Preparation of high selectivity silicalite-1 membranes by two-step *in situ* hydrothermal synthesis

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High selectivity silicalite-1 membranes were synthesized on silica tubes by *in situ* hydrothermal synthesis. Using a two-step synthesis, a membrane with a separation factor of 99 was prepared for separating an ethanol/water mixture at 60°C. The average ($n=4$) flux and separation factor of the membranes were $0.47 \text{ kg m}^{-2} \text{ h}^{-1}$ and 89, respectively. The membranes exhibited high reproducibility, and the relative standard deviation of the average ($n=4$) flux and separation factor were only 5.3% and 9.2%, respectively. These results suggest that silica is a suitable support for synthesis of high-performance silicalite-1 membranes.

high-selectivity, silicalite-1 membrane, hydrothermal synthesis, pervaporation, silica tube

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In recent years, much progress has been made in the preparation, characterization, and industrial application of zeolite membranes [1–3]. Zeolite membranes with excellent separation performance in a wide range of industrial processes, including gas separation, catalysis, pervaporation, and membrane reactors, have been produced [4–6]. Zeolite membranes can be used to separate different mixtures, and have low energy consumption and are environmentally friendly. Consequently, zeolite membranes have attracted attention in the field of separation technology [7–9].

In 2001, Morigami group [10] reported the first large-scale pervaporation plant made of 16 NaA membrane modules, which produced 530 L/h of solvents at less than 0.2 wt% of water from 90 wt% solvent at 120°C. Compared with NaA or FAU membrane, FMI (including ZSM-5 and silicalite-1) membranes are still prepared and used within different laboratories up to now, and this may be caused by the following reasons: one is the higher preparation cost compared with NaA or FAU membranes, and another reason is

that MFI membranes should be calcined in order to remove the templates, and this often results in the formation of cracks, which decreases the separation performance of the as-synthesized membranes [11]. Furthermore, the low separation performance and low reproducibility may be the main reason to limit the preparation of MFI membranes in large-scale [12].

An important potential application of hydrophobic silicalite-1 membranes is the separation of organic compounds, such as ethanol, 1-butanol, and other fermentation products, from fermentation broth [13,14]. In this application, silicalite-1 membranes show higher separation performance than polymer membranes [15]. Hydrophobic silicalite-1 membranes may also be used to extract small organic molecules from wastewater for recycling and to reduce environmental pollution. In order to prepare silicalite-1 membranes, *in situ* hydrothermal synthesis is often used to prepare silicalite-1 membranes because the conditions are simple to control. However, it is not easy to obtain high-performance membranes with this method. High-performance silicalite-1 membranes can be obtained by using the secondary growth

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method, but reproducible deposition of a thin, compact and defect-free seed layer on different supports, especially large tubular porous supports, is not an easy work. Therefore, how to further improve the separation performance of silicalite-1 membranes is highly desirable, which will accelerate the industrial applications of zeolite membranes.

In this study, silicalite-1 membranes with high selectivity and reproducibility were prepared on silica tubes by *in situ* hydrothermal synthesis. The effect of aging and the crystallization times on membrane performance was investigated.

1 Experimental

1.1 Synthesis of silicalite-1 membranes

Porous silica tubes were prepared in our laboratory by the casting method. The silica tubes had the following dimensions: outer diameter, 11 mm; inner diameter, 7 mm; length, 9 cm; pore diameter, 0.3 μm ; and porosity 45%. Before hydrothermal synthesis, all the tubes were polished with sand paper, washed ultrasonically with deionized water, and calcined at 500°C for 5 h to remove organics adsorbed on the surface.

Two synthesis solutions were prepared by mixing TPABr, NaOH, silica sol (SiO_2 mass fraction 26%), and deionized water at room temperature in the following amount-of-substance ratios: TPABr: Na_2O : SiO_2 : H_2O =1:0.25:10: X ; solution 1, $X=600$, and solution 2, $X=1000$. Solution 1 was used for a one-step *in situ* hydrothermal synthesis. Before each hydrothermal synthesis, a section of the silica tubes was filled with a mixed solution of water and glycerol or left empty, and then the tubes were sealed with a Teflon caps at each end. After adding the synthesis solution, the autoclaves were aged at 75°C for 0–12 h, and then the oven temperature was increased to 180°C. The crystallization time for one-step synthesis was 24 h, and the crystallization times for the two-step synthesis were 8–16 h (solution 1, first crystallization) and 10 h (solution 2, second crystallization). After each crystallization, the synthesized membranes were washed with deionized water, dried at 80°C overnight, and then calcined at 500°C for 12 h to remove the templates.

