Separation of ethanol/water mixture by silicalite membrane on pervaporation

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Abstract

Pure silicalite membranes were prepared on porous supports of sintered stainless steel or alumina discs. The silicalite layer was characterized by X-ray diffraction, SEM and mercury porosimetry. Individual crystals were intergrown in three dimensions into the polycrystalline phase. The membranes were not disintegrated by thermal treatment in vacuo or calcination for removing the organic amine occluded in the channels of silicalite, indicating high thermomechanical stability of the membrane. The liquid separation potential of the membrane was investigated by pervaporation of an aqueous ethanol solution. The high ethanol permselectivity with a separation factor \(\alpha(\text{EtOH}/\text{H}_2\text{O})\) of more than 60 was achieved for a 5 vol\% aqueous ethanol solution at 30°C, indicating no cracks and pores between the silicalite grains within the membrane. From adsorption experiments of ethanol and water on silicalite, it was found that the high permselectivity is attributable to the selective sorption of ethanol into the silicalite membrane.

Keywords: Separation; Ethanol; Silicalite membrane; Pervaporation

1. Introduction

Great interest has been focused on preparation of zeolite membranes from the standpoint of application to gas or liquid separation. Most of the zeolite membranes have been made by embedding the zeolite crystals in polymer or ceramic matrixes, or by in situ crystallization on porous substrates. Recently, several researchers succeeded in preparing pure zeolite membranes of silicalite, ZSM-5, ZSM-35, mordenite, NaA and SAPO [1-9]. Although zeolite membranes are polycrystalline films and very fragile, the gas separation potential of zeolite membranes is indicated in Refs. [10-12]. However, only few studies have been dedicated to the separation of liquid mixtures.

Te Hennepe et al. reported that the membrane performance of the silicon rubber membrane, which is effective for separation of ethanol/water mixtures, is considerably improved by addition of silicalite crystals to the silicon rubber matrix [13]. At 70 wt\% silicalite content a high separation factor \(\alpha(\text{EtOH}/\text{H}_2\text{O})\) of \(~20\) was achieved. This result suggests that if a pure silicalite mem-
brane were synthesized, a higher separation factor would be obtained.

From these standpoints, we have investigated the liquid separation potential of the zeolite membrane on pervaporation. It was already reported that the silicalite membrane is very effective for the separation of ethanol/water mixtures \[14\]. In this paper, the pervaporation performance of silicalite membrane for separation of ethanol/water mixtures was studied in detail.

2. Experimental

The hydrothermal synthesis of silicalite membranes was performed as follows. Colloidal silica (Cataloid SI-30 from Shokubai Kasei Co.; 30.4 wt% SiO\(_2\), 0.38 wt% Na\(_2\)O, 69.22 wt% water) was added to a stirred solution of tetrapropylammonium bromide (TPABr) and sodium hydroxide, to give a hydrogel with a composition of 0.1:0.05:1:80 TPABr-Na\(_2\)O-SiO\(_2\)-H\(_2\)O. Then the hydrogel was transferred to a 300 ml stainless steel autoclave. A porous support of sintered stainless steel or alumina disc (5 cm diameter) with an average pore diameter of 0.5–2 \(\mu\)m was placed on the bottom of the autoclave. The autoclave was placed in an air-heated oven at 170°C for 48 h. After the completion of the 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 100°C. Then the silicalite membrane was heated at 300–380°C under vacuum, or calcined at 500°C for 20 h in order to decompose the organic amine occluded in the zeolite framework. The silicalite membrane was not disintegrated by these processes.

The characterization of the membrane was achieved by X-ray diffraction (Mac Sci. MXP18) with the incident beam at a glancing angle of 1.00°. The surface and the cross section of membrane were characterized by scanning electron microscopy (SEM, Hitachi H-800) with an energy-dispersive X-ray analysis system (EDX). The pore size distribution of the membrane was measured by a mercury porosimeter (Micromeritics AutoPore 9200).

