

## Synthesis of Zeolite Beta Membrane and its Pervaporation Properties

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Zeolite beta membranes have been synthesized on 10-cm-long mullite tubular supports by seed-assisted hydrothermal crystallization. The membranes were characterized by XRD, FE-SEM and showed high alcohol permselectivity for pervaporation separation of ethanol/ethyl tert-butyl ether (ETBE) and methanol/methyl tert-butyl ether (MTBE) mixtures. This was achieved from sols: 0.06 Na<sub>2</sub>O: 0.28 TEAOH: 0.01 Al<sub>2</sub>O<sub>3</sub>: SiO<sub>2</sub>: (18~22) H<sub>2</sub>O at 150 °C in most cases for 3~6 days of hydrothermal reaction. For example, for EtOH (10 mass %) /ETBE (90 mass %) feed mixture, the maximum separation factor of 2140 with a total flux of 0.54 kg/m<sup>2</sup>·h at 50 °C was obtained. Moreover, preliminary investigation was carried out on zeolite beta membrane for separation of the quaternary mixture of H<sub>2</sub>O/EtOH/tert-butyl alcohol (TBA)/ETBE at 70 °C.

Key words: Membrane separation, Zeolite beta membrane, Pervaporation, Ethyl tert-butyl ether, Methyl tert-butyl ether

### 1. INTRODUCTION

Zeolite membranes have attracted much attention due to the potential applications for the highly selective separation and purification, catalytic membrane reactors, host-guest system and chemical sensors, etc. The majority of the zeolite membranes reported is of highly silicious silicalite type zeolite, although small pore membranes of A type zeolite can be applicable to separate mixtures of water and organic liquids such as alcohols by hydrophilic interaction and molecular sieving [1] and large pore membranes of Faujasite to separate mixtures of methanol / methyl tert-butyl ether or benzene / cyclohexane [2,3]. The main reasons are the accumulated knowledge in the synthesis of silicalite, the suitable pore diameter of 0.55 nm which is interesting for industrial application, the relative ease of preparation, the possible modifications and a relatively high thermal and chemical stability due to the high Si/Al ratio[4].

The synthesis of zeolite beta membranes is also quite limited until now. Tuan et al. for the first time reported in situ crystallization of zeolite beta membranes [5] and boron-substituted beta zeolite membranes [6] on a porous stainless steel tube. According to their findings no pure zeolite beta membrane could be ever fabricated on alumina supports and a long crystallization period was required for 3- or 5-time repetition of hydrothermal syntheses. Furthermore, the pervaporation separation performance of zeolite beta membranes was not high enough. In this study, we were able to prepare high performance membranes of zeolite beta by seeding method. The membrane is applicable to separate mixture of ethanol / ethyl tert-butyl ether (ETBE).