1.2 Membrane characterization

The surfaces and cross sections of the silicalite-1 membranes were characterized by scanning electron microscopy (SEM, JEM-1200, Jeol, Tokyo, Japan). The thickness of each silicalite-1 membrane was estimated from the cross section SEM.

1.3 Pervaporation measurements

Evaluation of the separation performance of the membranes for ethanol/water (ethanol mass fraction 3%) mixtures was carried out at 60°C on standard pervaporation apparatus. A

centrifugal pump circulated the feed through the system to reduce concentration polarization. The permeation and feed concentrations of ethanol and water were measured by off-line gas-chromatography (GC, Agilent 5890). The total flux was calculated by weighing the condensed permeate. The separation factor was determined as $\alpha_{A/W} = (Y_A/Y_W)/(X_A/X_W)$, where X_A , X_W , Y_A , and Y_W denote the mass fractions of components A (ethanol) and W (water) on the feed and permeate sides, respectively.

2 Results and discussion

2.1 Effects of aging time

Figure 1 shows the SEM images of the silicalite-1 membranes prepared by the one-step hydrothermal synthesis with different aging times. There was an obvious hole in the membrane prepared without aging (Figure 1(a)), and the dimensions of the zeolite crystals were larger along the *a*- and *b*-axes than those of membranes that were prepared with aging. Li et al. [16] found that aging decreased the crystal size, and this is consistent with the results obtained in the present study. The thickness of the membrane prepared without aging was about 35–40 μm (Figure 1(b)). After aging for 4–12 h, the membrane thickness decreased, which should improve the membrane flux. After aging for 4 and 8 h (Figure 1(d) and (f)), the membranes thickness were about 30 μm . The membrane surface also became more compact after aging, and this can be seen in Figure 1(c), (e), and (g). A compact membrane surface can contribute to the improvement of the separation selectivity, and this was verified by the data shown in Table 1.

The membrane that was not aged (membrane S-1) showed high flux but low selectivity (Table 1), which may be caused by the pinhole or cracks. An earlier study by our group showed that aging before crystallization was effective for formation of crack-free membranes [17], which was useful for improving membrane selectivity. Compared with membrane S-1, all the aged (4–12 h) silicalite-1 membranes showed higher selectivity towards ethanol/water mixtures. Among all the membranes, membrane S-3 (aged 8 h) had the highest average separation factor (78) and average flux (0.41 $\text{kg m}^{-2} \text{h}^{-1}$), which shows that aging at 75°C for 8 h optimizes membrane separation performance. All the membranes prepared by the one-step hydrothermal synthesis in this study had lower separation performance than the membranes from our earlier study [17], which indicated that the present synthesis conditions needed to be optimized.

2.2 Effect of the first crystallization time

The effect of the first crystallization time in the two-step synthesis on the separation performance of the silicalite-1 membranes was evaluated (Table 2). For the membrane SS-1, the first crystallization time was not long enough, and

Figure 1 SEM images of silicalite-1 membranes prepared by one-step *in situ* hydrothermal synthesis with different aging times. (a), (b) 0 h; (c), (d) 4 h; (e), (f) 8 h; (g), (h) 12 h. Images (a), (c), (e), and (g) are of the surface, and images (b), (d), (f), and (h) are of the cross section of the membrane.

a complete membrane was not formed on the silica tubes. After extending the first crystallization time from 8 to 16 h, all the membranes showed high separation performance towards ethanol/water mixtures, and membrane SS-7 had the highest separation factor (99) (Table 3). These results show that shorter crystallization times can result in incomplete membrane formation, while longer crystallization times may increase the membrane thickness, which can

decrease the membrane flux. These results were used to select the optimum first crystallization time for preparation of high-performance silicalite-1 membranes.

2.3 Improvement of the silicalite-1 membranes

Figure 2 shows the SEM images of silicalite-1 membranes synthesized by the two-step *in situ* hydrothermal synthesis.

