including hydrocarbon, CO_2, and H_2 gases, but did not show any separation factor for CO_2/N_2 mixtures which are very difficult to be separated using membranes. Nanoporous/amorphous silica composite membranes have been also synthesized by sol-gel coating of a silica sol templated with noncovalently bonded TPABr in our laboratory, and this membrane has been shown to be highly effective for CO_2/N_2 separation.[9] However, the potential disadvantage of the template approach is that the template such as TPABr might be nonuniformly distributed and aggregated in the silica matrix, and consequently it is very difficult to make a uniform/crack-free microporous membrane. In order to successfully implement the organic template approach, Raman and Brinker suggested the strategy for the use of the template such as MTES covalently bonded with the silica matrix in detail.[10] One of the most important criteria is that the organic ligands must be uniformly incorporated in the inorganic matrix without aggregation or phase separation to avoid creating pores larger than the size of the individual ligands.

In the present study, the nanoporous silica composite membranes were synthesized by the sol-gel coating of silica sols templated with covalently bonded MTES as well as non-reacted TPABr on SiO_2/α-Al_2O_3 composite tubular supports to enhance the CO_2/N_2 separation factor. Their separation efficiency and the effect of the microstructure of supports on the gas separation efficiency were investigated. The variation of the CO_2/N_2 separation efficiency of synthetic silica membranes with silica surface modification was also examined by both the gas permeabilities of various gases and the separation factors of CO_2 over N_2 in their mixtures.

EXPERIMENTAL PROCEDURE

Preparation of MTES-Templating Silica Sol

The organic-templating silica sols were prepared from the mixture of a silica sol and an organic template MTES (methyltriethoxysilanes: 99%, Aldrich, USA) or TPABr (tetrapropylammoniumbromide: 98%, Aldrich, USA) at room temperature. Silica sols were prepared from TEOS (tetraethoxysilane: 98%, Fluka, Japan) by a two-step acid catalyzed procedure described in detail in the literature.[10] TPABr-templating silica sols were obtained by adding 6 wt% of TPABr to the silica sol with a final molar ratio of TEOS: 3.8 EtOH: 5.1 H_2O: 0.056 HCl (1 M solution), followed by aging for 6–18h at 50°C after mixing vigorously at room temperature for 6h. The final molar ratio of the MTES-templating silica sol was 0.1 MTES: 0.9 TEOS: 3.8 EtOH: 5.1 H_2O: 0.056 HCl (1 M). In general, since the hydrolysis/condensation rate of MTES is $\sim$7 times faster than that of TEOS, MTES was added after 6/7 of the normal total reaction time in the first step for inhibiting formation of more bulky polymers.[9] The above organic-templating sols were used after syringe-filtering the sols diluted with ethanol (vol ratio of sol/EtOH = 1/2). The silica-template hybrid composites were prepared by evaporating organic-templating silica sols in the polystyrene dish, and the unsupported membranes were also prepared by heating hybrid composites at 150–550°C (heating rate, 1°C/min, holding time 2h). Thermal behavior of MTES-silica hybrid composites was examined by TG/DTA (TG/DTA-92, Setaram, France) and FT-IR (JASCO FT/IR-300E Spectrometer, Japan).

Synthesis and Characterization of SiO_2 Composite Membranes

The SiO_2/α-Al_2O_3 composite supports (1.6 nm mean pore diameter) were prepared by the pressurized coating of colloidal silica sols on tubular α-Al_2O_3 supports (8 mm outside diameter, 0.8 mm thickness, 100 mm length, and 0.1 μm mean pore diameter) at 6 bar for 2h. The preparative methods of the α-Al_2O_3 supports, the colloidal sols (average particle size 16 nm), and the SiO_2/α-Al_2O_3 composite supports are given in detail in our previous papers.[11,12] The organic-templated silica composite membranes were manufactured by dip-coating (drawing rate 20 cm/min) the templating sols on the SiO_2/α-Al_2O_3 composite supports at room temperature, followed by heating to 550°C at a heating rate of 1°C/min and holding for 2h. The whole process of dip-coating, drying, and calcining was repeated several times to repair any defect in the first silica membrane layer. In order to tune the pore size, the surface of the silica composite membranes was modified by immerging the composite membrane in the TEOS-EtOH solution (vol ratio of TEOS/EtOH = 1/4) for 10 min, followed by heating to 300°C at a heating rate of 1°C/min and holding for 4h. If necessary, the surface-modification was repeatedly performed.

The microstructure of the nanoporous silica layers was observed by SEM (Hitachi, S4200, Japan). The CO_2/N_2 permselectivity (permeability ratio of pure CO_2 to N_2) and the separation factor, $Y_{CO_2}(1 - X_{CO_2})/X_{CO_2}(1 - Y_{CO_2})$, were also determined using the same apparatus and methods described in our previous papers.[1,12] The composition of the feed CO_2/N_2 mixture and the transmembrane pressure (ΔP) examined in this work were in the range of 20–50 vol% of CO_2 and 1.0–3.0 atm, respectively.