### 2. EXPERIMENTAL

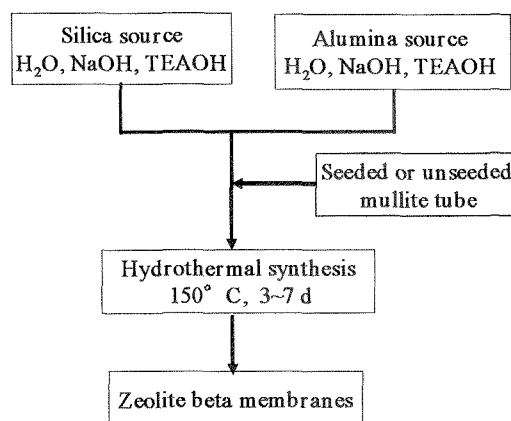


Fig. 1 Schematic representation of synthesis of zeolite beta membranes

zeolite beta membranes. The aluminosilicate sol used for hydrothermal crystallization was prepared by initially dissolving an appropriate amount of aluminium isopropoxide (Wako) in a fraction of an aqueous solution containing tetraethylammonium hydroxide (TEAOH, Aldrich, 35 mass%) as a template and NaOH (Wako) at 40~50 °C. Then a calculated amount of colloidal silica (CS, 30 mass% SiO<sub>2</sub>, Nissan Chemical Ltd.) was added to the remaining fraction of TEAOH solution under vigorous stirring. The Al solution was added dropwise to the Si solution to obtain the aluminosilicate sol with the molar composition of 0.06 Na<sub>2</sub>O : 0.28 TEAOH : 0.01 Al<sub>2</sub>O<sub>3</sub> : SiO<sub>2</sub> : (18~22) H<sub>2</sub>O. After vigorous stirring until homogenized, the sol transferred into an autoclave. The seed-coated mullite support (10 cm length, 12 mm o.d., 1.5 mm

thickness) with an average pore size of 1.3  $\mu\text{m}$  was then placed vertically in the autoclave, and hydrothermal crystallization was carried out at 150  $^{\circ}\text{C}$  for 3–6 days under autogenous pressure. After the hydrothermal treatment, the autoclave was quenched in cold water to stop the crystallization. The products were recovered, washed thoroughly with boiling distilled water and dried at 100  $^{\circ}\text{C}$  overnight. Zeolite beta membranes were ultimately calcined in air at 500  $^{\circ}\text{C}$  for 10 or 15 h at a heating and cooling rates of 0.15 and 0.2  $^{\circ}\text{C}/\text{min}$  respectively to decompose the occluded template in the zeolite pores.

X-ray diffraction (XRD) was collected with a Rigaku X-ray diffractometer (RINT 2000) using  $\text{CuK}\alpha$  radiation. Field Emission-Scanning Electron Microscopy (FE-SEM) was measured by a JEOL field emission SEM (JSM6350F).

Pervaporation experiments were carried out with a continuous counter-current system described elsewhere [1]. The effective membrane area in contact with the liquid feed was 18.84  $\text{cm}^2$ . The permeation side was kept under vacuum. The permeate vapor was collected by a cold trap condensed with liquid nitrogen. The compositions of the feed and the permeate were analyzed by a gas chromatograph (GC, Shimadzu 8A). The total flux was calculated by weighing the condensed permeate. The separation factor ( $\alpha$ ) was defined as  $\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$ , in which  $X_A$ ,  $X_B$ ,  $Y_A$  and  $Y_B$  represented the mass fractions of components A and B in the feed and permeate sides, respectively.

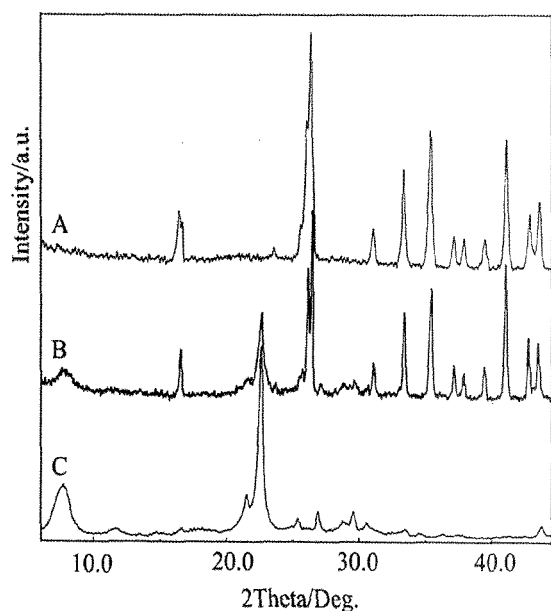


Fig. 2 XRD patterns of a mullite support (A), zeolite beta membrane (B) prepared at 150 $^{\circ}\text{C}$  for 5.5 days at a molar composition of 0.06  $\text{Na}_2\text{O}$  : 0.28 TEAOH : 0.01  $\text{Al}_2\text{O}_3$  :  $\text{SiO}_2$  : 21  $\text{H}_2\text{O}$  and beta powders (C) recovered from the bulk solution

