Synthesis of ZSM-5 zeolite composite membranes for CO$_2$ separation

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ZSM-5 type zeolites were synthesized by the hydrothermal treatment of the reaction mixture of silica sol, aluminum nitrate, sodium hydroxide, and TPABr at the temperature range of 150–180 °C in the autoclave. The shape of the ZSM-5 zeolite calcined at 450 °C was spherical or polyhedral and its crystalline size was 0.5–3 μm. The synthetic ZSM-5 was found to be highly hydrophobic and active for CO$_2$ adsorption. ZSM-5 zeolite composite membranes supported with porous α-alumina tubes have been synthesized by dip coating or pressurized coating of the reaction sol-mixture followed by hydrothermal treatment. The permeation mechanism of CO$_2$ through ZSM-5 membranes was a surface diffusion and the membranes prepared by the pressurized-coating hydrothermal treatment showed a fairly high CO$_2$/N$_2$ separation factor of 9.0 and a permeability of 10^{-8}–10^{-7} mol/m^2·s·Pa at room temperature. © *1999 Kluwer Academic Publishers*

1. Introduction

The ceramic composite membrane has been getting more attention and is being rapidly developed for the application of CO$_2$ separation/recovery in recent years. This is due to the worldwide restrictions against emission of CO$_2$ gas which causes the green-house effect. A 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 [1]. In particular, ceramic membranes have higher thermal, chemical, and biological stability and greater mechanical strength and regenerability than polymeric membranes, and thus are suitable for CO$_2$ separation in severe conditions. However, most existing ceramic membranes have failed to achieve high gas separation efficiency, because their separation mechanism has been mainly Knudsen diffusion [1, 2]. Many researchers have tried to reduce the pore size of ceramic membranes to less than 10 Å and also to modify their surfaces in order to enhance the CO$_2$/N$_2$ separation factor by gas transport mechanisms such as molecular sieving, activated diffusion, and surface diffusion instead of Knudsen diffusion. Research on the synthesis of microporous ceramic membranes and the enhancement of the CO$_2$ separation efficiency by silane coupling has also been done in our laboratory [3–6].

Special attention has been concentrated on ZSM-5 zeolite composite membranes for gas separation because of their very small and uniform pore structures and their strong hydrophobicity which is expected to prevent the decline in gas permeability due to moisture adsorption. Although many studies have been done on ZSM-5 crystals, their applications for membranes have not been much studied until recently [7–12].

Jia *et al.* [7] and Bai *et al.* [8] synthesized silicalite composite membranes using the hydrothermal treatment and obtained good separation factors for organic hydrocarbon vapors. Their synthetic process, however, was very complex and selectivities obtained for H$_2$, N$_2$, and He gases were quite low. The CO$_2$/N$_2$ permselectivity (ratio of single gas permeabilities) through ZSM-5 zeolite composite membranes synthesized by Yan *et al.* [9] was only 2.8 and their CO$_2$ permeability was also as low as 8.8×10^{-8} mol/m^2·s·Pa. Kusakabe *et al.* [10] synthesized ZSM-5 tubular composite membranes which showed a fairly high CO$_2$/N$_2$ permselectivity of 5–7, but they did not measure the separation factor for the gas mixture of CO$_2$ and N$_2$. Yan *et al.* [11] tried to improve the separation efficiency of ZSM-5 zeolite membranes using a post-synthetic coking treatment, but the reduction of gas permeation due to pore-blocking was too large to be used in practical applications. Most recently, ZSM-5 tubular

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membranes prepared by Coronas *et al.* [12] showed very high permselectivities for the mixtures of H_2/N_2 and hydrocarbons like butane, while not separating CO_2 and N_2 mixtures at all.

In this paper, the ZSM-5 zeolite composite membranes have been synthesized using a hydrothermal treatment of porous α-alumina tubes coated with the reaction sol-mixture which was optimized for making ZSM-5 crystals. The CO_2 separation efficiency of synthetic zeolite membranes has been evaluated through measuring and examining both the gas permeabilities of various gases and the separation factors of CO_2 to N_2 in their mixtures. The effect of process parameters on the CO_2 separation using zeolite membranes is also discussed.

2. Experimental
2.1. Synthesis of ZSM-5 crystals
The reaction sol-mixture (simply sol-mixture) for synthesis of ZSM-5 crystals and ZSM-5 composite membranes was prepared from the following components: sodium hydroxide (95%, Tedia Co.), aluminum hydroxide (98%, Junsei Chemical), colloidal silica sol (0.4 mol/1) being synthesized in our laboratory [3] by an interfacial hydrolysis reaction between TEOS (98%, Fluka) and high alkaline water, and TPABr (98%, Aldrich Co.) as a template. There were two methods for the preparation procedure of the sol-mixtures:

1. Sodium hydroxide and aluminum nitrate were completely dissolved in a colloidal silica sol, which was mixed with the template TPABr (method MM-1).
2. The colloidal silica sol was added in the solution of sodium hydroxide and aluminum nitrate, and then TPABr was added (method MM-2).

The compostion (mole ratio) of the mixed sol used in this work was $1.3Na_2O \cdot 10SiO_2 \cdot 0.1Al_2O_3 \cdot (500–1400)H_2O \cdot (0.5–2.5)(TPA)_2O$. These mixtures were aged for more than 2 d before they were hydrothermally treated. ZSM-5 crystallization was carried out in a 120 ml pressure vessel of an autoclave type at a temperature range of 150–180 °C for 12–48 h. As-synthesized ZSM-5 crystals were washed with DI water, filtered, dried at 150 °C, and calcined at 450 °C. The morphology and phase of ZSM-5 crystals were analyzed by SEM (H600, Hitachi) and XRD (PW1720, Philips). To examine the surface property of ZSM-5 over moisture, the amounts of water vapor adsorption on ZSM-5 and commercial 5A (Yakuri Pure Chemicals Co.) zeolites known as hydrophilic were measured at 30 °C and 35% relative humidity. The specific surface area and the isotherms of CO_2, O_2, and N_2 at room temperature were measured using BET apparatus (Gemini 2375, Micromeritics).