Table 1 Separation performance of silicalite-1 membranes prepared by one-step *in situ* hydrothermal synthesis with different aging times^{a)}

Membrane No.	Aging temperature (°C)	Aging time (h)	Synthesis time (h)	Filling	EtOH/H ₂ O (3 wt% EtOH)	
					Flux (kg m ⁻² h ⁻¹)	Separation factor
S-1	75	0	24	Yes	0.55	45
S-2	75	4	24	Yes	0.29	74
S-3	75	8	24	Yes	0.41	78
S-4	75	12	24	Yes	0.38	72

a) Average ($n=2$).**Table 2** Separation performance of silicalite-1 membranes synthesized by two-step *in situ* hydrothermal synthesis with different times for the first crystallization

Membrane No.	Aging temperature (°C)	Aging time (h)	Synthesis time (h)	Filling	EtOH/H ₂ O (3 wt% EtOH)	
					Flux (kg m ⁻² h ⁻¹)	Separation factor
SS-1 ^{a)}	75+75	8+8	8+10	Yes	—	—
SS-2 ^{a)}	75+75	8+8	10+10	Yes	0.75	43
SS-3 ^{a)}	75+75	8+8	12+10	Yes	0.51	60
SS-4 ^{b)}	75+75	8+8	14+10	Yes	0.47	89
SS-5 ^{a)}	75+75	8+8	16+10	Yes	0.42	78

a) Average ($n=2$); b) average ($n=4$).**Table 3** Separation performance of silicalite-1 membranes prepared by the optimized two-step hydrothermal synthesis

Membrane No.	Aging temperature (°C)	Aging time (h)	Synthesis time (h)	Filling	EtOH/H ₂ O (3 wt% EtOH)			
					Flux (kg m ⁻² h ⁻¹)	RSD ^{a)}	Separation factor	RSD ^{a)}
SS-6	75+75	8+8	14+10	Yes	0.49	5.3%	77	9.2%
SS-7	75+75	8+8	14+10	Yes	0.46		99	
SS-8	75+75	8+8	14+10	Yes	0.49		87	
SS-9	75+75	8+8	14+10	Yes	0.43		94	
SS-10	75+75	8+8	14+10	No	0.33		88	
SS-11	75+75	8+8	14+10	No	0.23		90	

a) RSD was calculated with STDEVP/average.

By compared Figure 2 with Figure 1 (e) and (f), the following obvious differences can be found: one is that the surface compactness of Figure 1 (e) is better than that of Figure 2 (a), and the crystal size of the former in *a*-axis and *b*-axis is larger than that of the later. Another difference is that the thickness of membrane Figure 2(b) is higher than that of membrane Figure 1(f). These differences indicate that the membranes produced by the one-step synthesis should show higher separation performance. However, in the experimental results, the membranes produced by the two-step synthesis showed higher separation performance than the one-step membranes (Tables 1, 2, and 3). This may have been a result of the crystal dimensions along the *a*- and *b*-axes, which determine the diffusion path of molecules through the membrane. The small holes and/or cracks in the membranes produced by the one-step synthesis would also decrease the separation selectivity of these membranes. Furthermore, the short first crystallization time for the two-step membranes may result in the formation of more inter-crystalline pathways. These pathways may be covered by the second crystallization, which would produce silicalite-1 membranes with high separation selectivity.

To improve the separation performance of the silicalite-1 membranes, the silica tubes were filled with water and glycerol, which has a high boiling point (bp 290°C). All the membranes produced by this method showed high separation performance for ethanol/water mixtures (Table 3), and membrane SS-7 had the highest separation factor (99) and flux (0.46 kg m⁻² h⁻¹). The average flux and separation factor of four of the membranes (SS-5 to SS-9) were 0.47 kg m⁻² h⁻¹ and 89, respectively. The results showed high reproducibility, and the relative standard deviations of the average total flux and separation factor were only 5.3% and 9.2%, respectively. The silica support may contribute to the high reproducibility because it has similar properties to silicalite-1 layer, and this may eliminate the formation of cracks during calcination. Furthermore, an earlier study by our group showed that membranes synthesized on silica tubes exhibited higher thermal stability than membranes synthesized on alumina tubes, and the separation performance of the later decreased obviously after calcination at 400°C for 5 h with a heating rate of 2°C min⁻¹ [18]. Compared with membranes synthesized with filled tubes, the average flux of the membranes prepared without filling was

Figure 2 (a) Surface and (b) cross section SEM images of silicalite-1 membrane prepared by the two-step *in situ* hydrothermal synthesis (SS-4, Table 2).

lower ($0.28 \text{ kg m}^{-2} \text{ h}^{-1}$), and the flux was improved by about 67% after filling the silica tubes. This result is similar to that in our earlier report [17]. These results show that choosing a suitable method for membrane preparation is important for improving the membrane flux, and the corresponding experiments, such as carbonizing polymer method, are carrying out.

3 Conclusions

Highly selective silicalite-1 membranes were synthesized on silica tubes by simple *in situ* hydrothermal synthesis. All the membranes showed high separation performance towards ethanol/water mixtures. The reproducibility of the separation with the membranes was high. These results suggest that silica is a suitable support for preparation of silicalite-1 membranes with high-performance and high-reproducibility.

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