### 3. RESULTS AND DISCUSSION

Figure 2 shows XRD of a zeolite beta membrane prepared on a mullite support and zeolite beta powders recovered from the bottom of the autoclave after hydrothermal synthesis of the membrane. The XRD patterns of the membrane consist of peaks corresponding to those of mullite support and zeolite beta. Zeolite beta was the only crystalline phase obtained either from the membrane or from the as-made powders collected from the bottom of the autoclave. The relatively strong support peaks

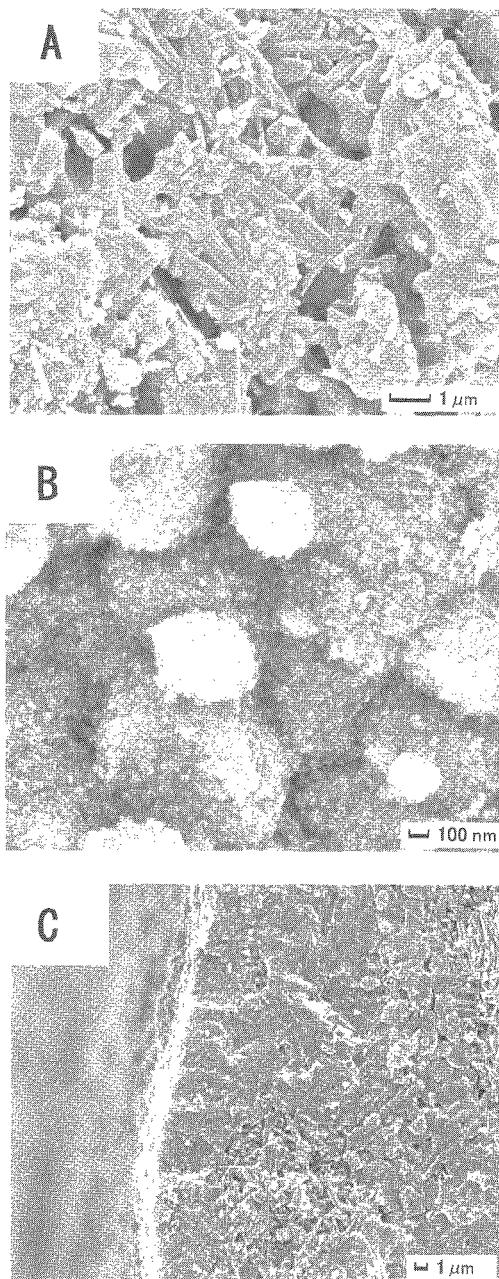


Fig. 3 FE-SEM images of surface view of mullite support (A), surface view of zeolite beta membrane (B) and cross-sectional view of the membrane (C) prepared at the same condition as in Fig. 2

in intensity indirectly revealed the thickness of zeolite beta membrane was small, which would be further confirmed by FE-SEM observation below.

After hydrothermal treatment, the surface morphology of zeolite beta membrane was clearly distinct from that of the support as shown in Fig. 3. The membrane surface was composed of numerous continuous well-intergrown agglomerates (ca. 1  $\mu\text{m}$  in diameter) with a grainy surface. The morphology of agglomerates appeared to be spherical with a primary particle diameter of below 100 nm. Judged from the cross-sectional view of the membrane in Fig. 2 (C), there was a dense top layer with a thickness of less than 10  $\mu\text{m}$ , while a lot of large cavities were observed in the support layer. It was very difficult to distinguish the interface between the zeolite beta layer and the mullite support not only because of the roughness of the support surface, but also because of the formation of zeolite beta crystals inside the support.

