Preparation of Low Silica X–type Zeolite Membranes on Porous Support by Microwave Heating

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Microwave heating was applied for the synthesis of faujasite zeolite membranes. Dense zeolite layers with very low Si/Al ratio (≈ 1.1) were formed on the seeded α–Al₂O₃ supports in a shorter synthesis time than the conventional method. Membranes showed high dehydration performance in the pervaporation of H₂O/ethanol (a = 387, Flux = 2.67 kg m⁻² h⁻¹) and H₂O/i–propanol (a = 2900, Flux = 3.53 kg m⁻² h⁻¹).

Key words : zeolite membrane / microwave heating / X–type zeolite / pervaporation / dehydration

1. Introduction

The interest in zeolite membranes has grown in the last decades driven mainly by the potentials that the membranes can be applied as a device for the separation of gases and liquids, as catalytic reactors, and as sensors. Zeolite membranes are conventionally synthesized by static hydrothermal synthesis. Successful scale–up and industrialization of such process is reported recently. Other methods, such as dry-gel conversion, vapor phase transport and microwave synthesis can also be employed. Microwave synthesis is getting more attention as it can drastically shorten the crystallization time of zeolites compared to the conventional heating systems. Various types of zeolite membranes, such as LTA, FAU, MFI, SOD and ETS, have been synthesized by microwave assisted heating. This method facilitates homogeneous heating of the synthesis gel and can also inhibit the formation of impurities. Due to the accelerated nucleation in the microwave heating, this approach can result in thinner and denser membrane morphologies from those formed in using the conventional heating methods.

The perm–selectivity of zeolite membranes is strongly affected by the zeolitic pore size, the composition of the zeolite and the morphology of the membrane. For example, lowering the Si/Al ratio of the zeolite framework increases the hydrophilicity of the membrane. While MFI zeolite membranes with infinite Si/Al ratio selectively permeate alcohol, MFI membranes with low Si/Al ratio show dehydration properties. In FAU zeolites, the Si/Al ratio can vary generally from 1 to 3 (FAU zeolite with Si/Al ratio lower and larger than 1.5 are also called X–type and Y–type zeolites, respectively). The possibility to control the Si/Al ratio of zeolite membranes will enable to optimize the membrane compositions for the applications.

Zhu et al. reported FAU membrane formation by applying “in situ aging”, where porous supports were immersed in the synthesis solution, followed by a microwave heating. We have reported the preparation of LTA and FAU membranes by combining the secondary growth method and the microwave system. In this case, supports were covered with seed crystals beforehand the hydrothermal synthesis. We found that the synthesis time can be reduced by applying the microwave heating compared to the conventional heating. The synthesis conditions of low silica zeolite X membranes by microwave heating were investigated in this study. The concentration of the synthesis gel is one of the parameters affecting the type of zeolite to be formed during the hydrothermal synthesis. For example, by doubling the water content of the gel, the main
zeolite type formed during the synthesis changed from X type to A type. In this report, the influence of the synthesis gel concentration on the membrane formation was investigated. Perm-selectivity of the FAU membranes was investigated in the dehydration of alcohol solutions.

2. Experimental

2.1 Membrane preparation

The chemicals used in the preparation of synthesis gels were water glass (sodium silicate solution, 26.5 wt% SiO$_2$, 10.6 wt% Na$_2$O, Aldrich), sodium aluminate (NaAlO$_2$, Al/NaOH = 0.80, Wako), sodium hydroxide (97 wt% NaOH, Wako), potassium hydroxide (85 wt% KOH, Wako) and deionized water. The starting gels with molar composition of 2.2 SiO$_2$: Al$_2$O$_3$: 5.5 Na$_2$O: 1.65 K$_2$O: xH$_2$O (x = 120 ~ 200) were prepared. NaAlO$_2$, NaOH and KOH were firstly dissolved in water until to form a clear solution. Water glass was then added under vigorously stirring. After stirred for about 1 h, the gel solution was sealed in a polypropylene bottle and aged under static conditions for 3 h at 70°C. Porous α-Al$_2$O$_3$ tubes with outer diameter of 1.2 cm, average pore size of 1.0 μm and porosity of 33% (provided from Nikkato) were rubbed with a water slurry of NaY zeolite seed crystals (HS–320, crystal size = 0.3 μm, Si/Al = 2.5, Wako) and then dried in air overnight. Then the seeded support was vertically placed in a PTFE-lined glass vessel and immersed in the aged gel. The reaction vessel was heated by a microwave oven (frequency = 2450 MHz, P$_{\text{max}}$ = 1.5 kW, Shikoku Instrumentation Co.; operated under auto-controlled peak power, duty cycle = 50% and period = 10 s) to 100°C in 10 min and held at 100°C for 2.5 h under atmospheric pressure. After the synthesis, membrane samples were cleaned thoroughly with deionized water and dried at 60°C for 6 h.