The pervaporation measurements using an aqueous ethanol solution as a feed were performed on a standard pervaporation apparatus as shown in Fig. 1. Liquid nitrogen was used as a cooling agent for the cold trap. The compositions of the feed and the permeate were determined by gas or liquid chromatography. Flux and

![Diagram of pervaporation apparatus](image)
separation factor $\alpha (\text{EtOH}/\text{H}_2\text{O})$ were calculated from:

$$\text{Flux (kg/m}^2\text{h)} = \frac{\text{weight of permeate, kg}}{\text{membrane area, m}^2 \times \text{permeation time, h}}$$

and

$$\text{Separation factor } \alpha (\text{EtOH}/\text{H}_2\text{O}) = \frac{[C_{\text{EtOH}}/C_{\text{H}_2\text{O}}]_{\text{Permeate}}}{[C_{\text{EtOH}}/C_{\text{H}_2\text{O}}]_{\text{Feed}}}$$

where $C_{\text{EtOH}}$ and $C_{\text{H}_2\text{O}}$ are the volume fractions of ethanol and water, respectively.

To evaluate the adsorption performance of the silicalite membrane, vapor-sorption experiments of water and ethanol on silicalite were carried out with a Belsorp 18 adsorption apparatus.

3. Results and discussion

3.1. Characterization of silicalite membrane

Fig. 2 shows X-ray diffraction diagrams of silicalite membranes supported on porous stainless steel and alumina discs. The reflection peaks corresponding to silicalite were observed in the X-ray diffraction diagrams. The peaks derived from the porous supports were not observed. Fig. 3 shows the scanning electron micrographs of the surface and the cross section of the membranes. The surface was formed by an aggregate of crystals of 10–25 μm. The growth on the porous support led to a randomly grown crystalline layer. The average thickness of the silicalite layer (400–500 μm) was confirmed by Si line analysis with EDX. These results indicate that the surface of the support was covered with densely packed silicalite crystals.

If there are cracks or pores between the silicalite grains within the membrane, separation performance cannot be expected. Therefore, the pore size distribution of the membrane was measured by mercury porosimetry. Fig. 4 shows the pore size distribution of the pure silicalite membrane detached from the stainless steel support by a mechanical method. One peak was observed at ~500 nm. To clarify where the peak originated from, a cross section of the membrane was measured by SEM at higher magnification (Fig. 5). The support side of the membrane consists of small crystals 2–4 μm in size. Pores or interstices between the silicalite grains were visible. The crystal sizes in the middle part of the membrane were larger than those on the support side. Pores or interstices were also observed. On the other hand, the solution side (the top layer) of the membrane was composed of a layer of highly intergrown zeolite crystals. Although the shape of

Fig. 2. X-ray diffraction diagrams of silicalite membranes on porous supports.
Fig. 3. SEM images and Si line analysis for surface and cross section of silicalite membranes on porous supports.
the crystal is not clear due to intergrowth, the crystal size appears to become larger. No pores originated from silicalite grains were observed. This indicates that the peak at 500 nm in the pore size distribution as shown in Fig. 4 is attributable to the pores between the silicalite grains in the middle and the support side of the membrane. These characteristics of the silicalite membrane prepared are consistent with those reported in the literature [10–12].

3.2. Pervaporation performance

As mentioned in the experimental section, the organic amine (TPABr) is used in the silicalite synthesis as a template. The organic amine remains in the channels of the silicalite crystals. In order to use the membrane as a pervaporation membrane, the amine must be removed from the channels by certain procedures. As the silicalite membrane experiences irregular stresses that arise from a difference in the thermal expansion between the support and the silicalite crystals and from removal of volatile materials from the zeolite framework, cracks are easily formed within the membrane during the treatment process.
Therefore, the influence of pretreatment conditions of the membrane on the pervaporation performance was studied. The pervaporation measurements were conducted at 60°C using an aqueous ethanol solution of 5 vol% as the feed. The results obtained are summarized in Table 1.

The silicalite membrane after air-drying at 100°C (containing the template still) showed a very low flux combined with a separation factor smaller than 1, indicating no cracks and pores between the silicalite grains within the membrane before the pretreatment. However, in the case of the membrane after thermal treatment under a vacuum, the flux and the separation factor increased with an increase in treatment temperature and time. The membrane calcined at 500°C to remove the template completely showed a high flux combined with a high separation factor of ~60. This separation factor is the most favorable one among organic and inorganic membranes which have been published so far. These results suggest that the membrane changes from a water-selective membrane to an ethanol-selective one by decreasing the amount of template occluded in the zeolite framework, and that the separation of ethanol/water takes place by transport through the zeolite channels.

