

# PL-1

## PREPARATION AND CHARACTERIZATION OF SILICALITE MEMBRANE

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### ABSTRACT

Pure silicalite membranes were prepared on porous sintered stainless steel and alumina supports. The silicalite membrane showed the high alcohol permselectivity, indicating no existence of cracks within the membrane. The high alcohol permselectivity is attributable to the high hydrophobic character of silicalite.

### INTRODUCTION

Zeolite and molecular sieves are widely used in many chemical and physical processes such as heterogeneous catalysis and gas separation. Recently, great interest has been focused on zeolite membranes or films due to their uniform pore sizes and resistance to high temperatures. However, under conventional synthesis conditions of zeolites, synthetic zeolites have been crystallized directly into powdery form. The preparation of zeolite membranes, which are made up of zeolite crystals themselves, is not achieved by conventional methods. Therefore, films or membranes containing zeolites have been made by embedding the zeolite crystals in plastic materials or by the in situ crystallization of zeolites on porous substrates[1]. We have studied the synthesis of pure zeolite film from the standpoint of understanding of growth process of zeolite crystals. As the Al distribution and the change in the morphology along the width of film reflect the time course of the crystal growth, we can get much more information regarding the crystal growth process by analyzing the film obtained. Recently, we succeeded in preparing pure ZSM-5 zeolite films of 30~100 $\mu$ m thickness, which are made up zeolite crystals themselves, by using a Teflon sleeve[2~4]. Large differences in the surface morphology and the surface Al concentration between both side of the film were observed. An amount of Al was hardly detected on the Teflon side. It was concluded that during the initial crystallization of ZSM-5 zeolite, the zeolite crystals with high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios are generated. The similar pure zeolite films were also synthesized by Tsikoyiannis et al.[5] and Anderson et al.[6]. In this paper, we investigate the performance of silicalite membrane deposit on porous substrate for separation of alcohol/water mixtures on pervaporation and gas separation.

## EXPERIMENTAL

The hydrothermal synthesis of silicalite membrane was performed as follows. Colloidal silica (Cataloid SI-30 from Shokubai Kasei Co.; 30.4wt% SiO<sub>2</sub>, 0.38wt% Na<sub>2</sub>O, 69.22wt% water) were added to a stirred mixture of tetrapropyleammonium bromide (TPABr) and sodium hydroxide in solution, to give a hydrogel with a composition of 0.1TPABr-0.05Na<sub>2</sub>O-SiO<sub>2</sub>-80H<sub>2</sub>O. Then, the hydrogel was transferred to a 300ml stainless steel autoclave. A porous stainless steel and alumina supports (5cm diameter) with an average pore diameter of 2μm was placed on the bottom of the autoclave. The autoclave was placed in an air-heated oven at 170°C for 48h. After the completion of crystallization under autogenous pressure without stirring, the autoclave was cooled down, and the support was recovered. The silicalite membrane on the support was washed with deionized water and dried at 120°C for 24h. After then the silicalite membrane was calcined at 300~500°C for 20h in order to decompose the organic base occluded in the zeolite framework.

The identification of the products was achieved by X-ray diffraction (MAC Sci. MXP-18). To analyze a membranes, the incident beam fell at a glancing angle of 1.0°. Observation of silicalite crystals and surface of the membrane was measure by energy-dispersive X-ray analysis (EDX) on a Kevex Delta system attached to a scanning electron microscope (Hitachi S-800) with an accelerating voltage of 15kv. The pore size distribution of the membrane was measured by BELSORP 36 nitrogen porosimeter and a Micrometrics AutoPore 9200 mercury porosimeter.

The pervaporation measurements using about 5 vol% ethanol solution as a feed were performed on a standard pervaporation apparatus. The pressure at the down stream side of the membrane was kept below 3 Torr. Liquid nitrogen was used as a cooling agent for the cold trap. The composition of the permeate was determined by gas chromatography. Single-component permeation experiments were performed on a silicalite membrane for several gases (H<sub>2</sub>, He, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>) using gas permeability apparatus (Gasperm-100; Japan spectroscopic Co., LTD.) at room temperature (25°C) and elevated pressure (~3kgf/cm<sup>2</sup>).

