Ion exchange of zeolite membranes by a vacuum ‘flow-through' technique

Seok-Jhin Kim, Christopher W. Jones, Sankar Nair, Yujun Liu, Jason S. Moore, Ravindra S. Dixit, John G. Pendergast Jr., Sagar Sarsani

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, GA 30332-0100, USA

Engineering & Process Sciences, The Dow Chemical Company, 2301 N. Brazosport Blvd, Freeport, TX 77541, USA

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Abstract

Ion exchange of nanoporous (e.g., zeolite) membranes is of increasing importance in their applications as separation devices and catalytic reactors. Ion exchange processes in zeolite membranes are significantly limited by slow hydrated-ion transport rates and the low liquid–solid interfacial area available in comparison to ion exchange of zeolites in powdered form, thereby leading to long membrane processing and regeneration times. Here, we consider ion exchange processes in zeolite membranes in more detail, and show the much higher efficacy of a vacuum-assisted liquid–vapor ‘flow-through' method in comparison to both the conventional ‘immersion/counter-diffusion' method as well as a liquid–liquid flow-through method. Na-MFI zeolite disk membranes, made by both in situ and seeded growth, were ion-exchanged with Ga³⁺, Zn²⁺, and Pt²⁺ ions in the temperature range of 23–70 °C and exchange times of 5–24 h. The penetration of these ions into the zeolite membranes was investigated in detail by energy-dispersive X-ray (EDX) spectroscopy. Surprisingly, the quantity of exchanged ions in the membranes via the vacuum-assisted ‘flow-through' technique is found to exceed that achieved by the other two methods by up to a factor of ten, with the liquid–liquid technique being the least efficient. Higher temperatures and longer ion exchange times increased the ion exchange efficiency in the vacuum-assisted method. Chemical analysis of the condensed permeate solution by inductively-coupled plasma (ICP) mass spectrometry revealed that both the original Na⁺ and replacement metal cations moved through the membrane in a co-current manner, unlike the conventional counter-current movement of ions in the immersion process. The Na⁺ ions in the membrane experience pressure-driven transport (along with water molecules) to the permeate side, and leave the membrane surface as hydrated vapor-phase cations, thereby allowing the maintenance of a high driving force for ion exchange. In contrast, the conventional counter-current flow technique leads to a decreasing concentration driving force with time. The liquid–liquid method, even though having the same ion concentration and applied pressure driving force as the liquid–vapor method, is very slow because of the large osmotic gradient opposing the permeation of ions and water from the feed to the permeate side. The liquid–vapor ion exchanged MFI membranes showed excellent integrity (as determined by H₂ and CO₂ permeation measurements).

1. Introduction

Nanoporous (e.g.) polycrystalline zeolite membranes supported on macroporous substrates have attracted large research efforts [1–3]. Zeolite membranes with a variety of crystal structures and pore sizes can effectively perform molecular separations by preferential adsorption and diffusion [4–5]. Zeolite membranes are also gaining increasing attention as catalytic membrane reactors combining reaction and separation in a single device [6–9]. There have been significant efforts to modify zeolite membranes in order to control their performance using methods such as ion exchange [10–17], chemical vapor deposition [18,19], coking treatments [20], and catalytic hydrothermal cracking [21–24]. Ion exchange is a particularly important route to modifying the adsorption, diffusion, and catalytic properties of zeolite materials and membranes [25], and a number of studies on the ion-exchange of zeolite membranes have appeared [26–33]. For example, Aoki et al. [29] studied the ion exchange of ZSM-5 zeolite membranes with H⁺, Na⁺, K⁺, Cs⁺, Ca²⁺ and Ba²⁺ cations. MFI zeolite membranes with Si/Al ratio of 25...
2. Experimental methods

