

초청강연 I

Synthesis and Permeation Characteristics of Zeolite Membranes

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Introduction

Membranes made from inorganic materials are generally superior to organo-polymeric materials in thermal and mechanical stability, and chemical resistance. Among inorganic materials zeolite is a promising candidate for a high performance membrane because of the unique characteristics of zeolite crystals such as molecular sieving, ion exchange, selective adsorption and catalysis. Although there are many recent reports¹ on the preparation of zeolite membranes and the gas permeation through the membranes, only a limited number of publications²⁻⁴ deal with pervaporation studies. Recently, we have reported a high pervaporation performance of NaA zeolite membrane for the separation of water/organic liquid mixtures^{4,5} and of NaY zeolite membrane for the separation of methanol/MTBE.^{6,7} Here, preparation of zeolite (LTA,^{4,5} ZSM-5⁶ and FAU⁶⁻⁸) membranes and their permeation properties are discussed.

NaA Zeolite Membrane

NaA membrane was grown hydrothermally on the surface of a porous cylindrical alumina support (10 or 12 mm outer diameter, 15 cm length and 1 μm average pore size). The hydrothermal synthesis of NaA zeolite membrane was performed as follows. An aluminate solution was prepared by dissolving sodium hydroxide and aluminium hydroxide in distilled water. A silicate solution was prepared by dissolving sodium silicate in distilled water. The aluminate solution was added to the silicate solution and the resulting mixture was stirred vigorously, producing a homogeneous gel. The molar composition of the resulting gel was $\text{SiO}_2/\text{Al}_2\text{O}_3=2.0$, $\text{Na}_2\text{O}/\text{SiO}_2=1.0$ and $\text{H}_2\text{O}/\text{Na}_2\text{O}=60$. The porous support coated by the seed crystals of NaA zeolite was placed in the gel. After hydrothermal treatment at 100°C for 3 hours, the support was taken out, washed by water and dried in reduced pressure.

The zeolite membrane was characterized by X-ray diffraction (XRD) and the surface morphology of the membrane was observed by a scanning electron microscopy (SEM). The XRD pattern of the membrane grown on alumina support consists of strong peaks corresponding to NaA zeolite and weak ones of alumina support. The surface of the alumina support was completely covered with NaA zeolite crystals, 2-4 μm in size. These crystals tend to be very closely bound together with little space between them. The thickness of the membrane was about 30 μm judging from the cross-sectional view of SEM observation.

Gas permeation and pervaporation experiments were carried out using the apparatus illustrated in Figure 1. Feed was introduced to the outer side of the zeolite membrane in the stainless-steel module that was placed in a thermostated air-bath. The effective membrane area was 47 cm^2 . Gas permeation rates through the membrane were measured by a soap film flow meter. Composition analysis for mixed gas was performed with a gas chromatograph. In pervaporation, the flow rate of the feed was held at 30-37 $\text{cm}^3\text{min}^{-1}$ and the downstream pressure was maintained below 13.3 Pa throughout the experiment.

Table 1 shows the flux and the separation factor of pervaporation for water/organic liquid mixtures through NaA zeolite membrane. The membrane was highly selective for permeating water preferentially with the high permeation flux because of the micropore filling of water in the zeolite pores or the intercrystalline pores between zeolite crystals to afford water-selective permeation through

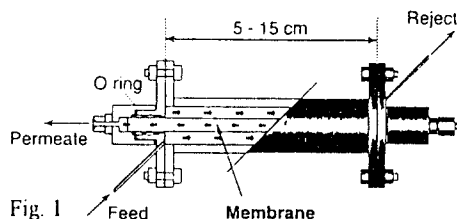


Fig. 1

Table 1 Pervaporation and vapor permeation performances of zeolite membranes

Zeolite	Feed solution (A/B) (wt% of A)	Temp (°C)	Separation factor (A/B)	Flux (kg/m ² h)
NaA	Water/Methanol (10)	50	2100	0.57
		105	5700	3.50
	Water/Ethanol (10)	75	10000	2.15
		105	30000	4.53
	Water/2-Propanol (10)	75	10000	1.76
	Water/Acetone (10)	50	5600	0.91
	Water/Dioxane (10)	60	9300	1.87
		105	8900	7.80
	Water/DMF (10)	60	8700	0.95

the membrane. Figure 2 shows the effect of methanol concentration of the feed mixture on the permselectivity of the membrane at 50°C. In water/methanol mixture, a high separation factor was observed. Furthermore, quite large flux and high separation factor were also observed for dehydration of DMF or dioxane, where most of the organo-polymeric membranes become very swollen, resulting in reduction of the selectivity.

