Surface silylation of silicalite membranes and their pervaporation performance for the separation of ethanol from ethanol-water mixtures

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The silicalite membrane, which is a type of zeolite membrane, has the highest hydrophobicity. An improvement in membrane selectivity would enhance the energy efficiency of the separation process. An enhancement in the hydrophobicity of silicalite membranes is possible by surface modification. Tubular silicalite membranes were hydrophobized by silylation, and their pervaporation (PV) performance for the separation of ethanol from a dilute ethanol-water mixture was investigated. The tubular silicate membranes were prepared by the secondary growth method, which consists of seeding by electrophoretic deposition and hydrothermal synthesis. Trimethylchlorosilane (TMCS), methyltrichlorosilane, propyltrichlorosilane, and 3,3,3-trifluoropropyltrichlorosilane were examined as the silylation reagents. The desired improvement in hydrophobicity and membrane performance were achieved only in case of TMCS. The contact angle increased from 20 to 130° and the PV performance improved after the silylation. A permeate EtOH concentration of 85.9 vol % with a total flux of 0.31 kg/m²⋅h from a 5 vol % EtOH aqueous solution at 30°C was obtained.

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1. Introduction

Membrane separation technology is attractive from the viewpoint of both energy cost and selectivity. Zeolite membranes have uniform, molecular-sized pores and are well suited for separating liquid phase mixtures.1–3 Mordenite framework inverted (MFI) zeolites such as silicalite and ZSM-5 have attracted a lot of attention.4–6 The performance of MFI zeolites often depends on the hydrophobicity of the pore surface.7–9 Silicalite, which does not contain aluminum, is more hydrophobic than any of the other zeolites. Therefore, silicalite is expected to be useful for the separation of organic materials dissolved in water. Silicalite membranes have been synthesized under various conditions, and their ability to separate organic materials from water/organic mixtures using pervaporation (PV) has been reported.4,6–9 PV is an emerging technology with significant potential to efficiently recover ethanol from fermentation broths.10–13 Previously, we reported the synthesis of tubular silicalite membranes on a porous stainless steel support tube by using hydrothermal synthesis and electrophoretic deposition, as a seeding technique, and evaluated their PV performance for ethanol and butanol separation.13–16 An improvement in membrane selectivity would increase the energy efficiency, thus making PV economically viable.14 The surface of membranes is usually modified to improve the membrane separation performance. The permselectivity of ethanol over water could be increased by improving membrane hydrophobicity. Zeolite surfaces modified using alkyltrichlorosilanes have been characterized by contact angle measurements.17 The surface of mixed matrix membranes, which are made up of zeolites and polymers for the improvement in membrane separation performance, have been reviewed.12 The surface hydrophobicity of the zeolite membranes could be improved by silylation. Silylation using trialkylsilane reagents is the most popular hydrophobization method.18–20 Trimethylchlorosilane (TMCS) reacts preferentially with isolated silanols as follows:20,21

\[
\text{SiOH} + \text{Si(CH}_3)_3\text{Cl} \rightarrow \text{SiOSi(CH}_3)_3 + \text{HCl}
\]  (1)

The hydrophobicity of disk-type membrane surfaces has been improved by reacting with silane coupling reagents, thus improving the separation performance of the membranes.22–24 Eslava et al. reported the silylation using TMCS.25 We also confirmed the silylation of silicalite crystals using TMCS by IR spectroscopy.25 In this study, we investigated the effect of surface hydrophobization of tubular silicalite membranes on their separation performance. The tubular silicate membranes were prepared by the secondary growth method, which consists of seeding by electrophoretic deposition (EPD) and hydrothermal synthesis. Four silylation reagents were used for the hydrophobization: TMCS, methyltrichlorosilane, propyltrichlorosilane, and 3,3,3-trifluoropropyltrichlorosilane. The hydrophobization of surfaces was characterized by the contact angle measurements and its effect was evaluated by PV separation of ethanol from a 5 vol % ethanol-water mixture.

