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PREPARATION OF SILICALITE PERVAPORATION MEMBRANE WITH ETHANOL PERMSELECTIVITY BY A 2-STEP HYDROTHERMAL SYNTHESIS

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ABSTRACT

The effect of a 2-step hydrothermal synthesis on the formation of silicalite membrane was investigated. Pervaporation performance of the membrane after the 2nd synthesis depended on its compactness after the 1st synthesis. Based on the cross-section of the membrane by scanning electron microscopy we suggested that the surface of the 1st step layer was made dense. The 2-step hydrothermal synthesis reduced the synthesis time by a factor of 2 while maintaining a high separation factor for the ethanol-water system.

Key Words: Silicalite; Zeolite; Ethanol permselectivity; Pervaporation; Hydrothermal synthesis

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INTRODUCTION

Recently, inorganic membranes have been the focus of much attention because they exhibit both high thermal stability and excellent resistance to organic solvents. Zeolite is an inorganic material that is an optimum candidate for being material of a molecular sieving membrane because it has uniform pore size. Silicalite, a type of zeolite, is more hydrophobic than any other zeolite because it has no aluminium inside its structure, and its zeolitic pore size is approximately 6 Å.

First, we prepared zeolite separation membranes that consisted only of silicalite crystals (1). We hydrothermally synthesized a pure silicalite membrane on a porous stainless steel support at 170°C for 48 hours and calcined at 500°C. The silicalite membrane exhibited very high ethanol permselectivity for a 5% (vol) ethanol aqueous solution (2). We then investigated the preparation conditions of silicalite membrane, such as the composition of the starting solution for hydrothermal synthesis and the calcination temperature and period, to prepare the silicalite membrane without cracks and intercrystalline regions. The prepared membrane showed separation factor α (EtOH-H_2O) of 120 with a total flux of 0.29 $kg/m^2 \cdot h$ for a 5% (vol) aqueous ethanol solution at 30°C (3). However, this synthesis method, in which generation of silicalite seed crystals and their growth occur at one hydrothermal synthesis, requires a long membrane preparation time. Furthermore, the preparation of membranes with high ethanol permselectivity were not highly reproducible. These are disadvantages for industrial manufacturing of silicalite membranes.

In this study, to shorten the period of the hydrothermal synthesis, we prepared silicalite membranes with a 2-step hydrothermal synthesis through the use of 2 synthesis mixtures of different compositions.

EXPERIMENTAL

The silicalite membranes were prepared on porous supports of sintered stainless steel (2 μm) by hydrothermal synthesis (4). The first synthesis was performed at 170°C for 6 to 48 hours with a synthesis solution where the ratio of H_2O to SiO_2 was 60 to 1 in view of crystal generation. After hydrothermal synthesis, the silicalite membrane was washed with distilled water and dried at 100°C for 24 hours. The second synthesis was performed at 170°C for 24 hours with a synthesis solution where the ratio of H_2O to SiO_2 was 90 to 1 or higher in view of crystal growth. After the second synthesis, the membrane was calcined for 60 hours at 375°C (heating rate: 15°C/h) in an electric furnace to remove the organic template.

After the first synthesis, the water permeability of the membranes was measured by ultrafiltration (UF) test, where applied pressure was under 3 kg/cm^2 by N_2 at room temperature.

After the second synthesis and calcination, the separation performance of the membranes was measured by pervaporation with a stainless steel cell previously developed in our laboratory (5). An ethanol aqueous solution of 5% (vol) was used as a feed at 30°C. The concentrations of permeate and feed were analyzed by gas chromatography. Pervaporation performance of silicalite membranes was evaluated by the separation factor α (EtOH-H_2O) and flux.

Scanning electron microscopy (SEM) observation was performed to characterize the membrane morphology. Special stainless steel supports were prepared for SEM observation so that a cross-section of a membrane with support could be seen.

RESULTS AND DISCUSSION

The generated silicalite grains were considered to be intergrown during the long hydrothermal synthesis period that resulted in a high separation factor α (EtOH-H_2O) of 120 as previously reported (3). In this study, the main purpose of the first synthesis was generating crystals and that of the second synthesis was making the membrane dense.

In the first synthesis the weight (g) of the generated silicalite crystals was increased with an increasing synthesis period. The water permeability of the membrane after the first synthesis decreased with increasing amounts of generated silicalite crystals, and the membrane synthesized for 48 hours shows almost zeros in fluxes. After the first synthesis no membrane could be measured by pervaporation performance because the fluxes were too high.

Table 1 shows the pervaporation performance of silicalite membranes. Silicalite membranes with ethanol permselectivity in pervaporation were success-

Table 1. Pervaporation Performance of Silicalite Membranes by a 2-Step Hydrothermal Synthesis

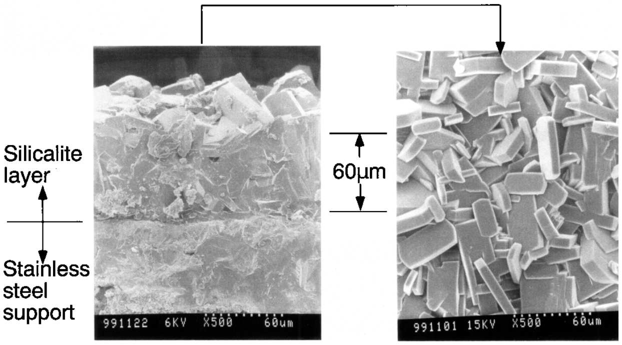
Membrane No.	Period of 1st Synthesis (h)	Water Permeability of the Membrane After 1st Synthesis ($t/m^2 \cdot D \cdot MPa$)	Total Flux in Pervaporation ($kg/m^2 \cdot h$)	Ethanol Concentration of Permeate (vol %)	Separation Factor α (EtOH-H_2O)
1	24	4.61	—	—	—
2	24	3.85	0.48	25.1	6
3	48	0.33	0.33	78.5	70
4	48	0.00	0.24	82.0	86