RESULTS AND DISCUSSION

MTES-Silica Hybrid Composite and Unsupported Silica Membrane

Since it is very difficult to evaluate the characteristics of a membrane layer separately in composite membranes, the characterization of the MTES-silica hybrid composites and the unsupported membranes must be performed prior to preparing composite membranes.

N_2 adsorption isotherms of the 10 mol% MTES-silica hybrid unsupported composites as a function of calcination temperature are given in Fig. 1. The hybrid composites calcined at 150°C, 400°C, and 550°C are found to be microporous from the type of N_2 adsorption isotherms. The N_2 volume adsorbed on MTES-silica hybrid composites decreased as the calcination temperature increased. This is likely due to the densification of the silica matrix at high temperature.

The TG/DTA data of the MTES-silica hybrid composites are given in Fig. 2. The weight loss occurs at 100–150°C due to continued evaporation of ethanol and water in the gel network. Between about 200°C and 400°C, the weight loss is attributed primarily to burning of residual organic materials

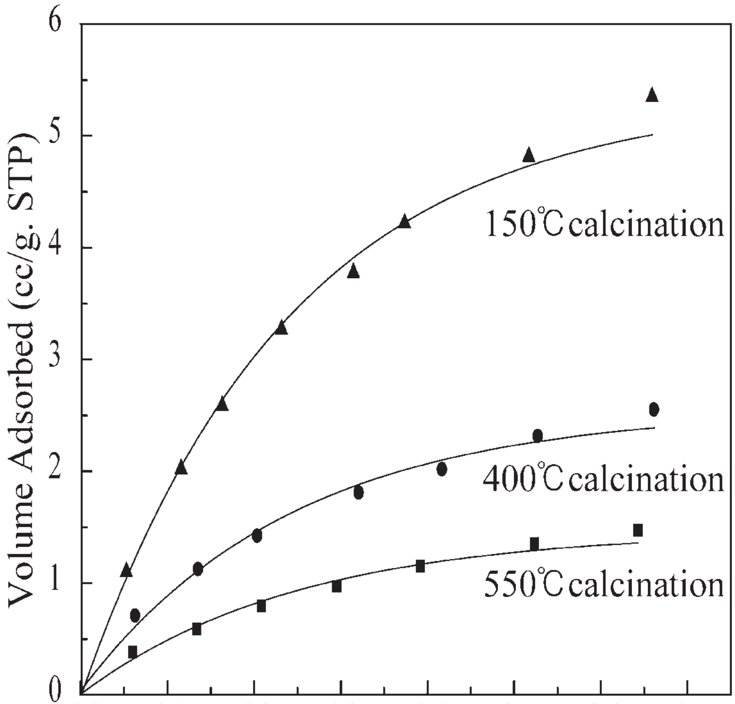

Figure 1. N_2 adsorption isotherms at room temperature of unsupported silica membranes prepared by MTES (10 mol%)-templating.

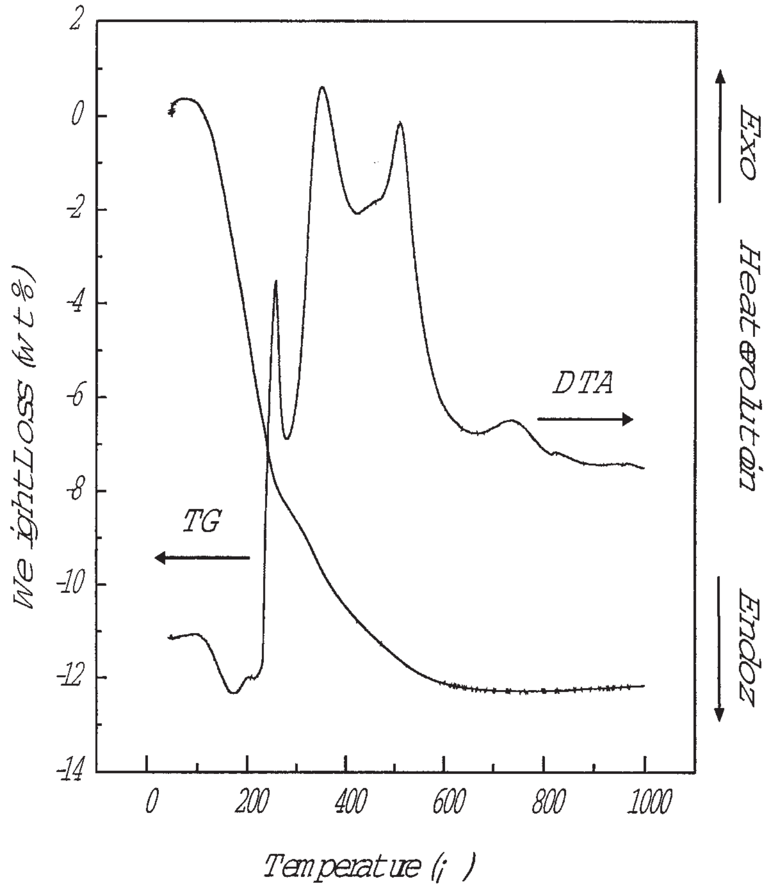

Figure 2. TG/DTA curves of the unsupported silica membrane prepared by MTES (10 mol%)-templating.

in the dried gel. The pores are finally produced by the oxidative pyrolysis of the MTES template as temperatures exceed 400°C.