2.1. Membrane synthesis by in situ crystallization

The aluminosilicate MFI zeolite membrane was synthesized on a porous α-alumina disk by the in situ crystallization method. Macroporous α-alumina disks (Coorstek) of 1 in. diameter, 1 mm thickness, and 25% porosity were used as supports for MFI zeolite membrane preparation. One side of the disk was polished by no. 600 SiC sandpaper for growing zeolite membrane. The synthesis solution was prepared as follows: tetrapropylammonium hydroxide (TPAOH, 1 M, Sigma–Aldrich) and NaAlO₂ (Sigma–Aldrich) were mixed in deionized water. After 30 min of stirring, tetraethyl orthosilicate (TEOS, 98%, Acros) was added dropwise to the solution under constant stirring. The molar composition of the gel was TEOS: 0.095 TPAOH: 35.42 H₂O: X NaAlO₂. The X value was varied from 0 to 0.040, corresponding to a range of Si/Al ratios from ∞ to 15. After the precursor was stirred for 3 h, it was transferred into the Teflon-lined stainless steel autoclave (Parr). The polished α-alumina disk was placed vertically at the bottom of the vessel and completely immersed in the synthesis solution. The synthesis experiments were performed at 150 °C for 17 h. After the hydrothermal reaction, the membrane was washed thoroughly with deionized water, dried, and calcined in air at 550 °C for 6 h to remove the template. The membranes were dried at 70 °C in an oven for overnight before ion exchange.

2.2. Membrane synthesis by seeded growth

To prepare a pure-silica MFI seed suspension, the synthesis solution was prepared by dissolving the fumed silica and NaOH pellets in 1 M TPAOH solution at 80 °C. It had a molar ratio of 0.33 SiO₂: 0.1 TPAOH: 0.035 NaOH: 5.56 H₂O [41]. The precursor was aged at room temperature for 4 h before receiving hydrothermal treatment. The hydrothermal synthesis was performed at 120 °C for 4 h. After hydrothermal synthesis, the resultant silicate nanoparticle slurry was washed in deionized water in a centrifuge. The seeds were then dip-coated on the alumina supports following the procedure described elsewhere [42]. After dip-coating, the disk was dried at 60 °C for 24 h in an oven. The seed layer coated disk was then calcined in air at 550 °C for 6 h to remove the template from the seed crystals and consolidate the seed layer. The precursor solution for secondary growth was the same as that used for in situ crystallization. The seeded α-alumina disk was placed and immersed in the synthesis solution. The secondary growth synthesis experiments were performed at 150 °C for 17 h.

2.3. Ion exchange methods

For the conventional ion exchange process, the zeolite membranes were immersed in the ion-exchange solution [16,25,30,31]. In some cases, the membrane was tied to a magnetic stirrer and placed at the bottom of a flask and stirred in the ion-exchange solution [11,17]. In this work, the zeolite membrane disk was attached to a magnetic stirrer bar with an epoxy adhesive, immersed in the ion exchange solution, and continuously stirred. For the vacuum-assisted liquid–vapor ‘flow-through’ process, the zeolite membranes were immersed with the membrane surface facing the ion exchange solution, and ion-exchanged by the pressure and concentration-induced total chemical potential.
difference created between the two sides of the membrane. The disk-supported zeolite membrane was attached to a bell-shaped glass tube with an epoxy adhesive, and with the membrane surface facing out of the bell-shaped tube (Fig. 1). The membrane surface was then immersed into the ion exchange solution bath. The other side of the tube was connected to a vacuum pump, to create a liquid–vapor pressure differential of approximately 1 atm across the membrane. Before ion exchange, the vacuum-tightness of the membrane assembly and all connections was verified. The pressure differential between the two sides of the membrane was monitored by a pressure gauge. For the liquid–liquid ‘flow-through’ process, the disk-supported zeolite membrane was attached to a bell-shaped glass tube with an epoxy adhesive, and with the membrane surface facing into the bell-shaped tube. The tube was connected to a water pump which introduces a pressurized ion exchange solution to the membrane surface with a liquid–liquid pressure differential of 1 atm across the membrane. The tube assembly was immersed into a bath containing deionized water at atmospheric pressure, which contacts the permeate side of the membrane.