Table 1 shows pervaporation performance for alcohol/ether separation through zeolite beta membranes together with those of other zeolite membranes. Although the zeolite beta membrane permeated water from water/organic mixtures, selectivity of the membrane is small due to the large pore diameter of zeolite beta (0.71X0.73 nm). On the other hand, the zeolite beta membrane showed a high alcohol-selectivity for feed mixtures with ethanol or methanol like hydrophilic zeolite membranes such as Faujasite zeolite (X and Y) membranes [2,3]. It is well known that the overall selectivity of a pervaporation process is determined by diffusivity selectivity and the sorption selectivity. In the case of alcohol/ether mixtures, the sorption process presumably determines the pervaporation

performance as suggested in Faujasite membranes [2,3]. Thus, pervaporation through zeolite beta and Faujasite membranes can break up the vapor-liquid azeotrope of ethanol/ETBE and methanol/MTBE and the pervaporation process is more selective than distillation. Recently, interests have been growing in the fuel industry for energy renewable product such as ethanol or as octane enhancer for ether derivatives [8]. Their low-cost production, therefore, has been investigated through the use of membrane processes [9,10]. Pervaporation is more able to induce substantial savings in separation steps involving azeotropes. The pervaporation process through zeolite membranes is a promising candidate for an application for ethanol/ETBE and methanol/MTBE separation.

ETBE can be produced by reacting ethanol with tert-butyl alcohol (TBA) [11]. This reaction is limited by the reaction equilibrium. An excess of ethanol is required to reach much higher conversion for the reaction. In addition the catalytic activity of the ion exchange resin catalyst is strongly inhibited by small amounts of water. For a quaternary mixture of 8.07 H<sub>2</sub>O / 37.67 EtOH / 38.40 TBA / 15.86 ETBE (by weight), the pervaporation selectivities for H<sub>2</sub>O/EtOH, EtOH/ETBE and EtOH/TBA pairs through the zeolite beta membrane at 70 °C were 3, 175 and 3263, respectively, with a total flux of 0.17 kg/m<sup>2</sup>·h. It could be seen that H<sub>2</sub>O component could be selectively removed from the quaternary mixture, thereby driving the forward etherification reaction favorably. Furthermore, the very low TBA permeation flux would be attributed to the occurrence of etherification reaction of TBA with EtOH driven by solid-state acid catalysis over beta zeolites in the membrane

Table I . Pervaporation performance for alcohol / ether separation through zeolite membranes

Membrane	Pervaporation				
	Mixture (A/B) (mass% of A)	Temp [°C]	Flux [kg·m <sup>-2</sup> ·h <sup>-1</sup> ]	$\alpha$	Ref
Beta (TEAOH/H <sub>2</sub> O/SiO <sub>2</sub> = 0.2/19/1, 150°C,82h)	MeOH/MTBE(10)	50	0.11	580	This study
	EtOH/ETBE(10)	50	0.044	1700	This study
Beta(TEAOH/H <sub>2</sub> O/SiO <sub>2</sub> = 0.28/19/1, 150°C,158h)	EtOH/ETBE(10)	70	0.17	3520	This study
Beta(TEAOH/H <sub>2</sub> O/SiO <sub>2</sub> = 0.28/19/1, 150°C,120h)	EtOH/ETBE(10)	70	0.54	2140	This study
		50	0.37	900	This study
Boron-beta	MeOH/MTBE(8)	30	-	8	6
Silicalite	MeOH/MTBE(8)	30	0.12	3	7
NaX	MeOH/MTBE(10)	50	0.46	10000	2,3
	EtOH/ETBE(10)	50	0.15	300	2,3
NaY	MeOH/MTBE(10)	50	1.70	5300	2,3
	EtOH/ETBE(10)	50	0.21	1200	2,3

layer. A systematic investigation of membrane preparation and the corresponding membrane reactor application for ETBE synthesis will be presented elsewhere in detail.

#### 4. CONCLUSIONS

1. Randomly oriented zeolite membranes with dense layer from zeolite beta were prepared by seed-assisted hydrothermal crystallization on porous tubular mullite supports at 150 °C for 3-6 days.
2. The membrane showed high separation selectivities for removing alcohol from alcohol/ether mixtures.

#### ACKNOWLEDGEMENT

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