

## Separation Organics/Water Mixtures by Pervaporation with Silicalite Membranes

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Silicalite membranes were prepared by *in-situ* crystallization on the outer surface of porous mullite tubes at 185°C for 40 h, using tetraethoxysilane and tetrapropyl ammonium hydroxide as a silica source and an organic structure directing agent, respectively. The surface of the support was completely covered with randomly oriented silicalite crystals. The crystals were also formed inside the support, where the thickness of the interface layer from silicalite and mullite was estimated about 5 to 10 μm. The membrane exhibits preferential organic compound permeation from alcohol/water or ketone/water mixtures. Especially, the separation factor and total flux for acetone/water and methyl ethyl ketone/water were 800 and 32,000, 0.52 kg/m<sup>2</sup>.h and 0.25kg/m<sup>2</sup>.h, respectively, for a feed concentration of 5 mass% ketone at 30 °C. Long term pervaporation operation and scale-up to 50 cm-membrane are also investigated.

**Key Words:** Silicalite, Zeolite membrane, Pervaporation, Organic/water separation

### 1. INTRODUCTION

Pervaporation is proposed to be one of the most challenging techniques for continuous organic component recovery from its aqueous solution [1,2]. Pervaporation is a membrane process in which liquid mixtures is in contact with the membrane on the feed side and the permeate is removed as a vapor because of a low vapor pressure existing on the permeate side. This low vapor pressure can be achieved by employing a carrier gas or using a vacuum. The pervaporation process involves a sequence of three steps [3]: 1. selective sorption in the membrane on the feed side, 2. selective diffusion through the membrane, 3. desorption into a vapor phase on the permeate side. The separation principle in pervaporation is based on differences in solubility and diffusivity, whereas separation in distillation is based on the vapor-liquid equilibrium. Thus, the problems of azeotropic distillation are avoided. The economical advantages of pervaporation plants can amount up to 30% in the investment and up to 50% in the operating cost in comparison to rectification plants [4]. Removal of water from liquid organic mixtures now becomes the largest segment of industrial pervaporation application. However, separation of organics from water has not found widespread distribution in the industry, mainly because of swelling, which is resulting in the low selectivity, and limited thermal stability of the polymeric membranes. Sano et al. first found that hydrophobic ZSM-5 membranes prepared on a porous stainless steel sheet showed a high alcohol selectivity in the pervaporation of alcohol/water mixtures [5]. Inorganic membranes, especially zeolite membranes, are promising candidates for high performance pervaporation membranes because of molecular sieving characteristics together with thermal and chemical

stabilities. Thus, it is necessary to develop reproducible and higher performance membranes on a large scale for more practical applications. Recently, we reported the silicalite tubular membranes showed both the high separation selectivity for ethanol over water and the high permeation flux [6]. In this work, separations of organic/water mixtures, such as acetone/water and MEK/water are investigated by silicalite membranes prepared on a porous, cylindrical tube. Long term pervaporation operation and scale-up to 50 cm-membrane are also investigated.

### 2. EXPERIMENTAL

#### 2.1 Silicalite membrane preparation

Silicalite membranes were prepared by *in situ*

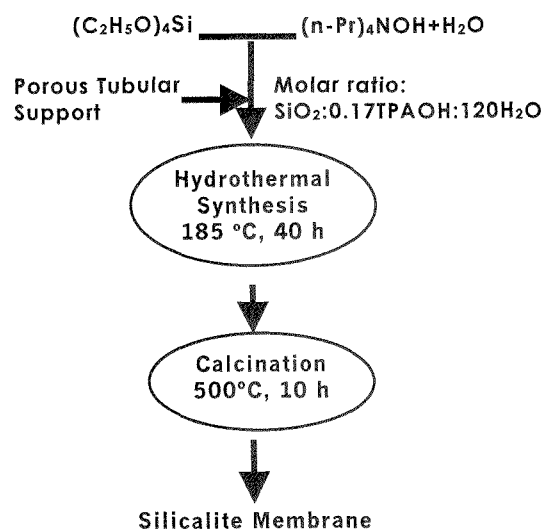


Fig. 1 Synthesis procedure of silicalite membrane

crystallization on the outer surface of a porous, cylindrical mullite support (Nikkato Corp., 10 and 50 cm in length, 12 mm outer diameter, 1.5 mm thickness, about 1  $\mu\text{m}$  average pore size) as shown in Figure 1.