2.2. Synthesis of ZSM-5 composite membranes
ZSM-5 composite membranes were synthesized as a tubular type by coating the support tube with the sol-mixture, and then hydrothermally treating them. The porous support tubes (OD = 8 mm, thickness = 0.8 mm) were fabricated by the usual slip-casting procedure using a slurry of α-alumina powder (AES-11, Sumitomo Co.). The details for the preparation of α-alumina tubes (0.1 μm average pore size and 35% porosity) were given in our previous paper [3].

The sol-mixture of 0.4 mol/l SiO_2 was selected to be suitable for synthesizing ZSM-5 composite membranes from the result of the shape and size of ZSM-5 crystals. Especially, the mole ratio of SiO_2/TPABr was changed in the range of 1/0.1–1/0.5 to examine the influence of the TPABr amount on microstructures and gas permeation characteristics of ZSM-5 composite membranes. The ZSM-5 composite membranes were prepared by both of the two methods of dip coating-hydrothermal treatment (DH) and pressurized coating-hydrothermal treatment (PH).

2.2.1. Dip coating-hydrothermal treatment
The sol-mixture was transferred to a pressure vessel (140 ml) of an autoclave. The α-alumina support consisting of porous and dense parts was then immersed in the sol-mixture. The formation of the ZSM-5 zeolite layers on the support was carried out for 40 h–5 d in the autoclave at 180 °C under autogeneous pressure. After hydrothermal treatment, ZSM-5 composite membranes were taken out, washed thoroughly with DI water, dried at 150 °C, and finally calcined.

The organic amine (TPABr) in the sol-mixture serves as a template for zeolite growth, and remains in channels of ZSM-5 crystals. In order to remove TPABr inside pores and to make pore channels open fully, the membrane was calcined in air at 450 °C for 12 h. The calcination was carefully controlled to avoid cracking due to decomposition and removal of process organics including TPABr and due to irregular stress on the crystal lattice coinciding with Hoffman degradation of TPABr [13]. XRD was used to determine whether the synthesized layer of the composite membrane was ZSM-5 or not. The morphology of the composite membrane, compactness among ZSM-5 crystals, and adhesion between ZSM-5 crystals and the α-alumina support were observed by SEM.

2.2.2. Pressurized coating-hydrothermal treatment
The pressurized coating technique developed in our laboratory [3, 4] was applied to produce a zeolite composite membrane in which the degree of gas-tightening could be promoted by the increment of compactness among the ZSM-5 crystal layers deposited inside pores of the support as well as on its surface. ZSM-5 composite membranes were first fabricated by introducing the sol-mixture inside the support tube, followed by pressurization at 250 kPa for 30 min. The conditions of hydrothermal treatment, washing, drying, and calcination were the same as those in the DH method.
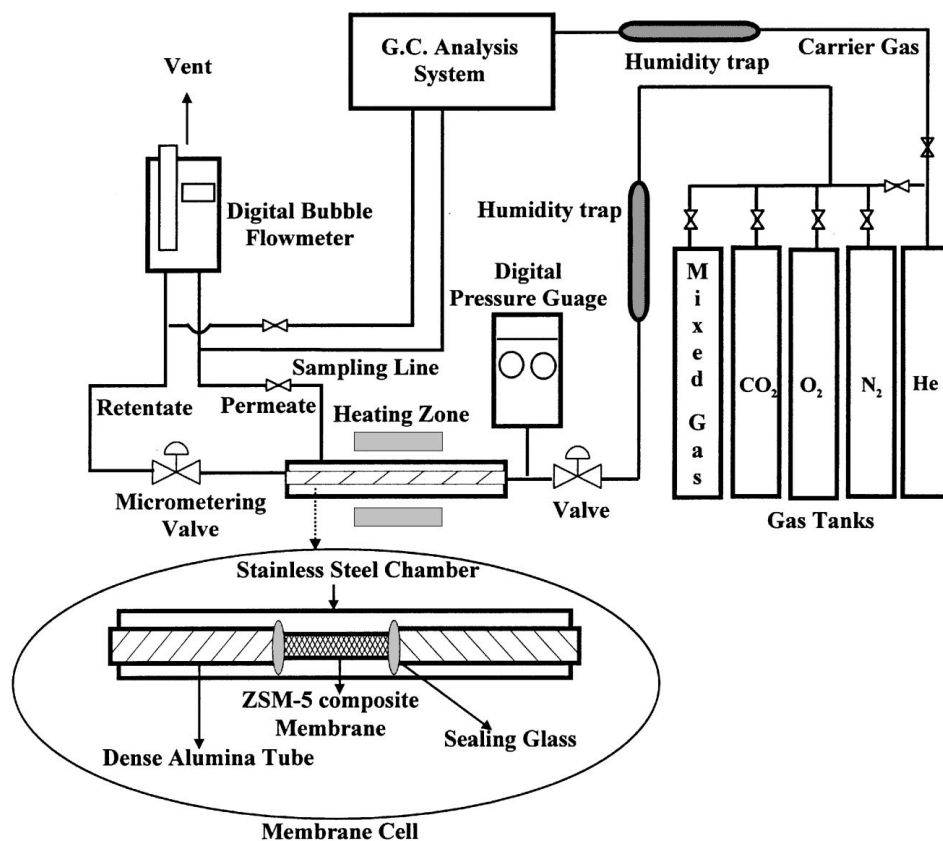
Figure 1 Schematic diagram of the gas permeability measurement apparatus including the membrane cell.

2.3. Gas permeability/separation factor measurements

The gas permeability and the separation factor were determined using an apparatus for gas permeation measurements coupled with a gas chromatograph as shown in Fig. 1. Each end of the membrane, installed inside the membrane cell system, was connected to a dense alumina tube (ID = 8 mm) which was fabricated by the same procedure as in the case of the porous support tubes and sintered at 1550 °C. The connection was completely done using a sealing glass and the length of the actual permeating part was 40 mm.

The gas-tightening among zeolite crystals deposited in the porous support has been well known to be the most important factor which determines gas permeation and separation characteristics of synthetic zeolite membranes. In particular, the key in synthesizing ideal zeolite composite membranes lies in making the intercrystalline phase perfectly gas-tightening or non-porous. In real zeolite membranes, however, both intracrystalline pores and intercrystalline voids might always exist. If the size of the latter is larger than that of the former, gases move mainly through pores larger than zeolite pore openings (e.g., about 6 Å of ZSM-5), and consequently a high separation efficiency can not be expected. In previous literature [7–12], the exact criterion of gas-tightening has not yet been established and is somewhat arbitrary, depending on researchers. A particular value of the N_2 permeability at room temperature before calcining membranes is usually chosen as a required gas-tightening criterion. By the same token, the nitrogen permeability through the membrane layer only, which is below 10^{-8} mol/m²·s·Pa before

calcining, was selected in this work as the criterion of gas-tightening.

