



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



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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).

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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

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and 600 were stirred in the exchange solution at 95 °C for 2 h. For Si/Al ratio of 25, permeation properties of the Na-ZSM-5 membrane changed with ion exchange while, for Si/Al ratio of 600, no correlation between permeance and ion size was observed. Tarditi et al. [25] ion-exchanged the ZSM-5 membranes with Cs⁺, Ba²⁺, and Sr²⁺ cations by immersing the membranes in the exchange solution at 80 °C for 24 h. The single-gas permeation of N₂ was conducted before the ion-exchange, and before and after the xylene permeation tests, but no significant changes in N₂ permeation were observed. Zhang et al. [30] studied the catalytic activity of MFI zeolite membranes by subjecting the membrane to H⁺ ion-exchange treatment and used the H⁺ ion exchanged H-MFI zeolite membranes for m-xylene (MX) isomerization. Takata et al. [31] reported the effect of repeated ion-exchange from Na⁺ to H⁺ on the permeances for He, N₂ and SF₆ at 100 °C for silicalite membrane. Since the cation size of Na⁺ is larger than that of H⁺, the gas permeances in the H⁺ form were consistently larger than for the Na⁺ form. Kusakabe et al. [32] ion exchanged the NaY-type membranes with K⁺ and Li⁺ ions. The NaY-type membranes exchanged with K⁺ and Li⁺ ions gave higher and lower CO₂/N₂ selectivities than the fresh NaY-type membrane. Hasegawa et al. [33] ion exchanged NaY-type zeolite membranes with K⁺, Rb⁺ or Cs⁺ ions. Permeation properties of the ion-exchanged zeolite membranes were investigated at 35 °C with a CO₂/N₂ equimolar mixture, and the CO₂/N₂ selectivity was in the order: Rb⁺ = K⁺ > Cs⁺ > Na⁺.

None of the above studies addressed directly the rate and extent of ion exchange of membranes. As discussed by Murad et al. [34], the rate of ion exchange depends upon the driving force for the ion exchange as well as the energetic barriers for the ions to enter/leave the membrane through the zeolitic pores. However, with the conventional ion-exchange method (which involves immersion of the zeolite membrane into an ion exchange solution), only a limited fraction of ions are exchanged. This is due to the slow concentration-driven transport of hydrated metal cations (which have an effective kinetic diameter of 4–8 Å [35]) in the zeolite pores and the lower liquid–solid interface area of a zeolite membrane in comparison to a powdered zeolite. For example, a 1-μm thick zeolite membrane has considerably lower interfacial area than an equal mass of 1 μm zeolite crystals, since the inter-crystalline boundaries in a good-quality membrane are not easily accessible to permeating species. In addition, the location and spatial gradient of the exchanged ions in such membranes have not been systematically studied.

The main motivation of this work is to investigate methods to increase the efficiency of ion exchange of zeolitic membranes. To this end, a vacuum-assisted liquid–vapor ‘flow-through’ technique is described in this work, using MFI zeolite membranes as an example system. The influence of ion-exchange parameters, such as different cations, temperature, and ion-exchange time on the MFI zeolite membranes with various Si/Al ratios are described using several characterization techniques. The magnitude of ion-exchange is found to be considerably larger than that achieved by conventional immersion methods. As discussed in more detail below, the liquid–vapor technique is shown to rely upon the pressure-driven co-current transport of hydrated metal ions through the membrane, in contrast with other ion-exchange techniques such as the conventional ‘immersion’ method and a liquid–liquid flow-through method. In addition, the stability of the ion-exchanged membranes at high operation temperature was evaluated. The liquid–vapor technique is potentially useful for applications such as catalysis and separations, since it can provide high loadings of ions such as Pt²⁺, Ga³⁺, and Zn²⁺. Metal-exchanged zeolites have been widely studied for catalytic processes such as propane aromatization, dehydrogenation of paraffins, and hydroamination [36–38]. For example, the introduction of Ga, Zn, and Pt species as exchanged cations into ZSM-5 catalysts was found

to increase the rate and selectivity of light-alkane conversions and to inhibit cracking side-reactions [39]. Ion-exchanged zeolite membranes have potential as catalytic membrane reactors to intensify such processes [40].

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 silicalite 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

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