A synthesis solution was prepared by mixing tetraethoxysilane (TEOS, 98.3 mass%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 20 ~ 25 mass% in water, Tokyo Kasei) and distilled water. The molar ratio of the composition of synthesis solution was:  $\text{SiO}_2\text{:TPAOH:H}_2\text{O}=1\text{:}0.17\text{:}120$ . Although the initial solution mixture was turbid, the solution became clear after 1 hour. Then, the solution was poured into a stainless steel autoclave. The support tubes were vertically placed in an autoclave. The autoclave was placed in a convection oven preheated at 185°C. After the hydrothermal treatment, the tubes were removed, washed with distilled water, dried at 100 °C for several hours, and calcined at 500 °C in air for 10 hours at a heating rate of 0.15 °C/min and then cooled down to room temperature at a rate of 0.25 °C/min.

## 2.2 Characterization and permeation experiments

The X-ray diffraction (XRD) with Cu-K $\alpha$  radiation was measured using a Shimadzu XD-3 instrument. The surface and the cross section of the membranes were observed by JEOL JSM6350F Field Emission Scanning Electron Microscopy (FE-SEM).

Pervaporation experiments were carried out with a batchwise system as described elsewhere [6]. The inside of the membrane tube was evacuated through a vacuum line. The permeated vapor was collected by a cold trap cooled with liquid nitrogen. The downstream pressure was maintained below 13.3 Pa. The effective membrane areas were about 28 cm<sup>2</sup>. The amount of the feed solution was about 2500 g. During pervaporation, a proper amount of organic component was added to the feed solution at intervals of 60-120 min to keep the constant feed concentration due to high flux of the membranes. The compositions of the feed and the permeate were analyzed by a gas chromatograph equipped with 3 m column packed with Polarpack Q. The permeation flux was calculated by weighing the condensed permeate. The separation factor was determined as  $\alpha_{A/B}=(Y_A/Y_B)/(X_A/X_B)$  where  $X_A$ ,  $X_B$ ,  $Y_A$ , and  $Y_B$  denote the mass fractions of components A (organics) and B (water) in the feed and the permeate, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Morphological characterization

The XRD patterns of the membranes grown hydrothermally on the porous mullite support consist of peaks corresponding to those of the support and MFI zeolite, respectively. The intensities of the diffraction peaks corresponding to MFI zeolite increased with an increase in the crystallization time. Figure 2 shows FE-SEM views of the support and the membrane prepared on the support at 185 °C for 40 h. After hydrothermal treatment, the surface of the support was fully covered with silicalite crystals. The crystals in the surface layer are hexagonal and their size is in the range of 10-15 %m. The thickness of the surface layer is about 15-20 %m. The silicalite crystals randomly