Hydrothermal synthesis conditions at 170°C for 48 hours (1st synthesis), for 24 hours (2nd synthesis). Synthesis solution $H_2O/SiO_2 = 60$ (1st synthesis), 90 (2nd synthesis).
Water permeability was measured by UF test.
Total flux was measured by pervaporation using a 5 %(vol) EtOH aqueous solution at 30°C as a feed.
Flux was too large to measure pervaporation performance.

fully prepared by a 2-step hydrothermal synthesis method. The effect of the membrane compactness after the first synthesis on the pervaporation performance of the membrane after the second synthesis was investigated. The membrane prepared from the high water permeable membrane, as determined by UF test after the first synthesis, showed low ethanol permselectivity in pervaporation because the membrane could not be made dense during the second synthesis. However, the membrane prepared from the membrane with low water permeability (values of near zero by UF test after first synthesis) showed high ethanol permselectivity in pervaporation; the concentration of permeate was about 80% (vol). We concluded that the compactness of the membrane after the first synthesis controls membrane pervaporation performance after the second synthesis.

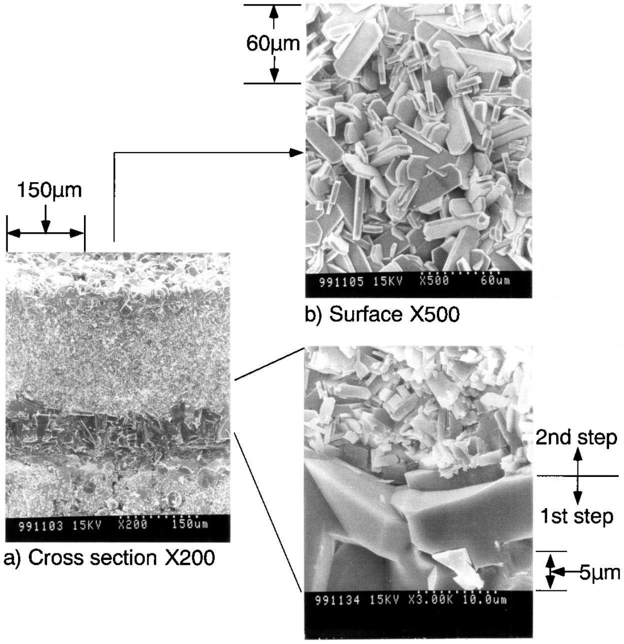
The effect of the H_2O-SiO_2 ratio of the second synthesis was investigated. Silicalite membranes with high ethanol permselectivity could be obtained with a H_2O-SiO_2 ratio of approximately 90–100. However, flux of a membrane synthesized with a H_2O-SiO_2 solution ratio of 150 for the second synthesis was too high to be measured by pervaporation performance. The silica amount in the mixture with a H_2O-SiO_2 ratio of 150 was too low to make the membrane dense.

The surface and cross-section of a silicalite membrane were observed by SEM. The photographs of a membrane after the first synthesis are shown in Fig. 1. A membrane consisted of large crystals. Figure 2 shows the photographs of the membrane surface and cross-section after the second synthesis. The membrane prepared by the 2-step hydrothermal synthesis method consisted of 2 layers. A clear boundary between the first synthesis layer and the second synthesis layer was observed. Small silicalite crystals were observed in the second synthesis layer. The sizes of the surface crystals were approximately 10 μm, and no inter-



a) Cross section X500 b) Surface X500

Figure 1. SEM images of the surface and the cross-section of the silicalite membrane on a stainless steel support after first synthesis. The hydrothermal synthesis condition was 170°C for 48 hours, and the synthesis solution was $H_2O/SiO_2 = 60$.



a) Cross section X200

b) Surface X500

c) Cross section X3000

Figure 2. SEM images of the silicalite membrane surface and cross-section on stainless steel support after the second synthesis. The hydrothermal synthesis condition was at 170°C for 48 hours (first synthesis) and 24 hours (second synthesis), and the synthesis solution was $H_2O/SiO_2 = 60$ (first synthesis) and 100 (second synthesis).

grown layer could be observed. Based on the SEM photographs, we suggest that the formation process of silicalite membrane is as follows: In the first synthesis, silicalite crystals generate on the stainless steel support. We believe that, because it could not be measured by pervaporation, in this step the membrane was not dense. During the second synthesis, many small crystals fell out of the bulk mixture. Because no intergrown layer could be observed in the second step layer and the membrane after the first synthesis did not show pervaporation performance, we suggest that the surface of first step layer was made dense by both the intergrowth of silicalite grains and the deposition of small silicalite crystals from the bulk mixture during the second synthesis.

From the above results, we concluded that through the 2-step hydrothermal synthesis method, the synthesis period was reduced to one-half (72 h) that previously reported (3). Furthermore, reproducibility was improved because the compactness of the membrane after the first synthesis could be estimated.

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