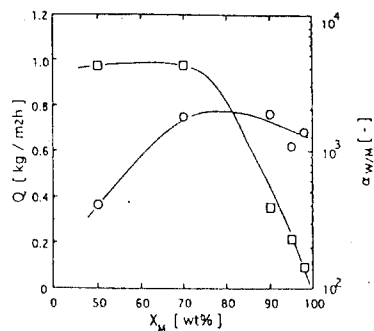


Figure 2 Pervaporation flux and selectivity of zeolite membrane for water(W)/methanol(M) mixtures as a function of the feed concentration at 50 °C.

Figure 3 shows gas permeation rates through NaA membrane are depend on the inverse of square root of molecular weight of gases. This dependence seems to suggest Knudsen diffusion. However, water vapor can permeate at about 2 order larger rate than these gases. Furthermore, adsorption of water to the membrane results in a decrease of the gas permeation rates. Vapor permeation properties of the membrane are also shown in Table 1. The NaA zeolite membrane showed a high performance also in the vapor permeation for water/organic liquid mixtures. Vapor permeation is considered to be applicable to a reversible reaction such as esterification in order to shift the equilibrium in favor of the product and to improve the conversion of the reaction. The combined process provided almost complete conversion in a short reaction time by removal of water vapor through NaA membrane from the gaseous mixture consisting of alcohol and water.⁹ The membrane was quite stable at 200°C and no change in separation performance was observed after a few months.

The versatility of NaA zeolite membrane for dehydration of aqueous ethanol is shown in Table 2. The performance of NaA zeolite membrane is the most favorable one for pervaporation membranes which have been published so far. Thus, a tubular type module for dehydration of organic liquids are now on sale. Figure 4 shows an example of module where length of the tubular membrane is 80 cm and 17 tubes are bundled.¹⁰

ZSM-5 Zeolite Membrane

ZSM-5 zeolite membranes were prepared by hydrothermal synthesis as described in the literatures.³ The membrane was further calcined at 500°C for 20 h in order to remove tetra-n-propylammonium bromide used as a template for ZSM-5 growth. ZSM-5 membrane preferentially permeated alcohol from aqueous solution as suggested by Sano et al.³ The separation factor of ZSM-5 membrane prepared on the alumina support was smaller than that of silicalite membrane with high hydrophobic properties prepared on a porous stainless-steel support. For organic liquid mixtures pervaporation through ZSM-5 zeolite membrane was not suitable since the flux was very low due to the strong adsorption of organic molecules (Table 3).

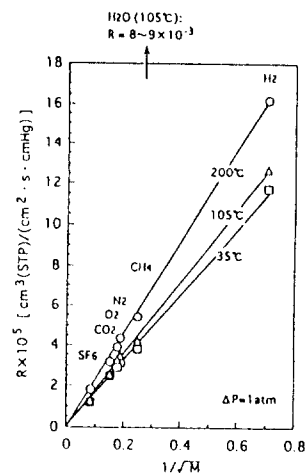


Figure 3 Permeation rates through NaA zeolite membrane vs. the inverse of square root of molecular weight of gases

TABLE 2. Pervaporation performances of representative membranes for water/ethanol system

Membrane	Temp [°C]	Feed [H ₂ O Wt%]	Q [Kg/m ² h]	α [-]
Zeolite (this study)	75	10	2.15	>10000
	75	5	1.10	>10000
Modified-porous glass	79	5	0.10	1630
Silica/Acrylamide	50	10	0.3	3200
GFT	80	5	0.01	9500
CMC(Na ion)	30	10	0.052	2430
PAA/Polymion complex	60	5	1.63	3500
Chitosan	60	10	0.1	6000
Polyimide	75	10	0.01	850
Polyimide(Asymmetric)	60	10	0.22	200