Ion-exchange solutions with 1 mM concentration containing Ga\(^{3+}\), Zn\(^{2+}\), or Pt\(^{4+}\) ions were prepared from Ga(NO\(_3\))\(_3\)·H\(_2\)O, Zn(NO\(_3\))\(_2\)·H\(_2\)O, and Pt(NH\(_3\))\(_4\)Cl\(_2\)·H\(_2\)O, respectively. The ion-exchange solution was heated to 23–70 °C under constant stirring. All three ion-exchange methods were carried out in the temperature range of 23–70 °C for time periods of 5–24 h. After ion exchange, the membrane was washed in deionized water at 70 °C overnight, and calcined at 550 °C for 6 h.

2.4. Characterization

Scanning Electron Microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) analyses were obtained on a JEOL LEO-1530 at a landing energy of 15 kV using the ‘InLens’ mode detector. The membrane samples were coated with gold to prevent surface charging effects. X-ray diffraction (XRD) patterns of the membranes were obtained using a PANalytical X’pert diffractometer. Elemental analysis by inductively-coupled plasma (ICP) was carried out by Columbia Analytics (Tucson, AZ). All membranes were dried at 70 °C for 12 h in an oven before gas permeation measurements. The membranes were mounted in a stainless steel cell with the zeolite surface facing the feed side, placed in a temperature-programmable oven, and further degassed under vacuum for 2 h at 23 °C. Before calcination, the integrity of the zeolite membrane was checked via He permeation measurements, for which a transient permeation setup with upstream pressure of 25–30 psi at room temperature was employed. The membranes had very low He permeances (less than \(1.0 \times 10^{-10}\) mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)). For calcined membranes, H\(_2\) and CO\(_2\) permeation measurements were carried out at 23, 75, 125, and 175 °C. The feed side was maintained at 30 psi, and the permeate side was evacuated to 0.1 psi. The gas permeance was measured by isolating the vacuum and recording the rate of pressure rise in a collection vessel of known volume on the permeate side.

3. Results and discussion

Fig. S1a (Supporting information) shows SEM images of a typical pure-silica MFI seed layer obtained by dip-coating. MFI nanocrystals with an average particle size of ~100 nm were obtained by conventional heating at 120 °C for 4 h. Fig. S1b and S1c show SEM images of the Na–MFI (or Na–ZSM-5) zeolite membrane after in situ crystallization in precursors with Si/Al = 25 and the MFI membrane after secondary growth in precursors with Si/Al = 25. The thickness of the zeolite membranes are 4–6 \(\mu\)m as estimated from the cross-section SEM images. The XRD patterns of the zeolite membranes are shown in Fig. S2 (Supporting information). The MFI zeolite membranes made by in situ crystallization showed (h00)/(0k0) out-of-plane orientation, and the MFI zeolite membranes from secondary growth method showed (h0l) orientation.