The existence of cracking in the entire membrane tube was examined by the pressure dependency of permeabilities of inert gas through the membrane layer only at room temperature as described by Hyun *et al.* [3,14]. Single gas permeabilities of N_2, O_2, He, and CO_2 were measured, and the CO_2/N_2 permselectivity (PS) was determined from the ratio of sigle gas permeabilities. The separation factor of CO_2 to N_2 (SF), $Y_{CO_2}(1-X_{CO_2})/X_{CO_2}(1-Y_{CO_2})$, was determined by analyzing the compositions of feed (X_{CO_2}) and permeate (Y_{CO_2}) gas mixtures using a gas chromatograph after the equilibrium state between feed and permeate gas phases was established. Helium was used as a carrier gas, and the sampling loop was installed in the chromatograph for automatic injection of a gas sample. The variations of the separation factor according to the feed composition, temperature, pressure, and the stage cut (θ) which was defined as the volume ratio of permeate to retentate were measured.

3. Results and discussion
3.1. ZSM-5 crystals

The morphology variations of ZSM-5 crystals with synthetic conditions were observed by SEM in order to select the optimum conditions for making the composite membrane in which zeolite crystals were embedded on/in a porous support. Fig. 2 shows two distinct types (hexagonal plate or spherical) of zeolite crystals after being calcined at 450 °C depending on concentrations of silica sol, mixing methods of the
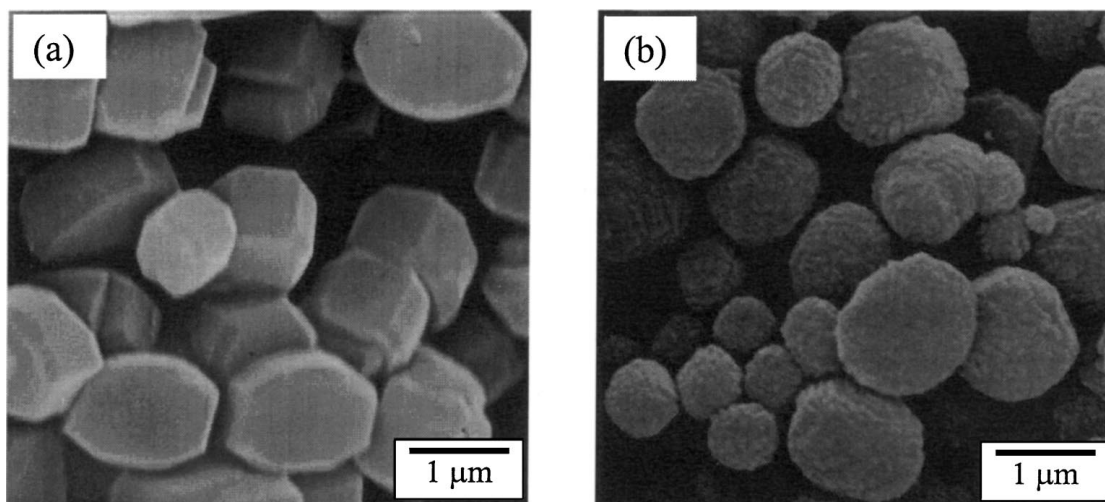
Figure 2 SEM micrographs of ZSM-5 zeolites calcined at 450 °C: (a) synthesized at 170 °C for 18 h from the sol (0.6 mol/l SiO$_2$)-mixture prepared by the MM-1 method and (b) at 170 °C for 24 h from the sol (0.4 mol/l SiO$_2$)-mixture by the MM-2 method.

TABLE I Specific surface area and water vapor adsorption of zeolites

Zeolite type	Surface area (m^2/g)	Total pore volume (cm^3/g)	Water vapor adsorption[b] (wt%)
ZSM-5	360	0.1981	3
Molecular sieve 5A[a]	300	0.1896	13

[a]Commercial molecular sieve 5A pellets (Yakuri Pure Chemicals Co.).
[b]Values at 30 °C and 35% relative humidity.

sol-mixture, and hydrothermal treatment temperatures. It was known that ZSM-5 crystals of Fig. 2b, hydrothermally synthesized at 160 °C for 24 h from the dilute silica sol (0.4 mol/l SiO$_2$)-mixture mixed by the MM-2 method, are more desirable because of their small sizes (0.5–3 μm) and spherical shapes. Therefore, the synthesis of ZSM-5 zeolite composite membranes in this study was tried on the basis of these conditions.