The decomposition temperature of MTES is analyzed in detail by the FT-IR spectrum. As seen in Fig. 3, the —CH_2— and —CH_3— of MTES are removed mostly around 550°C but not completely removed. This could be well understood by the color change of heat-treated unsupported membranes. It was observed that the MTES-unsupported membranes heat-treated above 600°C had turned black, while the TPABr-unsupported membranes heat-treated at the same temperature remained transparent. The main reason

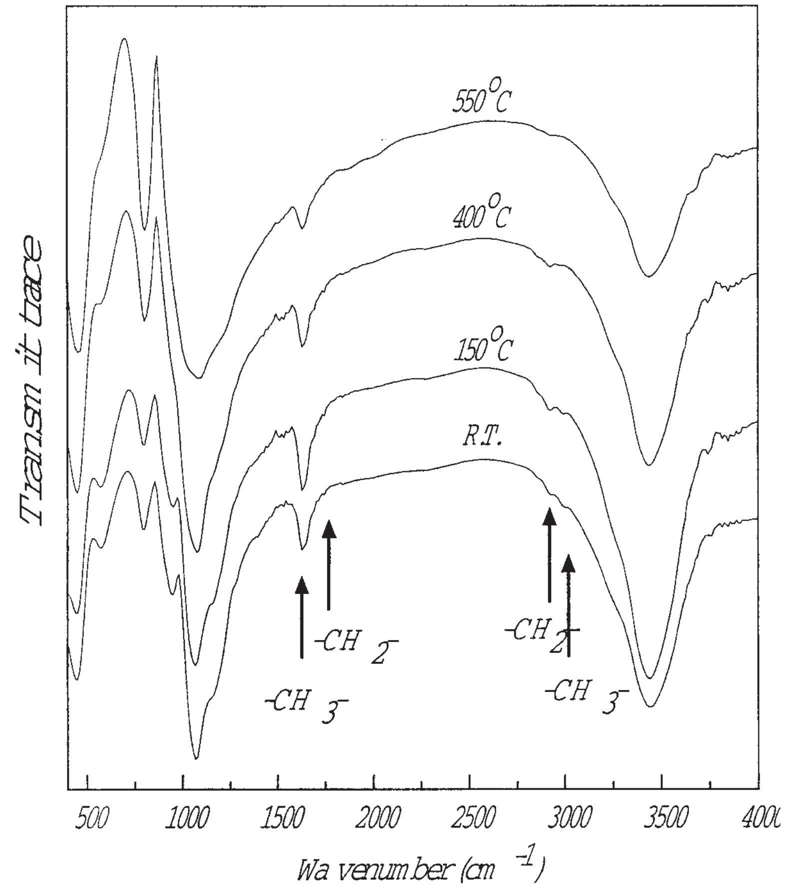

Figure 3. FT-IR spectra of the unsupported silica membrane prepared by MTES (10 mol%)-templating.

for this phenomenon is thought to come from ligands of MTES covalently bonded with TEOS that are strongly trapped within the matrix network which then leaves carbon inside after calcining.

SiO_2/α-Al_2O_3 Composite Support

SiO_2/α-Al_2O_3 composite supports having porous silica layers inside pores of the support created by a pressurized sol-gel coating (so-called pore-filled coating) technique were used in this work. A pressurized sol-gel coating technique could reduce the probability of cracking because of the discontinuity of the coating layer under stress during drying and firing, and also enhanced the adhesion force between the SiO_2 layer and the support.