## RESULTS AND DISCUSSION

### Preparation and characterization of silicalite membrane

Silicalite membrane was prepared on a porous stainless steel and alumina disk. Figure 1 shows the X-ray diffraction diagrams of silicalite membrane. The distinct peaks corresponding to silicalite was observed in the X-ray diffraction diagram of silicalite membrane. No peak corresponding to the porous substrate.

Figure 2 shows the scanning electron micrographs of silicalite membrane. The surface of silicalite membrane became with silicalite crystals 20~50mm in size and the thickness of the membrane was about 500μm confirmed by Si line analysis by EDX. The large difference in the crystal size between substrate side and solution side was observed from the scanning electron micrographs of cross sectional view of silicalite membrane teared off from porous

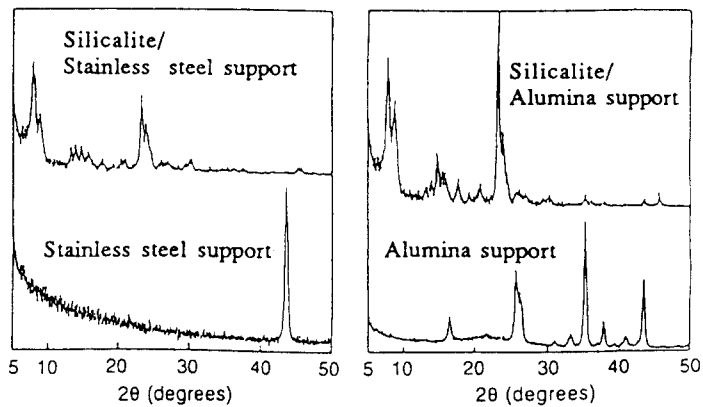


Figure 1 XRD diagrams of silicalite membranes on porous supports

stainless steel disk by mechanical force. The porous substrate side of the membrane was formed of silicalite crystals about 1~2 $\mu\text{m}$  in size. On the other hand, the solution side of the membrane was formed of silicalite crystals about 10~50 $\mu\text{m}$  in size. The increase in the size of silicalite crystals from the porous substrate side to the