Since the surface property of membrane materials has been considered an important factor influencing the gas permeation and separation efficiency, the adsorption amounts of water vapor, CO$_2$, N$_2$, and O$_2$ were measured. As shown in Table I, even though ZSM-5 zeolites had high specific surface areas of about 360 m^2/g, they adsorbed very small amounts of water vapor (3 wt %), compared with commercial Molecular Sieve 5A of 13 wt % adsorption and 300 m^2/g specific surface area. This result means that ZSM-5 zeolite surfaces are much more hydrophobic than those of Molecular Sieve 5A. The surface hydrophobicity prevents water vapor/moisture from condensing into pores, and enhances gas permeabilities as well as gas separation efficiencies, particularly in the low temperature region. The adsorption amount of CO$_2$ at room temperature and 1 bar (50 cm^3 STP/g) was about ten times as much as those of N$_2$ and O$_2$, and the isotherm slope for CO$_2$ over the entire pressure range was larger than those of other gases. From the above results, if the separation mechanism of CO$_2$ from gas mixtures like combustion gases is an adsorption-surface diffusion, ZSM-5 zeolites are expected to be a suitable membrane material for CO$_2$ separation.
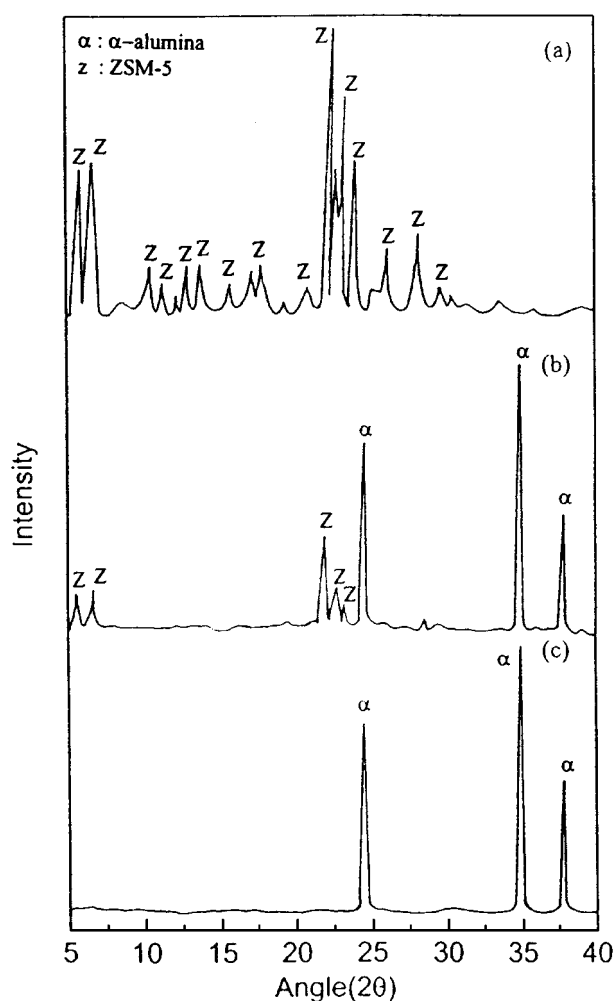

Figure 3 XRD patterns of (a) ZSM-5 crystal, (b) ZSM-5 composite membrane, and (c) α-alumina.

3.2. ZSM-5 composite membranes
3.2.1. Membranes by dip coating-hydrothermal treatment
3.2.1.1. Synthesis and microstructures. The phases of the ZSM-5 zeolite composite membrane synthesized by the DH method was analyzed by XRD as shown in Fig. 3, in which XRD patterns of ZSM-5 crystals and
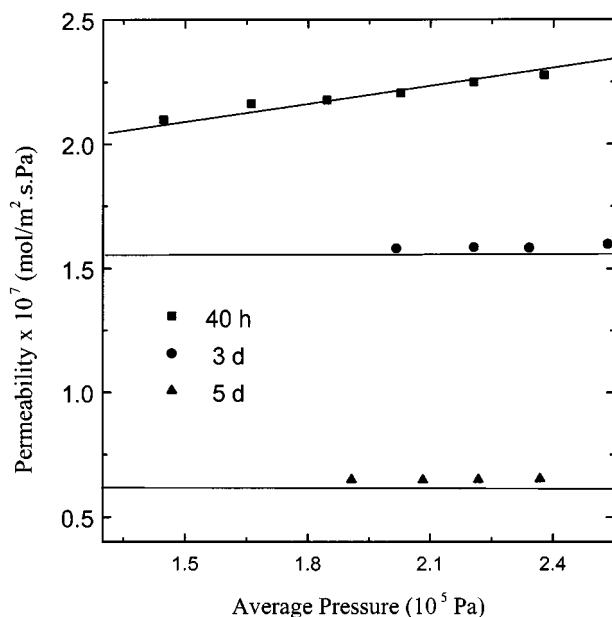
Figure 4 N_2 permeabilities of ZSM-5 membrane layers prepared by the DH method with different hydrothermal treatment times.

Figure 5 N_2 permeabilities of ZSM-5 membrane layers prepared by the DH method (180 °C, 3 h) with different TPABr concentrations.

Figure 6 N_2 permeabilities of ZSM-5 membrane layers prepared by the DH method with different calcining conditions: (a) fast calcining, (b) slow calcining, and (c) before calcining (solid line: N_2 permeability and dotted line: calcining route).

α-alumina were also given for comparison. The XRD pattern for the composite membrane of Fig. 3b indicates the coexistence of ZSM-5 and α-alumina phases, which means the formation of ZSM-5 crystals in the porous alumina support, and the same result was observed in the membrane synthesized by the PH method.

The criterion of gas-tightening through the composite membrane was chosen in this study as a N_2 permeability less than 10^{-8} mol/m^2·s·Pa. before calcining. However, the N_2 permeabilities of composite membranes synthesized by DH and PH methods before calcining were about 10^{-8} mol/m^2·s·Pa and 10^{-9} mol/m^2·s·Pa, respectively, which were found to be low enough to satisfy the gas-tightening criterion. Hereafter, the gas permeabilities mentioned in this paper will be those only through membranes calcined at 450 °C for 12 h.

Fig. 4 shows N_2 permeabilities through ZSM-5 membrane layers only in composite membranes synthesized with different hydrothermal treatment times by the DH method. The pressure dependency of N_2 permeation in the case of 40 h can be explained by loose compaction of crystals in the membrane layer because the treatment time for crystallization is too short for many ZSM-5 crystals to be formed. The defect-free layers in the whole tube could be synthesized when hydrothermal-treating longer than 3 d as shown in Fig. 4a and b which showed Knudsen flow only. Considering the separation efficiency of the membrane, the treatment for 3 d is preferable to 5 d because of considerable reduction in the permeability.