Figure 4 shows the microstructure of the SiO_2/α-Al_2O_3 composite support (average pore size 1.6 nm) prepared by pressurized gel-sol coating using the colloidal silica sol. Silica layers were formed inside the support pores with an average depth of about 1.5 μm, and the imperfect thin top layer, through which the surface micro-structure of the support could be seen, could be also obtained. This type of coating was found to be well in agreement with the model of the pressuring sol-gel coating.[12]

The gas permeability data of the composite supports given in Fig. 5 proved that micro-defect did not exist in the composite supports, through which only the Knudsen flow could occur. It was concluded from these results and preliminary

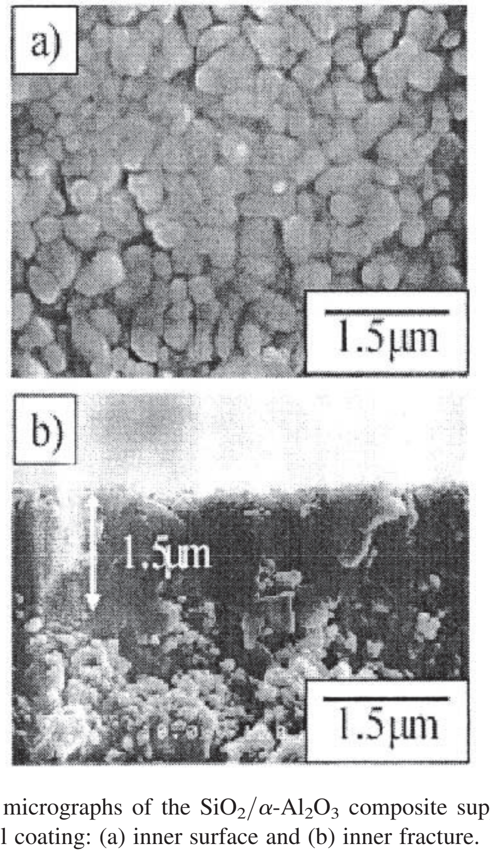

Figure 4. SEM micrographs of the SiO_2/α-Al_2O_3 composite support prepared by pressurized sol-gel coating: (a) inner surface and (b) inner fracture.

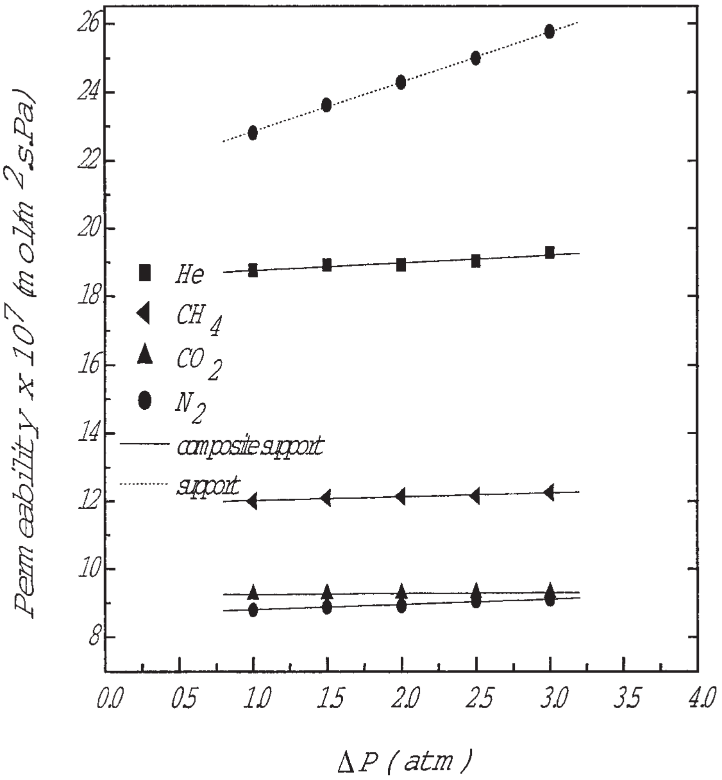

Figure 5. Gas permeabilities of the $SiO_2/\alpha\text{-}Al_2O_3$ composite support at room temperature.

coating experiments that the $SiO_2/\alpha\text{-}Al_2O_3$ composite supports were more suitable than $\alpha\text{-}Al_2O_3$ supports for defect-free sol-gel coating.

Silica Composite Membrane

Gas Permeability

To minimize defects such as cracks or pinholes in the templated silica layer, the sol-gel coating of the organic-templating silica sol on the $SiO_2/\alpha\text{-}Al_2O_3$ composite support was performed several times, and the influence of the number of coating times on N_2 permeabilities of the SiO_2 composite membranes templated by TPABr and MTES are given in Figs. 6 and 7,