2.2 Membrane characterization and perm-selectivity tests

The structure of zeolite membranes and crystals were characterized by X-ray diffraction (XRD, Rigaku, Smartlab) with Cu–Kα radiation. The morphology of the membranes was observed by field emission scanning electron microscopy (FE–SEM, JEOL JSM 6335F). The Si/Al ratio of the powder samples formed in the reaction vessel during the membrane preparation was determined using an inductively coupled plasma-atomic emission spectrometer (ICP–AES, Perkin–Elmer 4300 DV). The Si/Al ratio of the membrane was analyzed by Energy dispersive X-ray spectroscopy (EDAX).

Pervaporation (PV) experiments were carried out using apparatus described elsewhere. The effective membrane area was 18.8 cm$^2$ and the downstream pressure was maintained bellow 100 Pa. Synthetic mixtures of water/ethanol (EtOH) and water/iso–propyl alcohol (IPA) were used as feed solutions and applied to the outer surface of the membrane at 75°C. The membrane performance was evaluated by a total permeation flux (J [kg m$^{-2}$ h$^{-1}$]) and a separation factor ($\alpha$ [–]).

3. Results and discussion

One of the challenges to synthesize low-silica FAU zeolites is to avoid impurities such as LTA zeolite. Contamination of undesirable phases can be avoided by optimizing the gel compositions, aging time and synthesis conditions. Fig. 1 shows the XRD patterns of the Faujasite zeolite (X-type) standards (international center for diffraction data (ICDD)), α–Al$_2$O$_3$ and zeolite membranes from gels with molar composition of 2.2 SiO$_2$: Al$_2$O$_3$: 5.5 Na$_2$O: 1.65 K$_2$O: xH$_2$O: x = 122 (a), x = 180 (b) and x = 200 (c). ▼, A-type zeolite peak.
lite besides peaks of the α-Al₂O₃ support. For the membranes synthesized in the gel having the lowest water amount (x = 122), very weak peaks at 2θ = 7.2° and 14.4° appeared (Fig. 1(a)) which correspond to LTA zeolite. Peaks related to LTA zeolite were not found in membranes prepared in higher water content. Higher alkalinity with less water content in the synthesis gel may have accelerated the dissolution of alumina support. Increased aluminum concentration at the support surface may have favored the nucleation of A type zeolite.

The morphology of membranes were observed by SEM. Fig. 2 (a), (c) and (e) show the surface SEM images of the membranes obtained in gels with various H₂O content. In all cases, membranes were completely covered with micron meter sized crystals. A clear difference in the surface morphology by the synthesis gel composition can be noticed. The membrane formed in the most concentrated gel (Fig. 2 (a), (b)) was covered by aggregated octahedron FAU crystals and with some larger cubic zeolite crystals. These cubic crystals were the typical morphology of A-type zeolite which also agreed with the result of XRD analysis (Fig. 1 (a)). On the contrary, the size and shape of the crystals were rather uniform on the membranes formed in gels in x = 180 and x = 200 (Fig. 2 (c) and (e)). Dense zeolite layers were formed on the support surface with thickness about 6 μm as seen in the cross-sectional SEM images (Fig. 2 (b), (d) and (f)).