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2. Experimental

The silicalite membranes were prepared by using the secondary growth method on seeded supports as reported previously. The preparation method is explained briefly as follows. EPD was used for the seeding on the porous substrate. The average particle diameter of the silicalite seed was about 2 μm. The EPD bath consisted of n-propanol and silicalite seed powder. The concentration of the silicalite seed powder in the EPD bath was 0.5 g/100 cm³. A porous tubular stainless steel support (outer diameter: 10 mm, length: 100 mm, and pore size: 0.5 μm) was used as the deposition substrate, and a stainless steel mesh was used as the opposite electrode. In the EPD process, a DC voltage of 20 V was applied for 5 min using a regulated DC power supply (Takasago, TP035-2D, Kanagawa, Japan). The starting hydrogel for the synthesis of the silicalite membrane consisted of tetrapropylammonium bromide (TPABr, Tokyo Chemical Industry Co., Ltd.) as the structure-directing agent, colloidal silica (Cataroid, SI-30, JGC Catalysts and Chemicals Ltd., Kanagawa, Japan), SiO₂, 30.7 %, sodium hydroxide (NaOH, 0.42 %; H₂O, 68.88 %), sodium hydroxide, and distilled water in the ratio SiO₂:TPABr:NaOH:H₂O = 1:0.005:0.05:80. This hydrogel was stirred for 2 h at room temperature. The seeded tubular support was placed vertically in the chamber. When TMCS was used for the silylation of tubular silicalite membranes. The silicalite membrane was 20°. After silylation using TMCS as the silylation reagent, the contact angle was 130°. This result showed that the surface of the silicalite membrane has been modified.

Four silylation reagents: TMCS (Wako pure chem. Ind. Ltd., Japan, 98%), methyltrichlorosilane (MTCS; Gelest Inc., USA, 99%), propyltrichlorosilane (PTCS; Gelest Inc., USA, 99%), and 3,3,3-trifluoropropyltrichlorosilane (TFPTCS; Sigma Aldrich Co, USA, 97%) were examined. The abbreviated name and the chemical structure of organosilanes, the silylation reagents, and their abbreviations are shown in Table 1. The apparatus shown in Fig. 1 was used for the silylation of tubular silicalite membranes. The silicalite membrane was installed into the chamber. When TMCS was used for silylation, 30 cm³/min of He gas was bubbled through TMCS, and the gas was supplied to the chamber at 60°C for 3 h. After silylation, 30 mL/min of pure He gas was flown in the chamber for 12 h to remove the generated hydrochloric acid (HCl) gas. When other silylation reagents were used, the silylation reactions were carried out at 300°C for 1 h and repeated three times. When MTCS was used, methanol vapor was used to remove the generated HCl gas after the third round of silylation. Similarly, n-propanol vapor was used to remove the generated HCl gas when PTCS and TFPTCS were used.

The surface morphology of the membranes was observed using a confocal laser scanning microscope (Keyence, VK9500, Osaka, Japan). The contact angles on the surfaces were measured using a contact angle meter (DropMaster DM500, Kyowa Interface, Saitama, Japan). The batch PV experiments were carried out at 30 and 60°C. The composition of feed solution is ethanol: water = 5.95 vol %. The ethanol concentrations both in the feed and in the permeate were determined using a model GC 380 gas chromatograph (GL Sciences Inc., Tokyo, Japan). Here, the flux is defined by the following equation: 

\[ J = \frac{Q}{A \cdot t} \]

where \( J \), \( Q \), \( A \), and \( t \) are the permeation flux (kg/m²·h), total amount of permeation (kg), membrane area (m²), and operating time (h), respectively. The selectivity is expressed in terms of the separation factor \( \alpha \) (EtOH/H₂O), which is defined as follows:

\[ \alpha = \frac{C_{p(\text{EtOH})}}{C_{p(\text{H₂O})}} \cdot \frac{C_{f(\text{H₂O})}}{C_{f(\text{EtOH})}} \]

where \( C_{p(\text{EtOH})} \) and \( C_{p(\text{H₂O})} \) represent the volume fractions of ethanol and water (vol %) in the permeate, respectively. \( C_{f(\text{EtOH})} \) and \( C_{f(\text{H₂O})} \) represent the volume fractions of ethanol and water (vol %) in the feed solution.

3. Results and discussion

The photographs of silicalite membrane surface before and after the silylation treatment using TMCS are shown in Fig. 2. No impurities were observed on the crystal surface of the unmodified silicalite membrane. After the silylation, small dots adhering to the surface of the crystal were observed. Although these materials were not analyzed further, these results showed that the surface of the silicalite membrane has been modified. The effect of surface treatment on the silicalite membranes was evaluated in terms of wettability.