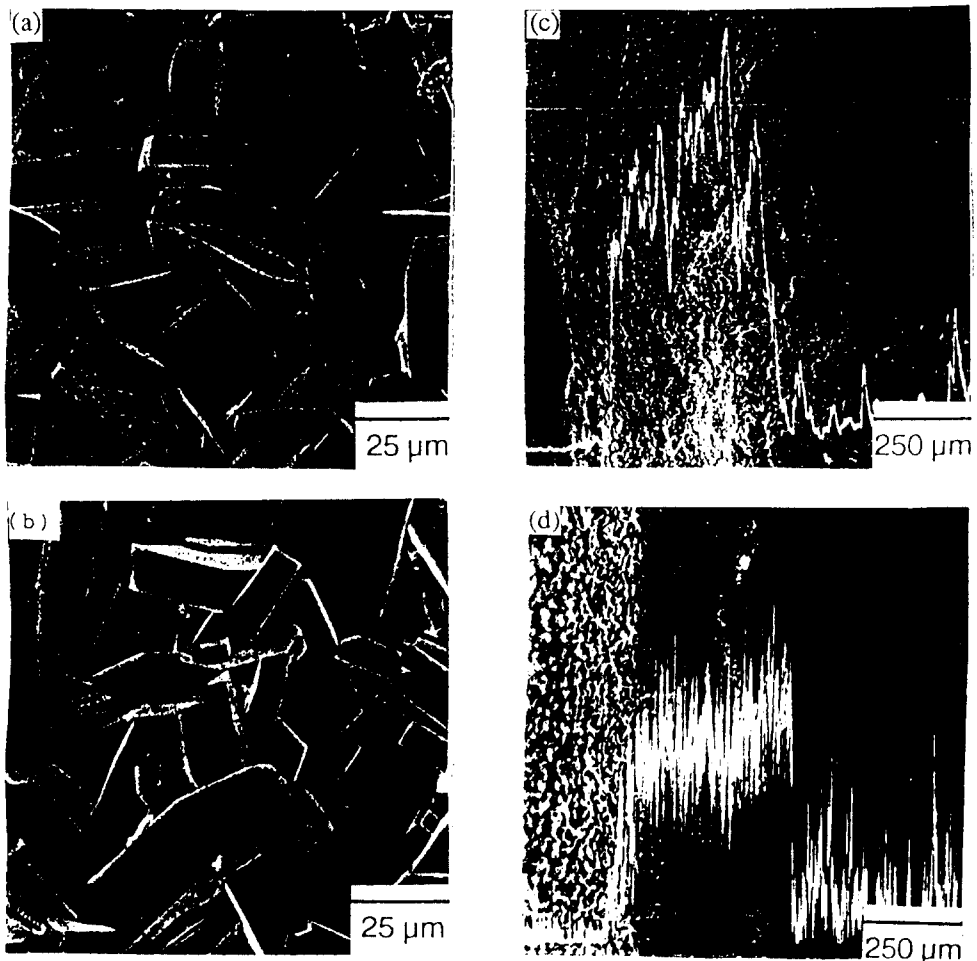


Figure 2 SEM images of silicalite membranes on porous supports

- (a) Surface of membrane on stainless-steel      (c) Surface of membrane on alumina  
 (b) Cross section of membrane on stainless-steel      (d) Cross section of membrane on alumina

solution side was observed. The membrane consist of large crystals next to each other with random orientation, and are thermomechanically stable upon calcination at 500°C in air to remove the TPA<sup>+</sup>, probably as a result of the strong chemical bonding of the silicalite phase to the porous substrate.

#### Separation performance of the silicalite membrane.

The performance results for ethanol/water mixture are illustrated in Figure 3. The separation factor  $\alpha(\text{EtOH}/\text{H}_2\text{O})$  hardly depended upon the feed temperature, while the flux increased with an increase in the feed temperature. The silicalite membrane exhibited over 60 of 0.18Kg/m<sup>2</sup>h at 30°C for 5 vol% ethanol aqueous solution as a feed. Figure 4 shows adsorption of ethanol and water on silicalite powder. Silicalite adsorption amount of the ethanol was about 3 times for the water. Furthermore, effect of operating temperature on the silicalite membrane performance using a varying alcohol are investigated(Figure 5). The high separation factor of approximately 90 was obtained for 1-propanol/water mixture at 30°C, although the flux was below 0.5 kg/m<sup>2</sup> h. On the other hand, the higher flux and the lower separation factor were obtained for methanol/water mixture. This can be explained by the differences in the molecular size and the interaction between alcohol and silicalite,

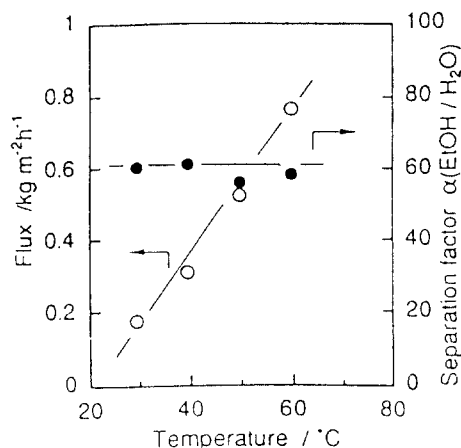


Figure 3 Effect of feed temperature on pervaporation flux and separation factor for ethanol/water mixture  
Feed ethanol concentration=5vol.%