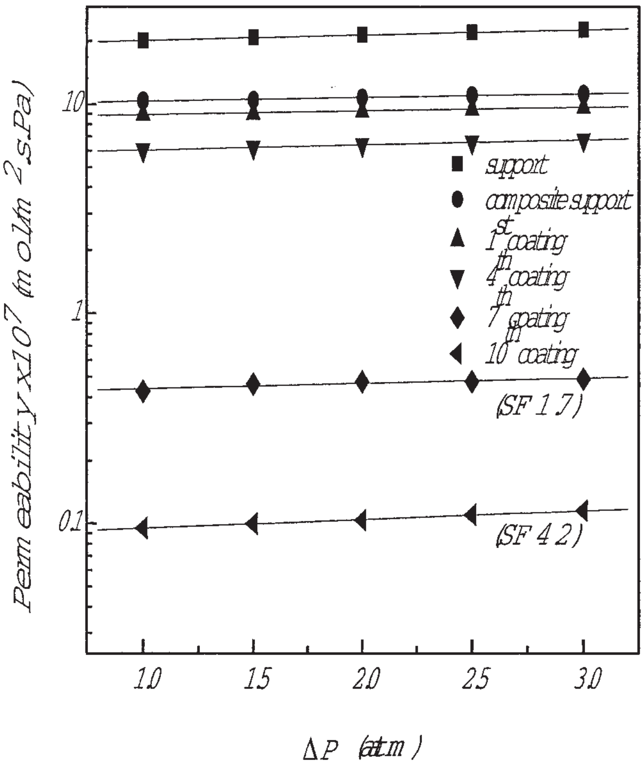

Figure 6. N_2 Permeabilities of TPABr-templated SiO_2 composite membranes on the SiO_2/α-Al_2O_3 support vs. coating time at room temperature (SF at $\Delta P = 3.0$ atm).

respectively. As the number of coating times increases, the N_2 permeabilities decrease since the thickness of the coating layer increases and the defects in the coating layer heal.

The TPABr-templated $SiO_2/SiO_2/\alpha$-Al_2O_3 composite membrane after being surface-modified with the TEOS-EtOH solution was further evaluated by the permselectivities of CO_2/N_2, He/N_2, and He/CH_4 as well as the CO_2/N_2 separation factor measured at 25°C. The permselectivities of the silica composite membranes after the 1st and 5th surface-modifications are given in Fig. 8. As seen in Fig. 8, CO_2/N_2, He/N_2, and He/CH_4 permselectivities increased from 2.4 to 6, 2.3 to 6.8, and 1.8 to 9, respectively, depending on the number of surface-modification times.

Figure 9 shows SEM pictures of silica top layers formed on the SiO_2/α-Al_2O_3 composite support. Any defect on the surface of the SiO_2 layer

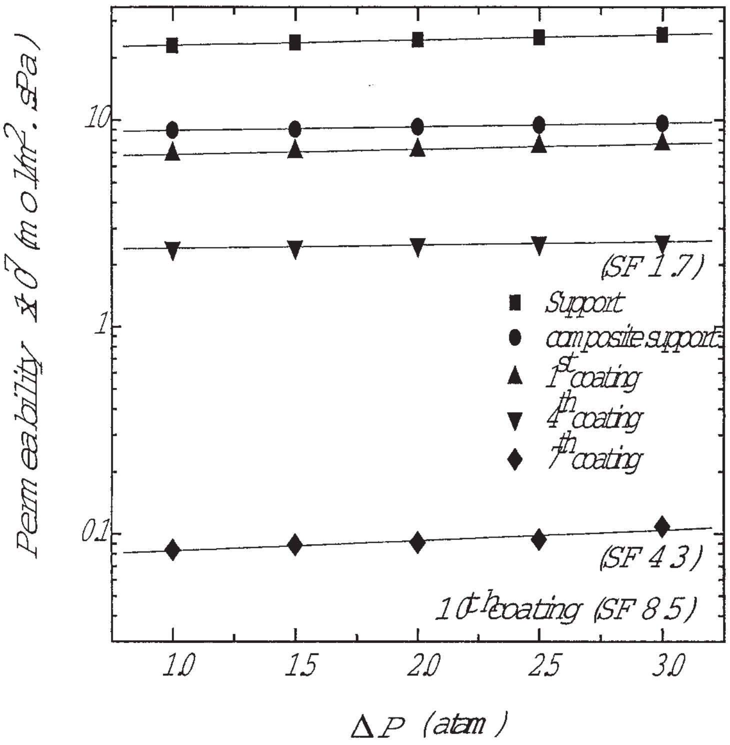

Figure 7. N_2 Permeabilities of MTES-templated SiO_2 composite membranes on the $SiO_2/\alpha\text{-}Al_2O_3$ support vs. coating time at room temperature (SF at $\Delta P = 3.0$ atm).

was not observed. Furthermore, the uniformity of the surface morphology was excellent. However, it should be noted that defect-free silica membrane layers could be more easily obtained using $SiO_2/\alpha\text{-}Al_2O_3$ composite supports as compared with the simple $\alpha\text{-}Al_2O_3$ supports. The differences between these two supports might be explained as being attributed to SiO_2 layers formed within pores of an $\alpha\text{-}Al_2O_3$ support and formed slightly on the support surface, which can control the surface morphology and reduce the probability of defect-occurrence during drying or calcining.