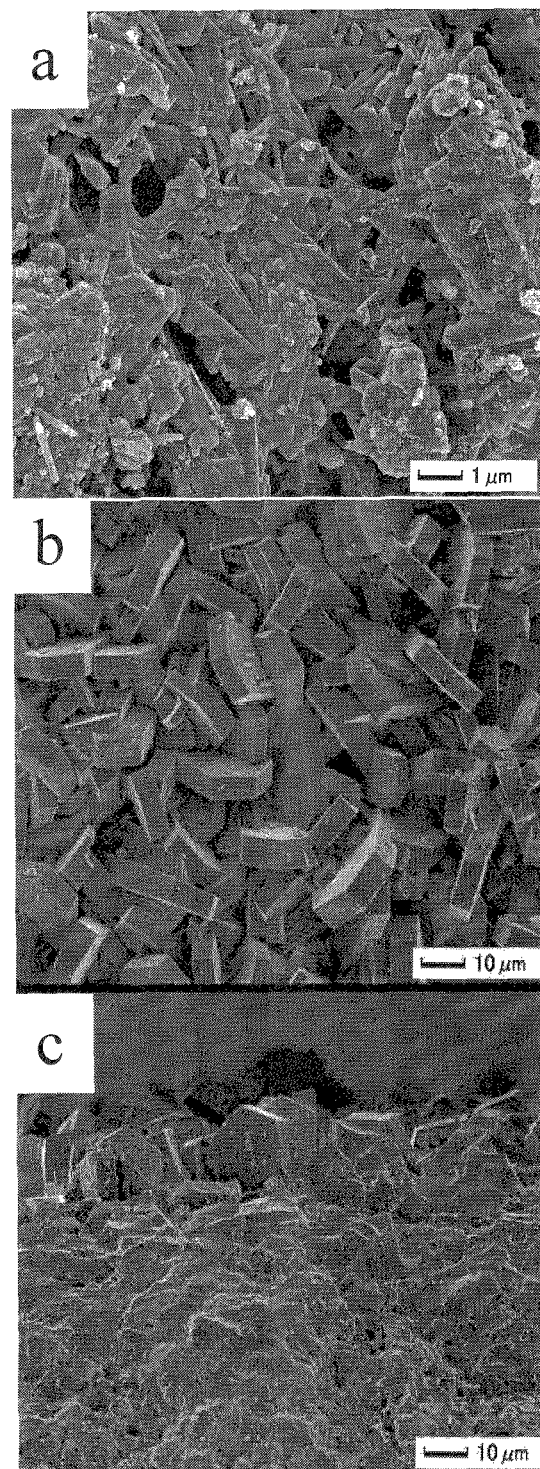


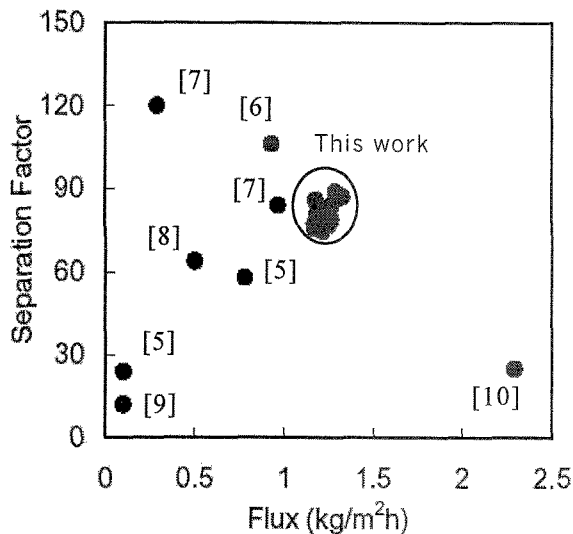
Fig. 2 FESEM photos of the surface of mullite support (a), the surface (b) and cross sectional (c) view of the membrane prepared on the mullite support tube at 185°C for 40 h.

grew onto the mullite support. It was also found that the crystals were formed inside the support. It was very difficult to determine the interface between the silicalite crystals and the mullite support. This indicates that a good interaction is present between the

silicalite crystals and the support. Compared with the cross section of the mullite support, the thickness of the intermediate layer was estimated about 5 to 10 %m.

**3.2. Pervaporation Performance**

Hydrophobic MFI (ZSM-5 and silicalite) zeolite



**Fig.3 Pervaporation performance for aqueous ethanol solution (4-10 mass%, 30-75°C) through MFI membranes.**

membranes exhibit preferential organic compound permeation from organic/water mixtures such as alcohol/water mixtures because MFI has not only strong hydrophobic property but also preferentially adsorbs organic compounds. Figure 3 summarizes the pervaporation performance of MFI zeolite membranes

**Table I**

Separation of acetone/water by pervaporation in various zeolite membranes

Feed mass%	Temp °C	Flux kg/(m <sup>2</sup> h)	Sep. Factor	Membr	Ref.
5.0	60	1.16	540	Silicalite	This work
5.0	30	0.52	800	Silicalite	This work
1.0	30	0.20	930	Silicalite	This work
5.0	60	0.15	440	B-ZSM-5	11
4.7	32	0.68	110	Silicalite	9
5.3*	30	1.06	110	Silicalite	12

\*vol%

for aqueous ethanol solution (5 mass%, 30-75 °C). 16 Membranes prepared in this study prepared under the same synthesis conditions at 185 °C for 40 h showed almost same pervaporation separation performances of an average of 85 in separation factor and 1.25 kg/(m<sup>2</sup>h) in flux, which suggests that the preparation of silicalite membranes are highly reproducible. Furthermore, randomly oriented silicalite membranes with a dense intermediate layer also shows higher separation

selectivities for removing ketones from their aqueous solution than other MFI membranes reported in literatures as shown in Table 1 and 2. Especially, the separation factor of MEK over water is more than two orders of magnitude higher than the reported values.