The variations of N_2 pemeabilities through the membrane layer with the amount of TPABr in the sol-mixtures are given in Fig. 5. Only when 1/0.3 mol ratio of SiO_2/TPABr being used, the defect-free composite membrane could be obtained. On the other hand, when sol-mixtures with mole ratios of 1/0.1 and 1/0.5 were used, N_2 permeabilities show pressure dependency (viscous flow) which resulted from the existence of de-
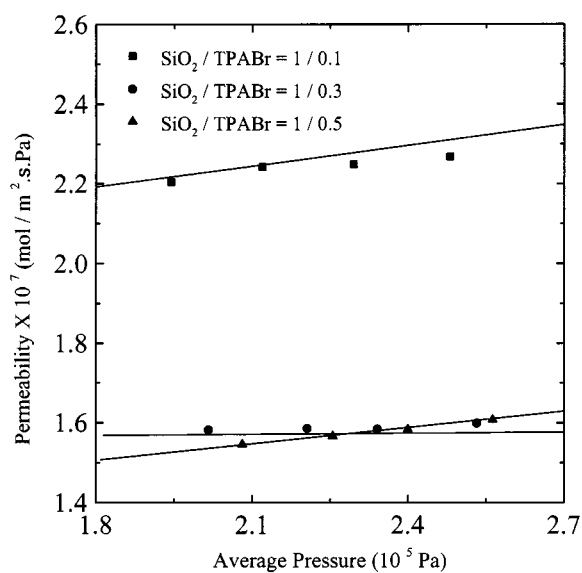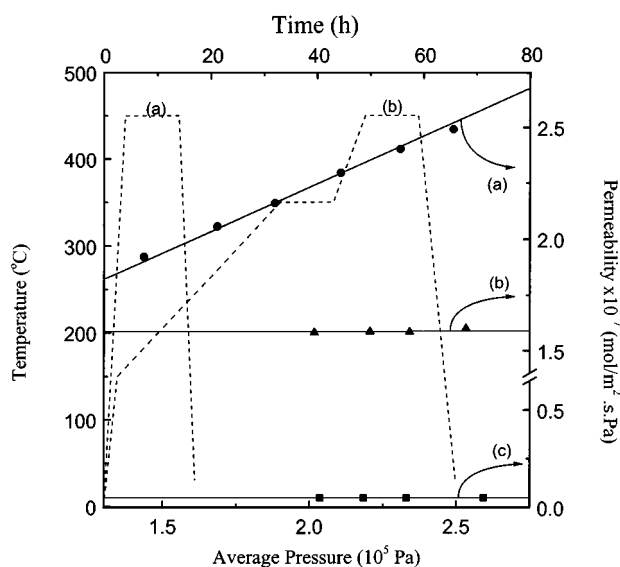
fects or large intercrystalline voids in ZSM-5 membrane layers. The amount of TPABr added as a template, if not enough, leads easily to large intercrystalline voids or cracks caused by incompletion of ZSM-5 crystallization, while the excess amount of TPABr filled between crystals also leaves defects or large voids after calcining.

In order to examine the effect of the calcination condition on microstructures of the membrane layer, N_2 permeabilities of the membrane synthesized by the DH method were measured as given in Fig. 6. The defect-free membrane was observed to be formed via slow calcining represented by the heating schedule (b).

Fig. 7 shows SEM micrographs of inner and fracture surfaces of the ZSM-5 composite membrane synthesized by the DH method with the optimum conditions mentioned above. It is reconfirmed that the membrane
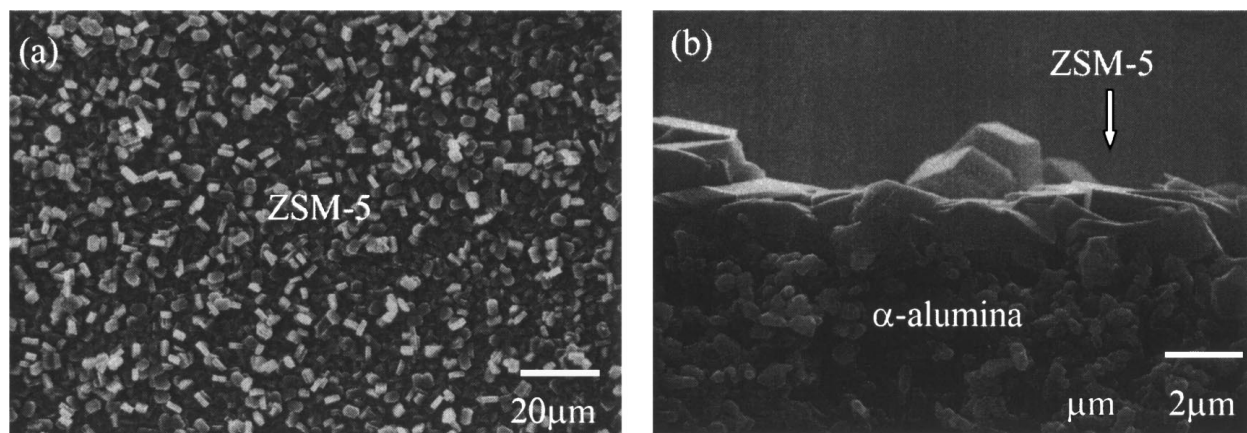
Figure 7 SEM micrographs of the ZSM-5 composite membrane prepared by the DH method: (a) inner and (b) fracture surfaces.
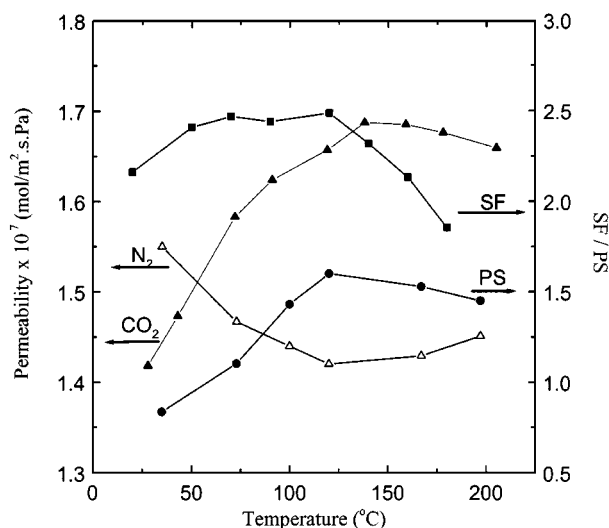

Figure 8 Gas permeabilities, CO_2/N_2 separation factors, and permselectivities of the ZSM-5 composite membrane prepared by the DH method as a function of measurement temperature.

layer consisted of uniform ZSM-5 crystals is formed as a top layer tightly adhered to the support.

3.2.1.2. CO₂ separation efficiency. For evaluating the CO_2 separation efficiency of ZSM-5 composite membranes by the DH method, single gas permeabilities, permselectivities, and separation factors of CO_2 and N_2 gases were measured and are given in Fig. 8. The permeability of the mixed gas (X_{CO_2} in feed $= 50\%$) at room temperature was about 1.23×10^{-7} mol/m^2·s·Pa, slightly smaller than that of N_2 or CO_2, and the separation factor of CO_2 to N_2 was 2.1, much higher than the Knudesen ideal separation factor of 0.8. The permeation mechanism of N_2 is considered to change from Knudsen flow to activated diffusion at about 130 °C.