Separation Factor of CO_2/N_2

The effects of the number of coating and modification times on the CO_2/N_2 permselectivities and separation factor of silica composite membranes are given in Figs. 6–8 and Table 1. The CO_2/N_2 separation factor of the

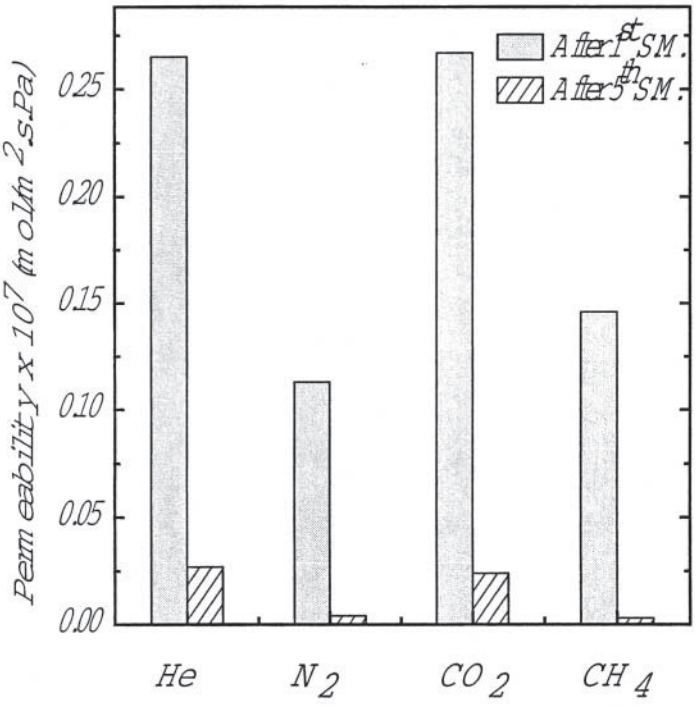

Figure 8. Various gas permeabilities of TPABr-templated silica composite membranes after 1st/5th surface-modification at 25°C and $\Delta P = 3.0$ atm.

MTES-templating composite membrane increased from 1.7 to 8.5 as the number of coating times increased from 4 to 10. However even through the number of coating times was 10, the CO_2/N_2 separation factor of more than 4.2 could not be obtained for the TPABr-templated composite membrane (Figs. 6 and 7). The CO_2/N_2 separation factor of the MTES-templating composite membrane almost doubled from 8.5 to 16.5 when the membrane surface was modified with the TEOS/EtOH solution five times, but further modification reduced the separation factor as seen in Fig. 10. The reason of this result is not clear at present. The CO_2/N_2 separation factor of TPABr-templated silica composite membranes also increased to 12.3 by surface-modifying five times.

To examine the effects of the separation process parameters on the performance of the membranes synthesized in this work, the variations of the CO_2/N_2 separation factor with transmembrane pressure (ΔP) and stage cut (θ) were measured. Figure 11 shows the representative results of the effect

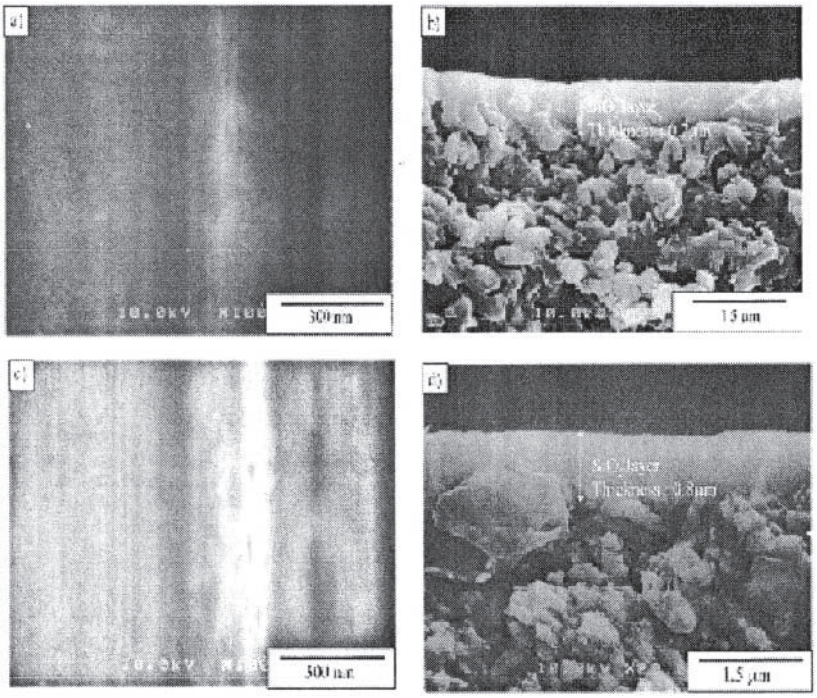

Figure 9. SEM micrographs of silica composite membranes on the SiO_2/α-Al_2O_3 composite support: (a) inner surface of MTES-templated membrane, (b) inner fracture of MTES-templated membrane, (c) inner surface of TPABr-templated membrane, and (d) inner fracture of TPABr-templated membrane.

of the transmembrane pressure for composite membrane modified with five surface coatings. The CO_2/N_2 separation factor increased with the increase of 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 and (ii) back diffusion, caused by collision between gases having different molecular weights in gas mixtures that could be reduced by increasing the transmembrane pressure.