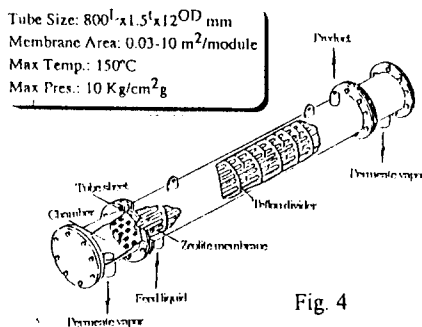


Figure 4

Table 3 Pervaporation and vapor permeation performances of zeolite membranes

Zeolite	Feed solution (A/B) (wt% of A)	Temp (°C)	Separation factor (A/B)	Flux (kg/m ² h)
ZSM-5	Methanol/Water (10)	50	10	2.65
	Ethanol/Water (10)	75	24	2.29
		105	1	1.33
	n-Propanol/Water (10)	75	100	0.62
	2-Propanol/Water (10)	75	32	0.59
	Acetone/Water (5)	50	107	0.34
	Dioxane/Water (5)	75	11	0.10
	DMF/Water (5)	75	1	0.18
	Methanol/Benzene	50	5	0.06
	Methanol/MTBE	50	3	0.02

NaY Zeolite Membrane

NaY membrane was also grown hydrothermally on the surface of a porous cylindrical alumina support. The aluminosilicate gel used in the synthesis of NaY zeolite membrane was prepared by mixing water glass solution and alkaline aluminate solution. After formation of the gel, the reaction mixture was stored for 12 hours. The molar composition of the resulting gel was SiO₂/Al₂O₃=10, Na₂O/SiO₂=1.4 and H₂O/Na₂O=60. After aging, the porous support coated by the seed crystals of NaY zeolite was placed in the gel. After hydrothermal treatment at 100°C for 5 hours, the support was taken out, washed by water and dried in reduced pressure. Gas permeation and pervaporation experiments were carried out using the apparatus described above.

The existence of NaY zeolite was also verified by XRD. The surface of the alumina support was completely covered with randomly oriented, intergrown NaY zeolite crystals, 0.5-1 μm in size. The thickness of the membrane was about 20 μm.

Figure 5 shows gas permeation rates through NaY membrane. The deviation from ideal Knudsen behavior was observed. High permeation rates for condensable gases such as CO₂ and CH₄ indicate the transport of the gases is enhanced by surface diffusion. The binary gas permeation was measured for CO₂/N₂ through the membrane. The N₂ permeation rate from the mixture was significantly reduced compared to that from pure N₂ due to the selective adsorption of CO₂. Thus, NaY zeolite membrane provides one of promising candidates for the separation of CO₂/N₂ mixture.

Table 4 shows the flux and the separation factor of pervaporation for liquid mixtures through NaY and NaX zeolite membrane. The membrane preferentially permeated water from water/alcohol mixtures. However, both the separation factor and the flux of NaY and NaX zeolite membrane were smaller than those of NaA zeolite membrane, probably due to the hydrophobic properties of the zeolite. On the other hand, NaY zeolite membrane showed a high alcohol permselectivity for several feed mixtures with methanol or ethanol. Especially high separation

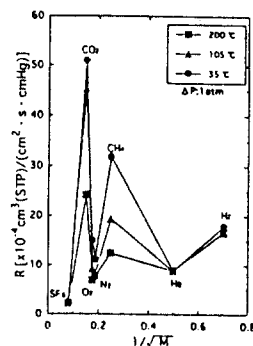


Figure 5 Gas permeation rates through NaY zeolite membrane vs. inverse of square root of molecular weight of gases