Fig. 2 shows the SEM micrographs of the surface and cross-section of the secondary grown zeolite membrane before and after vacuum-assisted ion-exchange. The secondary-grown zeolite membranes showed intergrown polycrystalline films and the thickness of the zeolite layer was 5–6 \(\mu\)m. The cross-section/surface microstructure of the ion-exchanged membrane was unchanged from that of the fresh membranes. In addition, the vacuum-assisted ion-exchanged zeolite membranes were kept in air at 550 °C for 0 h, 24 h, and 48 h, respectively, to check the high-temperature stability. The SEM images in Fig. S3 (Supporting information) were taken after aging at 550 °C. No significant change in membrane morphology was observed after high-temperature exposure. This suggests that the ion-exchanged zeolite MFI membranes are thermally stable, which make them useful for high-temperature applications. As shown in Fig. S4 (Supporting
The Si, Al, Na, Ga, Zn, and Pt compositions were measured using energy-dispersive X-ray (EDX) spectroscopy. The (oxygen-free) composition analysis taken from the top surfaces of the ion-exchanged membranes is shown in Table 1. Based upon the incident energy of the electron beam, the membrane depth over which the composition analysis is carried out is estimated as 1–2 μm. MFI zeolite membranes were obtained by secondary growth in precursors with Si/Al = 25, and ion-exchanged by the vacuum-assisted ‘flow-through’ technique with Ga³⁺, Zn²⁺, or Pt²⁺ ions. The EDX elemental analysis shows that the Ga/Al, Zn/Al, and Pt/Al ratios increased substantially after ion exchange indicating increase of exchanged ion density in the zeolite membrane. For the Ga- and Zn-exchanged membranes, the increase in Ga/Al, Zn/Al, and Pt/Al ratios showed good agreement with the corresponding decrease in Na/Al ratio. For example, in the case of exchange of monovalent Na⁺ ions with trivalent Ga³⁺ cations, the decrease in Na/Al ratio of 0.73 (i.e., from 0.79 to 0.06) is commensurate with the increase of Ga/Al ratio from 0 to 0.29. The Al atomic % and the Si/Al ratio did not change significantly after ion exchange, indicating that potential dealumination of the zeolite membrane was not a significant factor in comparison with the degree of ion exchange.

Fig. 3 shows the surface EDX analysis of Ga³⁺ ion-exchanged secondary grown membranes as a function of ion exchange time. The Ga/Na ratio of the membrane ion-exchanged at 70 °C was much higher than that of the membrane exchanged at 23 °C, and the differences became more significant as the ion exchange time increased. For the membrane exchanged by the vacuum-assisted ‘flow-through’ technique, Ga/Na was about five times higher than that of the membrane exchanged by the conventional immersion method. This clearly indicated a much larger driving force across the membrane in the vacuum-assisted process. Table 2 shows a direct comparison of the three ion exchange methods using secondary-grown membranes at 70 °C and a duration of 24 h. It is clearly seen that the vacuum-assisted liquid–vapor method provides 5–10 times more efficient ion exchange than the other two methods. Furthermore, the liquid–liquid method produces a much smaller level of ion exchange than the other two methods. The differences between these three methods, which are not immediately obvious, can be understood in terms of the type and direction of the driving forces for ion transport. In the vacuum-assisted liquid–vapor method, the pressure and concentration driving forces for permeation of water, Ga³⁺, and Na⁺ all exist in the same direction, i.e., from the feed side to the permeate side. This co-current flow of water and ions can be maintained throughout the ion exchange process. In the conventional immersion process, there is no pressure driving force for permeation. The concentration driving forces for Ga³⁺ and Na⁺ transport oppose each other. Finally, the liquid–liquid process is limited by the large osmotic differential (about 2.2, 2.4, and 1.7 atm for Ga³⁺, Zn²⁺, and Pt²⁺, respectively) that opposes the applied pressure differential (1 atm) and the ion concentration gradient. The large back-permeation of water prevents effective ion exchange, and a much larger feed pressure will be required for effective ion exchange.

Fig. 4 shows a comparison of the Ga/Al, Zn/Al, and Pt/Al ratios resulting from ion-exchange of in situ and secondary-grown Na-MFI membranes with two different Si/Al ratios (15 and 25). As expected these ratios increased with decreasing Si/Al ratios, because the membrane with lower Si/Al ratio has more ion-exchange sites. The membranes made by in situ crystallization consistently showed higher ion exchange than the secondary-grown membranes under the same ion exchange conditions (23 °C and 5 h). This is clearly due to the slower rate of transport of cations in the secondary-grown membranes (which are (h01)-oriented) in comparison to the in situ membranes (which are (h00) or (0k0) oriented and have the straight and sinusoidal pore channels.

Table 1
Elemental surface composition of Na-MFI membranes secondary-grown from precursor solutions with Si/Al ratios of 25, before and after vacuum-assisted ‘flow-through’ ion exchange with Ga³⁺, Zn²⁺, and Pt²⁺ ions at 70 °C for 24 h, 70 °C for 24 h, and 23 °C for 5 h, respectively. The atomic % values are on an oxygen-free basis.