After faster permeation of CO_2 gas by preferential adsorption and surface diffusion, N_2 gas remains in the feed gas stream. Consequently, the concentration polarization phenomenon such as an increase in the N_2 concentration on the feed side surface of the membrane or an increase in the CO_2 concentrations on the other side, could appear. This can be minimized by flowing a sweep gas into the permeate side and by reducing the stage cut, i.e., the ratio of

Table 1. Permselectivities and separation factors of silica composite membranes.

Type of membrane	N_2 Permeability ($mol/m^2 \cdot s \cdot Pa$)	CO_2/N_2 permselectivity	CO_2/N_2 separation factor
TPABr-templated			
Before modification	10^{-8}	1.89	4.2
After 5th modification	10^{-8}–10^{-9}	6.03	12.3
MTES-templated			
Before modification	10^{-8}	2.34	8.5
After 5th modification	10^{-8}–10^{-9}	—	16.5

the permeate flow rate to the retentive one. In this work, a sweep gas was not used, while the stage cut was controlled. Variation of the CO_2/N_2 separation factor with the stage cut for the silica composite membranes are shown in Fig. 12. It can be clearly observed from Fig. 12 that the smaller the stage cut the higher the CO_2/N_2 separation factor. As the stage cut decreases from 0.5 to 0.02, the CO_2/N_2 separation factors of the MTES-templated and TPABr-templated composite membranes increase from 16.5 to 18.7 and from 12.3 to 14.9, respectively.

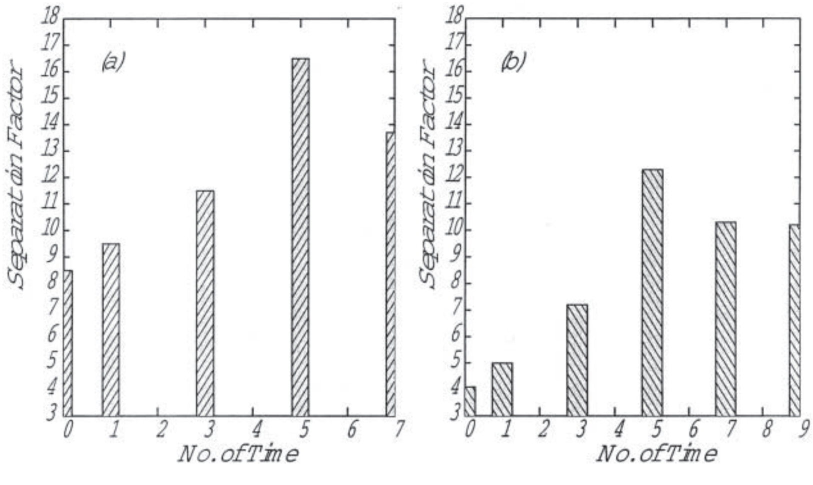

Figure 10. Variations of the CO_2/N_2 separation factor of templated silica composite membranes with a number of times of surface-modification: (a) MTES-templated and (b) TPABr-templated at 25°C and $\Delta P = 3.0$ atm.

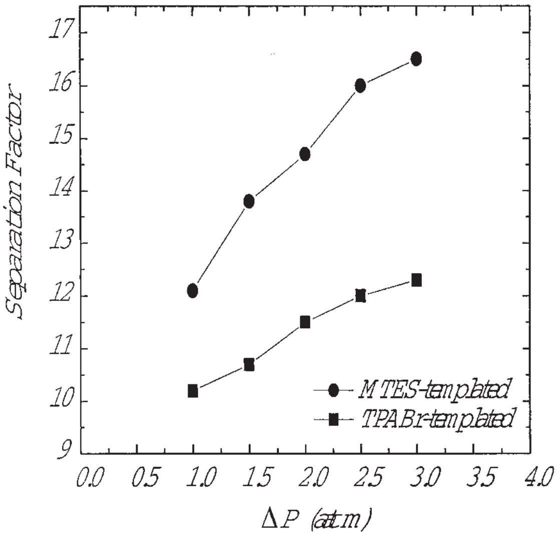

Figure 11. CO_2/N_2 separation factor vs. transmembrane pressure (ΔP) of surface-modified silica composite membranes at room temperature.