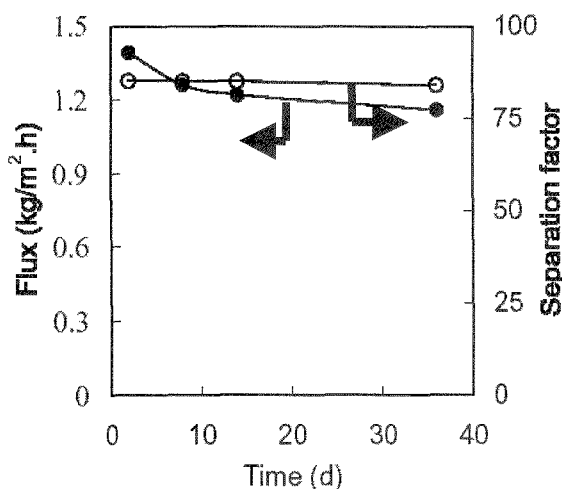
**Table II**

Separation of MEK/water by pervaporation in various zeolite membranes

Feed mass%	Temp °C	Flux kg/(m <sup>2</sup> h)	Sep. Factor	Membr	Ref.
5.0	60	0.73	2,400	Silicalite	This work
5.0	30	0.25	32,000	Silicalite	This work
5.0	60	0.055	380	B-ZSM-5	11
5.0	34	0.33	150	Silicalite	13
5.4*	30	0.41	270	Silicalite	12

\*vol%

Figure 4 shows the long time pervaporation behavior for aqueous ethanol solution (5 mass%) at 60 °C through the silicalite membrane. After more than one month, the flux of the membrane decreased slightly and the separation factor hardly changed.



**Fig.4 Stability of pervaporation performance through the silicalite membrane for aqueous ethanol solution (5 mass%, 60°C)**

In order to develop more energy efficient concentration of the biomass ethanol, tubular type module was designed. Figure 5 shows a schematic view of the pervaporation module [14]. The module is equipped with dividers for the purpose of accelerating the flow rate. Ethanol/water mixtures are fed to the outer side of the zeolite membrane and rushed across the bundle of silicalite membranes. The permeated gaseous mixture through the inside of the membrane is collected by a condenser. At present, a separation factor of 80 and a tall flux of 0.8 kg/(m<sup>2</sup>h)

were obtained through the 50 cm membrane.

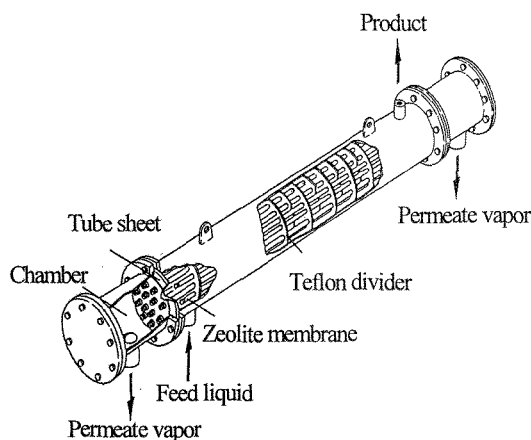


Fig. 5 Schematic view of the tubular-type pervaporation module.

Recently pervaporation module using zeolite A membranes have been successfully applied to remove the water, producing pure ethanol containing less than 0.5 mass% water. Thus, pervaporation using silicalite membranes may have an opportunity for making a significant contribution to more energy efficient production of the ethanol from biomass.

#### 4. CONCLUSIONS

1. Randomly oriented silicalite membranes with dense intermediate layer from silicalite and mullite were prepared reproducibly by *in situ* crystallization on porous tubular mullite supports at 185 °C for 40 h.
2. The membrane showed higher separation selectivities for removing ketones from their aqueous solution than other MFI membranes reported in literatures.
3. The membrane was stable after more than one month. Pervaporation behavior for aqueous ethanol solution (5 mass%) at 60°C through the silicalite membrane hardly changed.

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