The Si/Al ratios of the crystals formed in the synthesis gel of x = 200 during the membrane preparation measured by ICP and that of the zeolite membranes measured by EDAX were about 1.1 even though the Si/Al ratio of the seed was 2.5. The results suggest a strong influence of nucleation in the gel on the membrane formation. The Si/Al ratio is smaller compared to the reported values of FAU membranes: e.g. ≤1.3 ~ 1.5[^11] and 1.3[^6]. Formation of low silica X-type zeolite (LSX) membranes may be attributed to the lower Si/Al ratio of the synthesis gel: the Si/Al ratios were 1.1 in this study and 1.3 in the former studies[^6].

Table 1 shows the total flux (J) and the separation factor (α) of PV for H₂O/alcohol mixtures through LSX zeolite membrane together with previously reported results of FAU and NaA zeolite membranes. FAU and NaA zeolite membranes were highly selective for permeating water with high permeation flux. We have reported that both the flux and the separation factor increased with decreasing the Si/Al ratio of the zeolite membrane in water/ethanol separation using FAU membranes[^10]. Similar trend can be seen when comparing the LSX membranes with other membranes prepared in a conventional heating system. Higher hydrophilicity of the membrane with less Si/Al ratio may have enhanced the adsorption of water and result-

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Si/Al ratio</th>
<th>Feed</th>
<th>Temp. [°C]</th>
<th>J</th>
<th>α</th>
<th>Heating system</th>
<th>Synthesis time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSX[^1]</td>
<td>1.1</td>
<td>H₂O:EtOH</td>
<td>75</td>
<td>2.67</td>
<td>187</td>
<td>Microwave</td>
<td>2.5</td>
<td>This work</td>
</tr>
<tr>
<td>LSX[^2]</td>
<td>1.1</td>
<td>H₂O:EtOH</td>
<td>75</td>
<td>3.53</td>
<td>2300</td>
<td>Microwave</td>
<td>2.5</td>
<td>This work</td>
</tr>
<tr>
<td>LSX[^3]</td>
<td>1.1</td>
<td>H₂O:EtOH</td>
<td>75</td>
<td>3.04</td>
<td>1800</td>
<td>Microwave</td>
<td>2.5</td>
<td>This work</td>
</tr>
<tr>
<td>NaA[^10]</td>
<td>1</td>
<td>H₂O:EtOH</td>
<td>75</td>
<td>2.15</td>
<td>10000</td>
<td>Conventional</td>
<td>5</td>
<td>18</td>
</tr>
</tbody>
</table>

[^1]: x = 122,[^2]: x = 180,[^3]: x = 200 (2.25SiO₂:Al₂O₃:5.5Na₂O:1.65K₂O:xH₂O).[^11] Si/Al ratios are not indicated in the reference paper.
ed in the increase of both flux and selectivity. Both the total flux and the separation factor were higher in water/IPA separations than in water/ethanol separations. The higher separation factor in water/IPA system may be due to the size effect: IPA is a larger molecule than ethanol, thus, having more difficulties entering the zeolitic pores. On the other hand, the diffusivity of water in the zeolitic pores is inhibited by the organics in the pores \(^{12, 13}\). Accordingly, ethanol entered in zeolitic pores suppressed the water flux and resulted in smaller total flux than that in water/IPA system. Synthesis time for the preparation of dense FAU membranes can be shortened by applying microwave heating as reported with LTA membrane syntheses \(^8\): while longer synthesis time than five hours are generally required \(^{10, 14, 15}\) in a conventional heating system, membranes with equivalent dehydration properties were formed in 2.5 hours in this study. LTA zeolites appeared on the membrane surface prepared in the most concentrated gel (x = 122) as observed by XRD and SEM. LTA and FAU zeolites cannot be connected in atomic scale and will create defects at the boundary. On the contrary, the water content of the synthesis gel had no significant influence on the membrane dehydration properties. This may be due to the high water adsorption of both LTA and FAU zeolites that plugs the small defects with water, or may suggest a pure and dense FAU layer formation underneath the surface.

4. Conclusions

FAU zeolite membranes with low Si/Al ratio as 1.1 were successfully prepared on porous \(\alpha\text{–Al}_2\text{O}_3\) supports by combining the secondary growth method and the microwave heating system. FAU zeolite membranes were prepared in shorter synthesis time with microwave than with conventional heating method. The low silica X-type zeolite (LSX) membranes showed high dehydration performances in the dehydration of ethanol and isopropanol with PV.

References


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