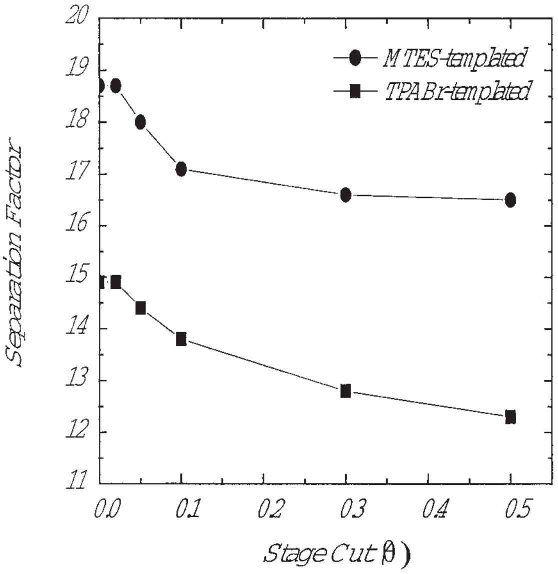

Figure 12. CO_2/N_2 separation factor vs. stage cut (θ) for surface-modified silica composite membranes.

CONCLUSIONS

Crack-free nano porous silica composite membranes could be manufactured by dip-coating (drawing rate 20 cm/min) the MTES- or TPABr silica sol with the mean particle size less than 10 nm on the $SiO_2/\alpha\text{-}Al_2O_3$ composite tubular support (average pore size 1.6 nm).

The $SiO_2/\alpha\text{-}Al_2O_3$ composite tubular supports pore-filled via pressurized sol-gel coating (coating time 2h, coating pressure 6 bar) were found to be more effective for homogenous and crack-free coating of nano particulate organic-templating silica sol than the simple $\alpha\text{-}Al_2O_3$ supports.

The CO_2/N_2 permeability and the separation factor of MTES-templated silica composite membranes were enhanced to about 10^{-8}–10^{-9} $mol/m^2 \cdot s \cdot Pa$ and 19 at room temperature, respectively, by surface-modifying the templated silica membrane with the TEOS-EtOH solution (volume ratio = 1 : 4).

ACKNOWLEDGMENT

This work was supported by grant No. R01-1999-000-00198-0 from the Basic Research Program of the Korea Science & Engineering Foundation.

REFERENCES

1. Hyun, S.H.; Song, J.K.; Kwak, B.I.; Kim, J.H.; Hong, S.A. Synthesis of ZSM-5 zeolite composite membranes for CO_2 separation. Mater. Sci. **1999**, *34* (13), 3095–3105.
2. Hasegawa, Y.; Watanabe, K.; Kusakabe, K.; Morooka, S. Influence of alkali cations on permeation properties of Y-type zeolite membranes. J. Membr. Sci. **2002**, *208* (1–2), 415–418.
3. Kwak, B.I.; Hyun, S.H.; Kim, G.T. CO_2 separation characteristics of ZSM-5 composite membranes synthesized by the hydrothermal treatment. Mater. Sci. Lett. **2001**, *20* (20), 1893–1896.
4. Bonhomme, F.; Welk, M.E.; Nenoff, T.M. CO_2 selectivity and lifetimes of high silica ZSM-5 membranes. Micropore Mesopore Mat. **2003**, *66* (2–3), 181–188.
5. De Vos, R.M.; Verweij, H. Improved performance of silica membranes for gas separation. Membr. Sci. **1998**, *143* (1–2), 37–51.
6. Tasi, C.-Y.; Tam, S.-Y.; Lu, Y.; Brinker, C.J. Dual-layer asymmetric microporous silica membranes. Membr. Sci. **2000**, *169* (2), 255–268.

7. Diniz Da Costa, J.C.; Lu, G.Q.; Rudolph, V.; Lin, Y.S. Novel molecular sieve silica (MSS) membranes: characterization and permeation of single-step and two-step sol-gel membranes. Membr. Sci. **2002**, *198* (1), 9–21.
8. Giessler, S.; Jordan, L.; Diniz Da Costa, J.C.; Lu, G.Q. (Max). Performance of hydrophobic and hydrophilic silica membrane reactors for the water gas shift reaction. Sep. Purif. Technol. **2003**, *32* (1–2), 255–264.
9. Yang, S.M.; Lee, Y.E.; Hyun, S.H.; Lee, C.H. Organic-templating approach to synthesis of nanoporous silica composite membranes(I): TPA-templating and CO_2 separation. Mater. Sci. **2002**, *37* (12), 2519–2525.
10. Raman, N.K.; Brinker, C.J. Organic "template" approach to molecular sieving silica membranes. J. Membr. Sci. **1995**, *105* (3), 273–279.
11. Hyun, S.H.; Jo, S.Y.; Kang, B.S. Surface modification of γ-alumina membranes by silane coupling for CO_2 separation. Membr. Sci. **1996**, *120* (2), 197–206.
12. Hyun, S.H.; Kang, B.S. Synthesis of nanoparticulate silica composite membranes by the pressurized sol-gel technique. Am. Ceram. Soc. **1994**, *77* (12), 3093–3098.

Received April 2004
Accepted July 2004