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>EDX atomic %</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>Ga/Al</th>
<th>Zn/Al</th>
<th>Pt/Al</th>
</tr>
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<tr>
<td></td>
<td>Si Al Na Ga Zn Pt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>25</td>
<td>Before</td>
<td>94.2</td>
<td>3.27</td>
<td>2.57</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>After</td>
<td>94.9</td>
<td>3.74</td>
<td>0.24</td>
<td>1.07</td>
</tr>
<tr>
<td>Zn</td>
<td>25</td>
<td>Before</td>
<td>94.1</td>
<td>3.27</td>
<td>2.67</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>After</td>
<td>94.5</td>
<td>3.48</td>
<td>0.84</td>
<td>–</td>
</tr>
<tr>
<td>Pt</td>
<td>25</td>
<td>Before</td>
<td>93.6</td>
<td>3.93</td>
<td>2.43</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td></td>
<td>After</td>
<td>94.5</td>
<td>3.81</td>
<td>0.93</td>
<td>–</td>
</tr>
</tbody>
</table>

a) Si/Al ratio in precursor solution.
b) Si/Al ratio in the resulting zeolite membrane.
is the maximum possible selectivity lower than unity\[^4\]. The gas
and CO\(_2\) ideal selectivity is well-known as a criterion to test the
+ and some
were measured before and after
3+ (4.5–4.7 Å) > Zn
sured the spatial distribution of the exchanged metal ions along
three different ion exchange methods at 70
(concentration of the metal ion (Ga
174
To gain further insight into the ion exchange process, we mea-
sed the liquid–liquid, applied \(A_P = 1\) atm
= 25 was ion-
exchanged with Ga
2+ ion by the flow-through technique at 23 °C
for 24 h. In this case, the total flux through the membrane was
0.21 kg m\(^{-2}\) h\(^{-1}\) during 24 h of ion exchange, based upon the mass
of solution collected in the cold trap. Before and after Ga
3+ ion-
exchange, the Ga content of the feed solution showed no signifi-
cant change, since the Ga
3+ feed concentration is in large excess.
The condensed permeate solution after ion exchange showed
much higher Na content than in the feed chamber, as well as a sig-
nificant Ga content. Thus, we conclude that a large fraction of the
Na
+ ions are transported through the membrane and exit at the
permeate side in the form of vapor-phase hydrates, which are well
known to exist in water vapor [43–45]. These Na
+ ions are dis-
placed from the zeolite by Ga
3+ ions moving in from the feed side.
This observation implies that the vacuum-assisted method is co-
current, unlike the counter-current movement of ions in the
conventional immersion process. The cations (Na
+ and some Ga
3+) exit the membrane on the vacuum side, allowing the maintenance of a high driving force for ion exchange.

Gas permeation measurements were used to determine the
quality of the final ion-exchanged secondary-grown membranes
obtained from the vacuum-assisted flow-through method. The sin-
gle-gas permeances of H\(_2\) and CO\(_2\) were measured before and after ion-exchange. Fig. 7 shows detailed results for the Ga-exchanged membrane, whereas similar data for the Zn-exchanged and Pt-exchanged membranes are shown in Fig. S7 (Supporting infor-
mation). As shown in Fig. 7(a), the membranes exhibited ideal
(single-component) selectivity for CO\(_2\) over H\(_2\) > 1 at 23 °C. The
CO\(_2\)/H\(_2\) ideal selectivity is well-known as a criterion to test the
integrity of zeolite MFI membranes. Defective MFI membranes exhi-
bite a Knudsen-like CO\(_2\)/H\(_2\) selectivity lower than unity [46]. The gas
permeances slightly increase after ion exchange, due to two main
factors. Firstly, the effective zeolite pore size increases upon
replacement of the larger Na
+ ions with the other ions. Although
the order of hydrated ionic radii is: Ga
3+ (4.5–4.7 Å) > Zn
2+ and H
+ ions initially pres-