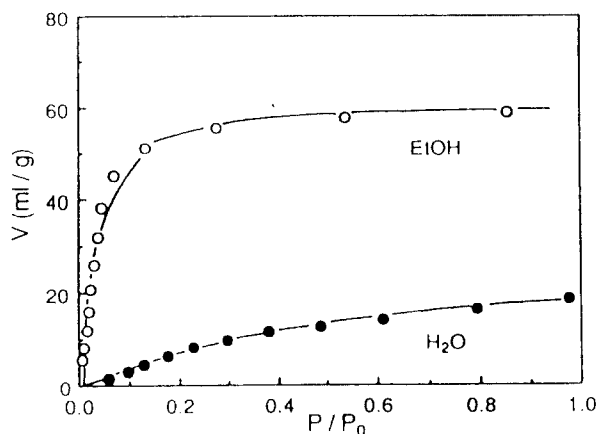


Figure 4 Adsorption of ethanol and water on silicalite

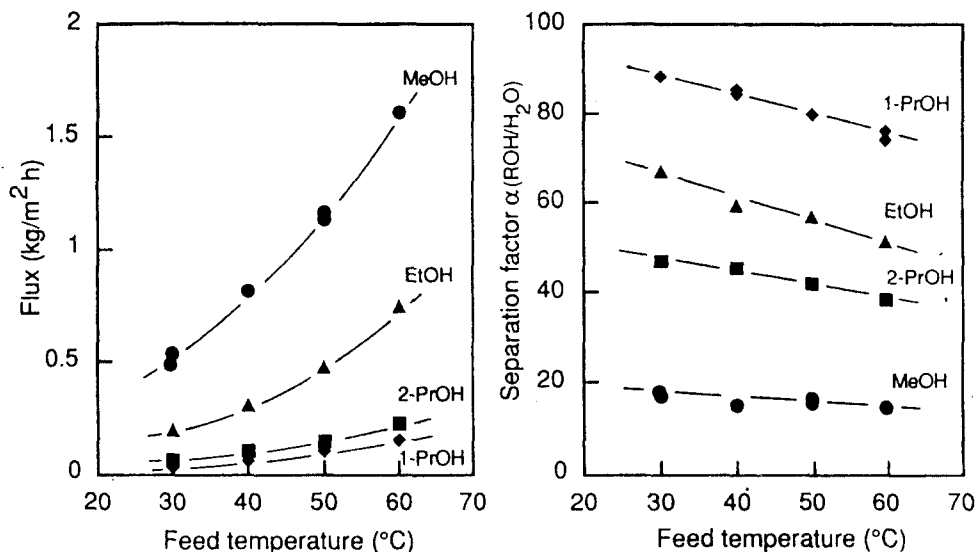


Figure 5 Pervaporation flux and separation factor  $\alpha$  for various alcohol/water mixtures. Feed alcohol concentration = 1 mol%,  $\alpha = [C_{ROH}/C_{H_2O}]_{perm} / [C_{ROH}/C_{H_2O}]_{feed}$

methanol being the smallest and the most polar molecule in the group of alcohols tested here. Amount of adsorbed alcohol on silicalite was larger than that of water, indicating the selective sorption of alcohol. This results suggests the high alcohol permselectivity is attributable to the high hydrophobic character of silicalite.

The permeation results with various single component gases are summarized in Table 1. As-synthesized (TPA<sup>+</sup>-containing) silicalite membrane (b) showed no flux for all gases indicating no cracks within the membrane at least 3 kgf/cm<sup>2</sup> pressure and even after 2h on stream. The calcined silicalite membrane (c) has high permeability for N<sub>2</sub>, the permeability ratios of CO<sub>2</sub>/N<sub>2</sub> and CH<sub>4</sub>/N<sub>2</sub> are 5.49 and 1.44, respectively. These values are bigger than those calculated for Knudsen diffusion. The results suggest that the separating layer of the