The N_2 permeability decreases in proportion to $T^{-1/2}$ up to 130 °C, but above 130 °C increases with temperature. This temperature effect on the N_2 permeability could be explained by both of the increase of the mean free path of N_2 with temperature and the predominance of activated diffusion instead of Knudsen diffusion above 130 °C. However, the permeation behavior of CO_2 depending on temperature is just the opposite to the case of N_2. As can be expected, this

might result from the fact that CO_2 gas moves through the membrane by the adsorption and surface diffusion process along the pore wall. In general, the mobility of CO_2 adsorbed on the pore wall of the membrane increases with temperature, but the adsorption amount of CO_2 decreases. Consequently, there might exist a particular temperature at which the rate of surface diffusion is maximum. The separation factor (2.5) and the permselectivity (1.7) for CO_2/N_2 show the most high values at 120 °C. The higher values of separation factors than those of permselectivities as shown in Fig. 8 are attributed to the decrement of N_2 permeability in the case of mixed gases because of reduction of the effective pore radius caused by adsorption of CO_2 on the pore wall. The mechanism of CO_2/N_2 separation in the ZSM-5 composite membrane synthesized by the DH method was considered to be a surface diffusion of CO_2 in conjunction with Knudsen diffusion of N_2.

3.2.2. Membranes by pressurized coating-hydrothermal treatment

3.2.2.1. Synthesis and microstructures. To enhance the gas-tightening by forming the ZSM-5 crystal layers inside the pore of α-alumina, the pressurized coating [3, 4] was first done for 30 min at 250 kPa and followed by the hydrothermal treatment using the sol-mixture of an optimal composition selected in the DH method. The final composite membranes were produced via calcining membranes including TPABr up to 450 °C at the same heating schedule as in the DH method. The overall procedure described above will be abbreviated in this paper to the PH method as distinct from the DH method. The variations of N_2 permeabilities at room temperature with hydrothermal treatment time and measurement pressure are shown in Fig. 9. A low N_2 permeability of about 10^{-9} mol/m^2·s·Pa before calcining and Knudsen diffusion through ZSM-5 membrane layers calcined at 450 °C for 12 h proved that defect-free composite membranes could be obtained by the PH method even though the hydrothermal treatment time was as short as 40 h in contrast to the case by the DH method (see Fig. 4). On the other hand, as the hydrothermal treatment time increased, the gas permeability decreased below 10^{-7} mol/m^2·s·Pa which is too low for practical

applications. Thus, all ZSM-5 composite membranes prepared by the PH method in this work were based on the treatment time of 40 h.

Fig. 10 shows the SEM micrographs of the ZSM-5 composite membrane prepared by the PH method. Comparing the inner surface of Fig. 10a with that synthesized by the DH method in Fig. 7a, the former is more rough and consists of larger cystals. The reason might be that the abrupt crystallization of ZSM-5 occurred on the high concentration region, i.e., the inner surface and
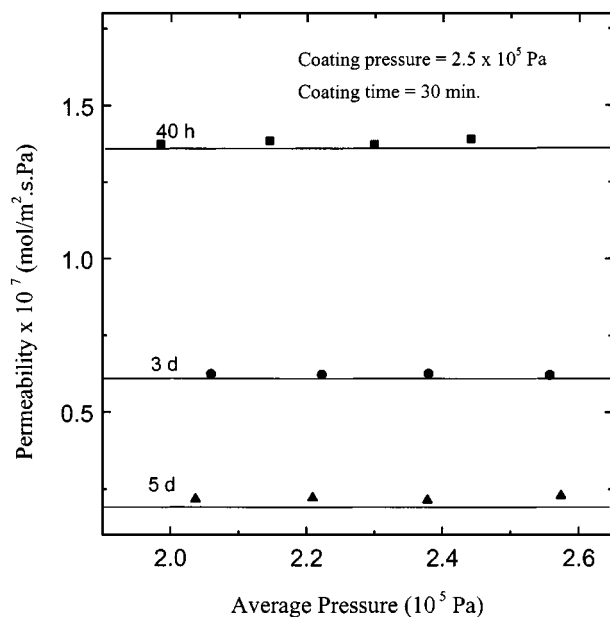

Figure 9 N_2 permeabilities of ZSM-5 membrane layers prepared by the PH method with different hydrothermal treatment times.

pores already coated with the reaction sol-mixture via pressurized-coating before hydrothermally treating in the sol-mixture solution. This could be also confirmed from the fact that the morphology of the outer surface simply coming into contact with the dipping solution is very similar to that of the inner surface prepared by the DH method. In zeolite composite membranes, it determines the gas-tightening whether the aperture among ZSM-5 crystals is formed or not. The smaller the aperture, the higher the separation efficiency of zeolite composite membranes. The separation efficiency of zeolite membranes, however, is remarkably degraded when the size of apertures is large enough to play a role as a defect. As can be seen in Fig. 10c and d, ZSM-5 crystals are not perfectly and closely packed in the top-layer. However, since an intermediate layer in which ZSM-5 crystals are tightly adhered to α-alumina is formed inside the pores of the support, it can be expected that the ZSM-5 composite membrane synthesized by the PH method will show a high separation efficiency of CO_2/N_2.