Figure 3 shows the images of contact angle measurements and the value of the contact angles. The silicalite separation membrane formed on the outer surface of the tubular support. Therefore, the contact angle was measured on the surface of the dense separation layer. The contact angle of the unmodified silicalite membrane was 20°. After silylation using TMCS as the silylation reagent, the hydrophobicity of the surface increased the most, and the contact angle was 130°. This result showed that the reaction shown in Eq. (1) took place. When MTCS, PTCS, and TFPTCS were used as the silylation reagent, the contact angles

![Fig. 1. Apparatus for silylation.](image-url)

![Fig. 2. Laser microscope images of silicalite membrane surface before and after silylation using TMCS. (a) Unmodified silicalite membrane surface, (b) modified silicalite membrane by TMCS.](image-url)
The separation factor was 81 (b) TMCS, (c) MTCS, (d) PTCS, and (e) TFPTCS. Feed solution: 5 vol % EtOH-water mixture. The contact angle of the treated surfaces was lower than the hydrophobicity of the surface treated with TMCS. Thus, the hydrophobicity of those treated surfaces decreased compared to the case where TMCS was used. Therefore, the density of the silylation reagents per unit area of the silicalite membrane surface decreased compared to the case where TMCS was used. Thus, the hydrophobicity of those treated surfaces was lower than the hydrophobicity of the surface treated by TMCS.

The fluxes of water and ethanol through the modified membranes and the separation factor are shown in Figs. 4 and 5, respectively. Here, each membrane was prepared independently, and the membrane performance was evaluated independently. The value of the membrane separation performance of the unmodified silicalite membrane is the geometric mean of multiple membranes separation performances, and the standard deviation of variation in their performance is indicated by an error bar. The total flux of the unmodified silicalite membrane was 0.32 (±0.02) and 1.38 (±0.12) kg/m²·h at 30 and 60°C, respectively, and the separation factor was 81 (±16) and 74 (±13) at 30 and 60°C, respectively. The total flux of the membranes after the silylation using TMCS, MTCS, and PTCS was almost the same as that of the unmodified silicalite membrane at 30°C. On the other hand, at 60°C, the flux of the modified membranes showed almost the same and/or slightly lower values. The flux of the membrane modified using TMCS was 0.31 and 1.38 kg/m²·h at 30 and 60°C, respectively, and the separation factor was 115 and 97 at 30 and 60°C, respectively. In the case of MTCS, the total flux was 0.34 and 1.35 kg/m²·h at 30 and 60°C, respectively, and the separation factor was 86 and 83 at 30 and 60°C, respectively. In the case of PTCS, the total flux was 0.31 and 1.28 kg/m²·h at 30 and 60°C, respectively, and the separation factor was 90 and 88 at 30 and 60°C, respectively. An improved separation factor was clearly observed only for the membranes modified using TMCS. The separation factor of the modified membranes increased because of the improvement in hydrophobicity of the membrane surface. It is apparent that the contact angle of the surfaces increased upon modification. The separation factor of the membranes modified using MTCS or PTCS slightly increased than that of the unmodified membrane. This result is consistent with that of the contact angle. However, because we do not have enough data to support these results, we do not discuss them in this paper. In the case of TFPTCS, total flux was 0.13 and 0.43 kg/m²·h at 30 and 60°C, respectively, and the separation factors were 10 and 9 at 30 and 60°C, respectively. The membrane performance in this case was significantly low. Fluorine atoms, which have excellent water and oil repelling properties, are present in TFPTCS. Therefore, the total flux decreased because the membrane reduced the permeation of ethanol. In order to clarify the detailed effect of silylation, it is still important to investigate the change in the pore-size distribution from gas permeation behavior, coverage of the silanol groups on the surface of the membranes, etc.

4. Conclusions

The improvement in the separation performance of tubular silicalite membranes was investigated by increasing their surface hydrophobization using silylation. The silylation of tubular silicalite membranes using TMCS was found be an effective method for hydrophobization. The PV showed high performance with permeate EtOH concentration of 85.9 vol % (separation factor α of 115) with a total flux of 0.31 kg/m²·h from a 5 vol % aqueous EtOH solution at 30°C.

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Fig. 3. Water drop contact angles on silicalite membrane surfaces. (a) Unmodified silicalite membrane, and silicalite membranes modified by (b) TMCS, (c) MTCS, (d) PTCS, and (e) TFPTCS.

Fig. 4. The flux of the silicalite membrane with various silylation reagents. PV at (a) 30°C and (b) 60°C; Feed solution: 5 vol % EtOH-water mixture.

Fig. 5. The separation factor of the silicalite membranes with various silylation reagents. Feed solution: 5 vol % EtOH-water mixture.
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