Fig. 6 shows the pervaporation performance of several silicalite membranes, which were prepared by the same method. It is noted that each membrane shows a slight different performance. We have considered that the difference in membrane performance is attributable to a slight difference in membrane thickness or to very small cracks formed during the thermal treatment of the membrane. It is also noted that the ethanol concentrations of the permeates for the alumina supports are slightly lower than those for the stainless steel ones. Taking into account that the hydrophobicity of the ZSM-5 type zeolite decreases when the content of framework aluminum increases \([15, 16]\), this suggests that the top layer of the membrane on the alumina support is not composed of silicalite crystals but composed of ZSM-5 ones. The difference between ZSM-5 and silicalite is the content of framework aluminum, which is nil for the latter. Although the synthesis mixture does not contain an aluminum source, it is reasonable to consider that a part of the surface of the alumina support is dissolved in the high-pH solution. Actually, the surface SiO2/Al2O3 ratio of the membrane on the alumina support measured by EDX was 392.

Next, the influence of the feed temperature on the pervaporation performance was studied using the silicalite membrane supported on a sintered stainless steel disc (Fig. 7). The flux increased linearly with an increase in the feed temperature due to the higher vapor pressure of the components of the feed. The separation factor \(\alpha(\text{EtOH}/\text{H}_2\text{O})\) decreased slightly with the temperature. A few introductory experiments were carried out to investigate the influence of the feed ethanol concentration on the pervaporation performance. Fig. 8 illustrates the relationship between flux and separation factor as function of the feed ethanol concentration. The flux decreased rapidly by adding ethanol to water and then increased slightly with the ethanol concentration. On the other hand, the separation factor \(\alpha(\text{EtOH}/\text{H}_2\text{O})\) reached a maximum value at a feed ethanol concentration of ~3 vol% and then

### Table 1
Influence of pretreatment conditions on pervaporation performance

<table>
<thead>
<tr>
<th>Treatment condition</th>
<th>Temp. (°C)</th>
<th>Time (h)</th>
<th>Flux (kg/m² h)</th>
<th>Separation factor (\alpha(\text{EtOH}/\text{H}_2\text{O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>air-drying</td>
<td>100</td>
<td>12</td>
<td>0.00303</td>
<td>0.38</td>
</tr>
<tr>
<td>in vacuo</td>
<td>300</td>
<td>6</td>
<td>0.00840</td>
<td>0.58</td>
</tr>
<tr>
<td>in vacuo</td>
<td>380</td>
<td>6</td>
<td>0.0394</td>
<td>7.8</td>
</tr>
<tr>
<td>calcination</td>
<td>500</td>
<td>20</td>
<td>0.760</td>
<td>58</td>
</tr>
</tbody>
</table>

Feed temperature: 60°C; feed ethanol concentration: 5 vol%.
Fig. 6. Pervaporation performance of silicalite membranes prepared. Feed ethanol concentration: 5 vol%; feed temperature: 30°C. (O) Alumina support; (●) sintered stainless steel support.

Fig. 7. Influence of feed temperature on pervaporation performance. Feed ethanol concentration: 5 vol%.

decreased with the ethanol concentration. The rapid changes in the flux and the separation factor $\alpha$(EtOH/H$_2$O) suggest that selective adsorption of ethanol on the surface of the silicalite membrane takes place.

3.3. Sorption property

It is well known that the transport mechanism in pervaporation through membranes can be described by the sorption–diffusion model [17]. The membrane performance depends upon (1) sorption of permeates in the feed side and (2) diffusion through the membrane. In the case of ethanol/water mixture, as the molecular sizes of ethanol and water are smaller than 5 Å (≈ the pore size of silicalite), the sorption process determines the pervaporation performance mainly. Therefore, in order to clarify the sorption properties of the silicalite membrane, adsorption isotherms of ethanol and water on silicalite powders were measured. Fig. 9 shows the adsorption isotherms of ethanol and water at 30°C. It is clearly shown that the amount of ethanol adsorbed on silicalite was ~3 times larger than that of water. It is indicated that the high hydrophobic property of silicalite enhances the selective
Fig. 9. Adsorption isotherms of ethanol and water on silicalite at 30°C.

Adsorption of ethanol into the membrane, resulting in the high separation factor.

4. Conclusions

(1) The pure silicalite membranes exhibit high ethanol permselectivity with a separation factor $\alpha$(EtOH/H$_2$O) of more than 60 for a 5 vol% aqueous ethanol solution at 30°C.

(2) Cracks or pores between the silicalite grains, which affect the pervaporation performance, do not exist within the membrane.

(3) The high ethanol permselectivity of the membrane is attributable to the high hydrophilic properties of silicalite.

References