3.2.2.2. CO_2 separation from CO_2/N_2 mixtures. To evaluate the CO_2/N_2 separation efficiency of ZSM-5 composite membranes prepared by the PH method, separation factors and mixed gas permeabilities according to the stage cut (θ) were first measured at room temperature for the feed gas containing 50% CO_2 as shown in Fig. 11. As the stage cut decreases from 0.37 to 0.03, the CO_2/N_2 separation factor increases from 5.4 to 9.0 and the mixed gas permeability also increases concurrently. The effects of the stage cut on them can be explained by the concentration polarization of N_2 at the pore entrance. In the case of high stage cuts, nitrogen which
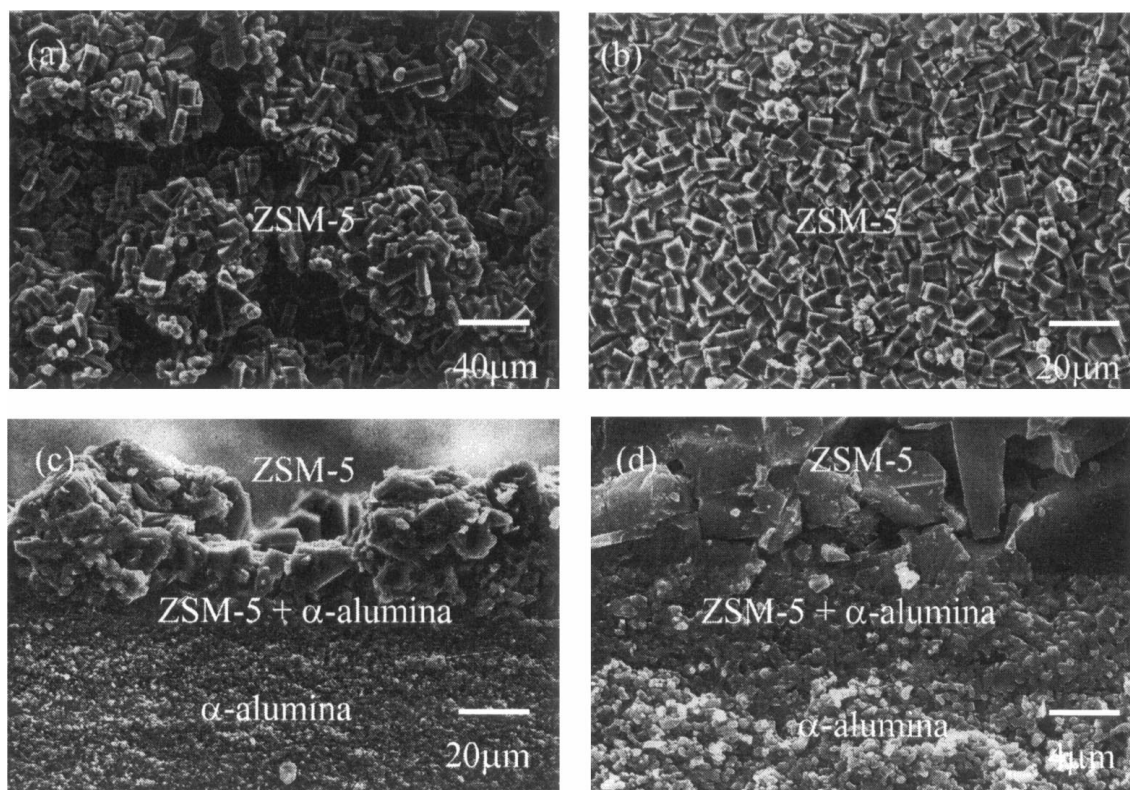

Figure 10 SEM micrographs of the ZSM-5 composite membrane prepared by the PH method: (a) inner, (b) outer, (c) fracture (low resolution), and (d) fracture (high resolution) surfaces.
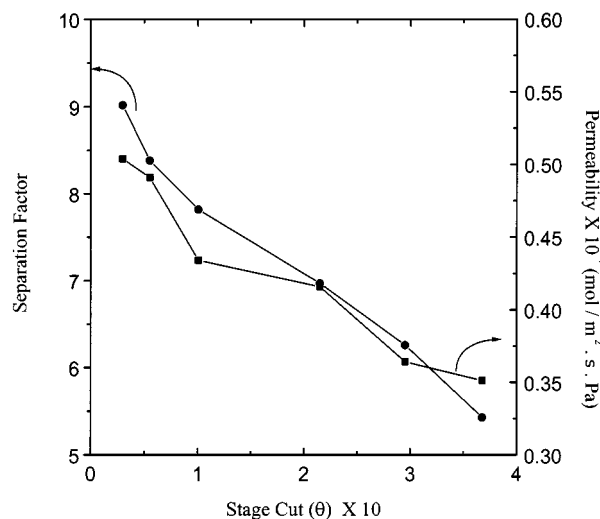
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Figure 11 CO_2/N_2 separation factors and mixed gas permeabilities as a function of the stage cut of the ZSM-5 composite membrane prepared by the PH method.
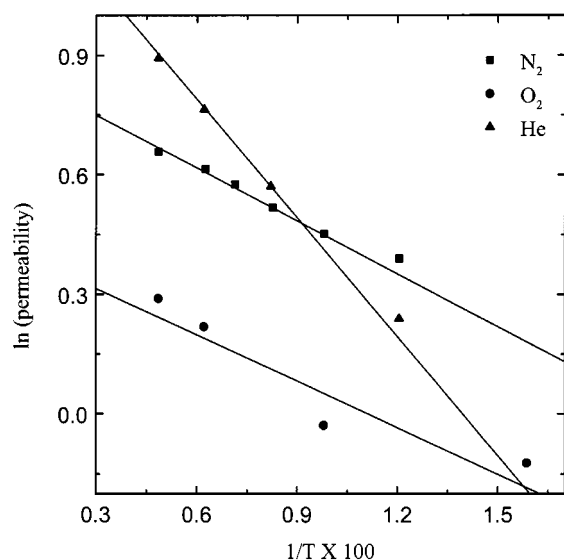

Figure 13 CO_2/N_2 separation factors and mixed gas permeabilities of the ZSM-5 composite membrane prepared by the PH method as a function of measurement temperature.

Figure 12 N_2, O_2, and He permeabilities of the ZSM-5 composite membrane prepared by the PH method as a function of measurement temperature.

Figure 14 CO_2/N_2 separation factors of the ZSM-5 composite membrane prepared by the PH method as a function of transmembrane pressure.

is accumulated at the pore entrance prevents CO_2 from adsorbing on the pore wall and migrating. Lowering the stage cut reduces the concentration polarization, so that the CO_2/N_2 separation factor and the mixed gas permeability increase. However, the stage cut was fixed at 0.1 in other experiments because the lower the stage cut, the more gas thrown away.