Table 4 Pervaporation performance of NaX and NaY zeolite membranes

Zeolite	Feed solution (A/B) (wt% of A)	Temp (°C)	Separation factor (A/B)	Flux (kg/m ² h)
NaX	Water/Ethanol(10)	75	360	0.89
	Methanol/Benzene(10)	50	24	1.25
	Methanol/MTBE(10)	50	320	0.26
NaY	Water/Ethanol (10)	75	130	1.59
	Methanol/Benzene (14)	50	1400	0.62
	Methanol/MTBE (10)	50	3300	1.11
		60	5300	1.70
	Ethanol/ETBE (10)	50	1200	0.21

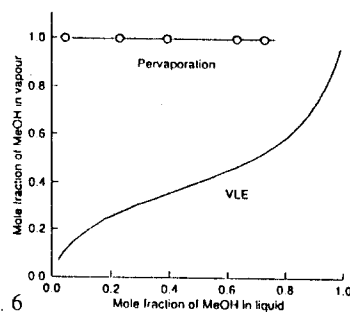


Fig. 6 Pervaporation selectivity at 50 °C through NaY zeolite membrane and vapour-liquid equilibrium (VLE) at 101 kPa in the methanol-MTBE system

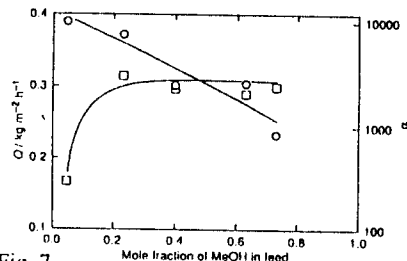


Fig. 7 Flux Q (L) and separation factor α (C) as a function of methanol feed concentration for pervaporation of methanol-MTBE mixtures through NaY zeolite membrane at 50 °C

factors were observed for methanol/methyl *tert*-butyl ether (MTBE) separation. In Figure 6 pervaporation selectivity expressed as methanol mol fraction in the permeate is shown as a function of methanol mol fraction in the feed mixture. It can be observed that pervaporation through NaY zeolite membrane ensures MTBE enrichment in the feed phase by preferential methanol transfer. The corresponding vapor-liquid equilibrium (VLE) curve is given in the same figure, which shows the methanol/MTBE system exhibits a minimum boiling azeotrope. It is clear that pervaporation through NaY zeolite membrane can break up the azeotrope and is more selective than distillation (VLE). The pervaporation of methanol/MTBE has attracted recent interest. Although methanol/MTBE mixtures were separated by pervaporation using polymer or inorganic membranes, membranes that have both high selectivity and high permeation flux were not available. The performance of NaY zeolite membrane is good enough to put this membrane into practical use (Table 5).

It is well known that the overall selectivity of a pervaporation process is determined by mobility selectivity and sorption selectivity. In the case of methanol/MTBE mixtures, the kinetic diameters of these two molecules are approximately 0.38 and 0.62 nm, respectively, and are smaller than intrinsic NaY zeolite pores of 0.74 nm. Therefore, the sorption process presumably determines the pervaporation performance. Methanol sorption into the membrane increases with increasing methanol feed concentration and an increasing sorption causes an increase in the pervaporation flux. When the methanol sorption approaches saturation, the flux becomes constant as shown in Figure 7. Thus, the high permselectivity of NaY zeolite membrane may be attributed to the selective sorption of methanol into the membrane.

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Table 5

Membrane	MeOH (wt %)	Temp (°C)	α (MeOH/MTBE) (-)	Flux (kg/m ² h)	Ref. ¹⁾
Cellulose acetate	0.83-6.9	23-49	14-454	0.05-1.41	1
Poly(vinyl alcohol)	5-30	45	3-4	0.12-0.16	2
BPDA Polyimide	4-1	60	1400	0.6	3
Poly(methylene oxide)	1-20	22	24-8	0.18-0.65	4
Nafion 417	3.2-5.3	50	35	0.64	5
Poly(styrene-co-styrenesulfonic acid)(Mg ion form)	14.3-5.0	25	25000-35000	0.02-0.001	6
Plasma polymer	9-21(EtOH)	80	40-350	0.2-1.7	7
Silicalite/Stainless steel	5-50	30	2-4		8
NaY zeolite/Alumina	1-50	50	840-10000	0.35-1.4	9

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