3+,Zn
2+, or Pt
+) could be
obtained by complete exchange of all Na
+ and H
+ ions initially pres-
ent near the acid sites of the Na-MFI zeolite membrane. The gradient of the exchanged Ga
3+ cation concentrations clearly
shows the direction of transport of the entering cations from the
feed to the permeate side. As shown in Fig. 5, the Ga
3+ ion concen-
trations increase with temperature and exchange time: 70 °C × 24 h > 70 °C × 5 h > 23 °C × 5 h, with the most dramatic changes occurring as a result of temperature increases. In contrast, higher temperatures and longer ion exchange times decreased the quantity of Na
+ ions in the membranes, which is consistent with the change of the quantity of Ga
3+ ions. The co-current movement of ions through the membrane is also evidenced by the Na
+ ion concentration profile in the membrane cross section. Fig. 6 com-
pares the Ga
3+ and Na
+ concentration profiles obtained from ion exchange by the vacuum-assisted and the conventional immersion
techniques using the secondary-grown membranes. The liquid–
liquid method does not lead to significant ion exchange and is not depicted in the figure. The concentration of Ga
3+ ions after vac-
uum-assisted ion exchange was much higher than that obtained
from the conventional immersion method. This implies that the
unidirectional ion exchange in the vacuum-assisted co-current
flow is better than conventional counter-current flow, which
involves counter diffusion of ions. In the conventional exchange
method, the Na
+ concentration profile near the membrane surface
showed opposite trend, which explains the counter-current move-
ment of ions.

running perpendicular to the membrane plane). When the mem-
brane was ion-exchanged by ‘flow-through’ technique at 70 °C
for 24 h, the Ga/Al showed improvement compared to the
conventional immersion method. The thermal stability of the
ion-exchanged membranes was further tested for an extended
time of 192 h at 550 °C. The Ga/Al, Zn/Al, and Pt/Na ratios as well
as the Ga/Na, Zn/Na and Pt/Na ratios showed excellent high-
temperature stability over 192 h of high-temperature temperature.

To gain further insight into the ion exchange process, we mea-
sured the spatial distribution of the exchanged metal ions along
the cross sections of the MFI membranes with EDX spectroscopy.
Fig. 5 shows the concentration profiles of Ga
3+, Zn
2+, and Pt
2+ ions
in the secondary-grown membrane cross-section for different vac-
uum-assisted ion exchange times and temperatures, with the most
detailed results shown for the Ga
3+ ions. The transition between the
‘membrane’ and ‘support’ regions is marked by the location
at which the Si/Al ratio changes abruptly. The concentrations are
expressed in terms of \(C/C_{\text{max}}\), where \(C_{\text{max}}\) is the maximum possible
concentration of the metal ion (Ga
3+, Zn
2+, or Pt
+) that could be
obtained by complete exchange of all Na
+ and H
+ ions initially pre-
sent near the acid sites of the Na-MFI zeolite membrane. The
gradient of the exchanged Ga
3+ cation concentrations clearly