Figs 12 and 13 show the effects of measurement temperature on permeabilities and CO_2/N_2 separation factors (feed composition of 50 vol % CO_2) of the ZSM-5 composite membrane prepared by the PH method. The pure gas permeabilities of non-adsorbable gases such as He, N_2, and O_2 are well descibed by Arrhenius plots corresponding to the activated diffusion model in micropores [15]. Unlike these gases, the permeation mechanism of adsorbable CO_2 (Fig. 13) is thought to be surface diffusion by the same token as in Fig. 8. The CO_2/N_2 separation factor of the high value of 7.8 at room temperature decreases as increasing measurement temperature, while the mixed gas permeability in-
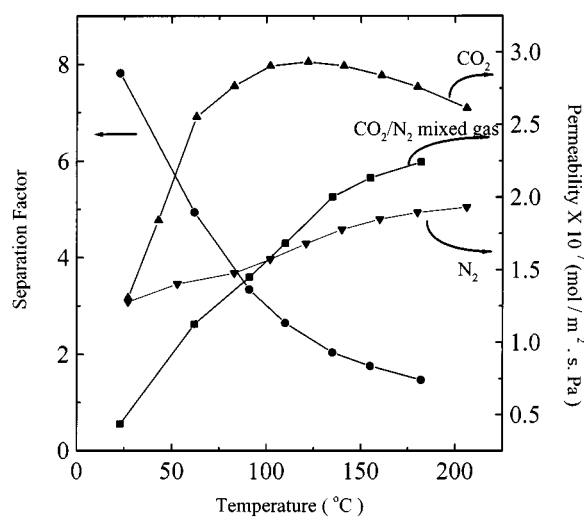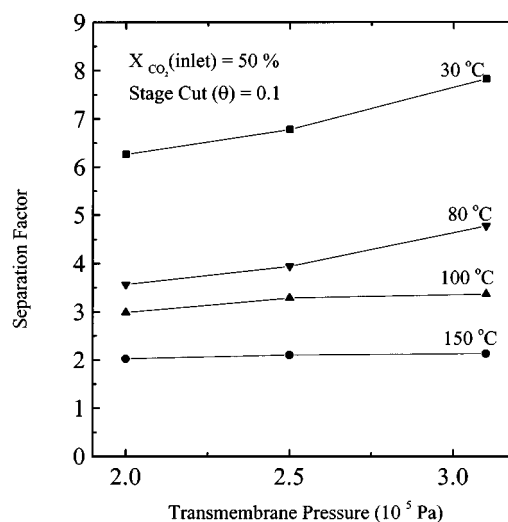
creases vice versa as shown in Fig. 13. When comparing Fig. 13 with Fig. 8, it is known that the ZSM-5 composite membrane prepared by the PH method shows a higher separation factor than those by the DH method. This means that gastightening among ZSM-5 crystals is effectively well done in the PH method, and consequently the effective average pore size of the membrane becomes smaller. The temperature dependency of the CO_2/N_2 separation factors is clearly different from each other. This is ascribed to different permeation mechanisms (Knudsen diffusion/activated diffusion) of N_2 as described in Figs 8 and 13.

The variations of CO_2/N_2 separation factors of the ZSM-5 composite membrane with transmembrane pressure are presented at different measurement temperatures in Fig. 14. At room temperature the separation factor increases from 6.3 to 7.8 according to the increase of transmembrane pressure from 200 to 310 kPa. The higher the temperature, the less the effect of transmembrane pressure on the separation factor. Fig. 15 shows the effects of the feed composition on
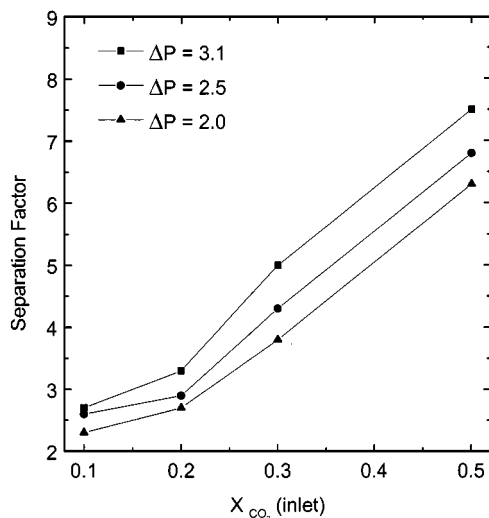
Figure 15 CO$_2$/N$_2$ separation factors of the ZSM-5 composite membrane prepared by the PH method as a function of inlet CO$_2$ concentration.

the CO$_2$/N$_2$ separation factor as a function of transmembrane pressure. As the amount of CO$_2$ in the feed gas increases, the separation factor also increases, which is attributed to the increment of the CO$_2$ adsorbed on the pore wall of the membrane. The separation factor increases from 6.3 to 7.8 with transmembrane pressure in the case of a feed composition of 50 vol % CO$_2$, but in a feed composition of 10 vol % CO$_2$, the separation factor increases slightly.

4. Conclusions
The ZSM-5 composite membrane could be produced by the dip coating-hydrothermal treatment (DH) and the pressurized coating-hydrothermal treatment (PH) methods. The main findings of this research are as follows:

1. ZSM-5 zeolites could be synthesized by the hydrothermal treatment of the sol-mixtures of colloidal silica sol, aluminum nitrate, sodium hydroxide, and TPABr at a temperature range of 150–180 °C. The synthetic conditions of the ZSM-5 zeolite with a spherical shape and a crystal size of 0.5–1.0 μm were adopted in producing zeolite composite membranes supported by a porous alumina tube.

2. The ZSM-5 composite membrane prepared by the PH method showed favorable gas-tightening for its N$_2$ permeability before calcining was 10^{-9} mol/m^2·s·Pa at room temperature.

3. The permeation mechanism of CO$_2$ through ZSM-5 membranes was a surface diffusion, and that of N$_2$, O$_2$, and He was Knudsen flow or an activated diffusion, depending on the synthetic method of the membranes.

4. The CO$_2$/N$_2$ separation factor of the membrane prepared by the DH method was 2.5 at about 120, while the ZSM-5 composite membrane by the PH method showed a high CO$_2$/N$_2$ separation factor of 9.0 and a permeability of 10^{-8}–10^{-7} mol/m^2·s·Pa at room temperature. It was concluded that the ZSM-5 composite membrane synthesized by the PH method developed in this work was highly effective for CO$_2$ separation.

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