Table 1 Single component gas permeation of silicalite membranes

Treatment conditions	P (cm <sup>3</sup> ·cm/cm <sup>2</sup> ·sec·cmHg)					
	H <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	He	CO <sub>2</sub>	CH <sub>4</sub>
(a) Al <sub>2</sub> O <sub>3</sub> substrate		4.80x10 <sup>-2</sup>	6.21x10 <sup>-2</sup>			
(b) 100°C-20h in air	Barrier*					
(c) 500°C-20h in air	4.22x10 <sup>-9</sup>	1.40x10 <sup>-9</sup>	1.27x10 <sup>-9</sup>	3.04x10 <sup>-9</sup>	7.68x10 <sup>-9</sup>	2.02x10 <sup>-9</sup>
Selectivity (P <sub>x</sub> /P <sub>N<sub>2</sub></sub> )	3.74	-	0.91	2.17	5.49	1.44

Temp. = 25°C, Applied pressure = 1.0 kg-G/cm<sup>2</sup>, Membrane area = 12.56 cm<sup>2</sup>, Membrane thickness = 500 μm

\* Applied pressure = 3.0 kg-G/cm<sup>2</sup>

silicalite membrane contains both zeolite channels and a void spacing of zeolite each other crystals resulted from defects, for the membrane are still permeable for molecules bigger than the zeolite pore openings. To have a better understanding on the zeolitic membranes more work has to be conducted.

[REFERENCES]

- [1] For example; (1) D.L.Wernick and E.J.Osterhuber., *J.Membrane Sci.*, **22**, 137 (1985),  
(2) M.Demertzis and N.P.Evmiridis., *J.Chem.Soc.,Farady Trans.*, **82**, 3647 (1986),  
(3) A.Ishikawa, T.H.Chiang and F.Toda., *J.Chem.Soc.Chem.Comm.*, 764(1989),  
(4) T.Bein, K.Brown and C.J.Brinker., *Stud.Surf.Sci.Catal.*, **49**, 887 (1989),  
(5) M.Goldman, D.Fraenkel and G.Levin., *J.Appl.Polym.Soc.*, **37**, 1791 (1989),  
(6) A.S.Michaels., *Chemtech*, 162, (1989),  
(7) E.R.Geus, A.E.Jansen, J.C.Jansen, J.Schoonman and H.Bekkm.,  
*Stud.Surf.Sci.Catal.*, **65**, 457 (1991),  
(8) S.Sakurada, N.Tagaya, T.Maejima and T.Yoshida., *Jpn. Kokai Tokkyo Koho*,  
59-213,615 (1984),  
(9) K.Miyazaki and T.Mitsumata., *Jpn. Kokai Tokkyo Koho*, 60-129,119 (1985),  
(10) H.Suzuki., *Eur. Pat. Appl.*, 180,200 (1985),  
(11) M.Ooyama., *Jpn. Kokai Tokkyo Koho*, 63-291,809 (1988),  
(12) I.M.Lachman and M.D.Patil., *US Pat.*, 4,800,187 (1989),  
[2] T.Sano, Y.Kiyozumi, M.Kawamura, F.Mizukami, H.Takaya, T.Mouri, W.Inaoka,  
Y.Toida, M.Watanabe and K.Toyada., *ZEOLITES*, **11**, 842 (1991),  
[3] T.Sano, Y.Kiyozumi, F.Mizukami, H.Takaya, T.Mouri and M.Watanabe., *ZEOLITES*,  
**12**, 131 (1992),  
[4] T.Sano, F.Mizukami, H.Takaya, T.Mouri and M.Watanabe., *Bull.Chem.Soc.Jpn.*,  
**65**,146 (1992),  
[5] J.G.Tsikoyiannis and W.O.Haag., *ZEOLITES*, **12**, 126 (1992),  
[6] M.W.Anderson, K.S.Pachis, J.Shi and S.W.Carr., *J.Mater.Chem.*, **2**, 255 (1992),