<table>
<thead>
<tr>
<th>Ion-exchange method</th>
<th>Ga/Na</th>
<th>Zn/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum-assisted liquid–vapor, applied (A_P = 1) atm</td>
<td>4.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Conventional immersion, no (A_P)</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>Liquid–liquid, applied (A_P = 1) atm</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Fig. 4. EDX elemental analysis of in situ and secondary-grown Na-MFI membranes after (A) Ga
3+, (B) Zn
2+, and (C) Pt
2+ ion-exchange by the vacuum-assisted ‘flow-
through’ technique at 23 °C and 5 h of ion-exchange time. The dashed lines depict the theoretical maximum elemental ratios assuming complete ion exchange.
(4.3 Å) > Pt\(^{2+}\) (4.0–4.4 Å) > Na\(^{+}\) (3.6 Å), the dehydrated ionic radii are in the reverse order: Na\(^{+}\) (1.16 Å) > Pt\(^{2+}\) (0.94 Å) > Zn\(^{2+}\) (0.88 Å) > Ga\(^{3+}\) (0.74 Å). The latter ionic radii are likely more appropriate in relation to the above permeation measurements, performed on calcined membranes that were further degassed overnight before permeation measurements. Secondly, it is also clear that the number of metal cations present in the membrane drastically decreases when the monovalent Na\(^{+}\) cations are replaced by divalent (Pt\(^{2+}\), Zn\(^{2+}\)) and trivalent (Ga\(^{3+}\)) cations. The CO\(_2\)/H\(_2\) permselectivities did not change significantly after ion exchange, indicating that the membrane integrity was not affected by the vacuum-assisted ion exchange process. The temperature dependences of the H\(_2\) and CO\(_2\) permeances for the Na-MFI and the Ga-exchanged-MFI membranes are also similar. The single-gas H\(_2\) and CO\(_2\) permeation properties were further tested at 550 °C after aging for 0 h, 48 h, 96 h, 144 h, 192 h, and 240 h, respectively, as shown in

Fig. 5. Ion concentration profiles measured by EDX spectroscopy along the zeolite membrane cross-section of Na-MFI membranes secondary-grown from precursors with Si/Al = 25, before and after (a1 and a2) Ga\(^{3+}\), (b1 and b2) Zn\(^{2+}\), and (c1 and c2) Pt\(^{2+}\) ion-exchange by the vacuum-assisted liquid–vapor ‘flow through’ method.

Fig. 6. Ga\(^{3+}\) and Na\(^{+}\) ion concentration profiles measured by EDX spectroscopy along the zeolite membrane cross-section of Na-MFI membranes secondary-grown from precursors with Si/Al = 25, after ion-exchange for 24 h at 70 °C by the vacuum-assisted liquid–vapor ‘flow through’ method and the conventional immersion method.

Table 3

| Concentrations of Ga and Na in the feed and (condensed) permeate solution as determined by ICP analysis, for a secondary-grown Na-MFI membrane with Si/Al = 25 before and after Ga\(^{3+}\) ion-exchange by vacuum-assisted ‘flow-through’ technique at 23 °C for 24 h. |
|---|---|
| | Ga (ppm) | Na (ppm) |
| Feed before ion-exchange | 52 | 7 |
| Feed after ion-exchange | 54 | 10 |
| Permeate after ion-exchange | 5 | 20 |
Fig. S8 (Supporting information). Both H2 and CO2 permeances increased over an aging time of 100 h, and then stabilized. For the Ga3+ ion-exchanged membrane, the H2 and CO2 permeances increased 40% and 50%, respectively, after 240 h of aging. The perm-selectivities of H2 over CO2 were nearly unchanged upon thermal aging, indicating that the ion-exchanged membranes are thermally stable and can function at high operating temperatures.

4. Conclusions

A vacuum-assisted liquid–vapor ‘flow-through’ technique was developed to effectively ion-exchange α-alumina-supported Na-MFI zeolite membranes. It was found that the vacuum-assisted technique greatly enhances the exchange of Na+ ions with other metal ions such as Ga3+, Zn2+, and Pt4+, in comparison to the conventional immersion method and a liquid–liquid flow-through method. Both the enhancement of total ion content and spatial distribution of ions along the membrane cross-section are attributed to the higher driving forces for ion transport in the vacuum-assisted method in comparison to the other two methods. For all the methods investigated, higher temperature and longer ion exchange times allowed a greater degree of ion exchange. It is shown that the vacuum-assisted process involves pressure and concentration-driven co-current transport of water and ions from the feed to the permeate side. The ion-exchanged zeolite membranes also showed excellent integrity after ion exchange and high stability under high-temperature operation. Because of its excellent efficiency, the vacuum-assisted ‘flow-through’ technique is valuable in producing and quickly regenerating ion-exchanged zeolitic membranes for separations and catalysis applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.10.017.

References


