Graphical abstract

Rapid Synthesis of Faujasite/Polyethersulfone Composite Membrane and Application for CO₂/N₂ Separation

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Abstract

Rapid growth of faujasitic membranes on polyethersulfone support was investigated. The membrane growth occurred in a novel zeolite reactor, where the extent of supersaturation of the synthesis gel 8.5 Na₂O: 1 Al₂O₃: 10.9 SiO₂: 487 H₂O was controlled by removal of water from the reaction system. The gel remaining after removal of half the water from the reaction was isolated and used as a coating on the polymer support. Along with this reactive gel, coating of a uniform film of nanozeolite seed deposition on the porous polymer support was also investigated. Eight variations of the gel-seed combinations were examined for membrane growth. The optimal membrane synthesis conditions was defined as coating of the PES support by a nanozeolite seed layer of 250-300 nm thickness, and then introduction into the reactor after water is removed, and continuing the reflux process with reintroduction of the water for another hour. Further characterization included X-ray diffraction, optical microscopy and detailed scanning electron microscopy. Leak test of a dye through the membrane and the mechanical stability of the membrane via a tape test were performed. The transport properties of these membranes for CO₂/N₂ separation were evaluated. There were three ways the membrane samples were prepared and handled for transport measurements. Prior to transport measurements, all samples were covered with PDMS. Initial attempts placed the seeded PES support into the growth reactor. These samples all exhibited poor transport properties with CO₂/N₂ selectivities less than 10. For the second group, the seeded PES supports were placed in a holder that ensured flatness during the zeolite growth process. There was significant improvement in the transport properties, with half of the membranes exhibiting CO₂/N₂ selectivity greater than 20. With the third group of membranes also grown in the flat geometry, care was taken to keep them flat through all the subsequent steps including washing, drying and putting on the PDMS layer. Transport properties improved further. The twelve membranes in this group exhibited CO₂/N₂ separation factor in the range of 16-110 with CO₂ permeance in the range of 180-2000 GPU (1 GPU = 3.3×10^{-10} mol/m²·Pa).

Keywords

Faujasite, Polyethersulfone, Membranes, Polydimethylsiloxane, CO₂/N₂ Separation

1. Introduction

Zeolites are microporous crystalline aluminosilicates, with well-defined pore sizes at the sub-nanometer level.[1–4] Because of the narrow pore size, thermal and chemical stability, zeolite membranes are attractive for pervaporation, gas and liquid separations.[2,4–10] There is currently great urgency in removal of CO₂ from flue gas emanating from coal-fired power plants, followed by sequestration to decelerate global warming effects. Selective CO₂ removal also can benefit other industries, such as in natural gas purification and in water gas shift reactions for hydrogen production.[2,11] Compared with traditional absorption-based separation, membrane separation is significantly more energy efficient.[12]

The faujasite framework, with its three-dimensional architecture and 7.4 Å pore opening is attractive for gas separations, and has been extensively studied.[1] Because of its large pore size, there is no steric hindrance for CO₂, N₂ or other similarly sized gas molecules to enter the zeolite framework. However, CO₂, because of its higher quadrupole moment exhibits preferential interaction with the zeolite framework and the extraframework cations.[13] Aided by such interactions, CO₂ molecules preferentially permeate through zeolite framework by surface diffusion, while N₂ is blocked due to pore constriction caused by CO₂ adsorption, and forms the basis for gas separation.[14,15]

Even though zeolite membranes have been studied for gas separation,[16,17] factors such as long synthesis time, membrane defects, high cost and poor reproducibility in zeolite membrane manufacture have limited their commercial use.[4] The only commercial use of zeolite membranes is in solvent purification by pervaporation.[7,18–22] Zeolite membranes

are typically grown on α -alumina or metal supports.[14,16,17,22–29] These supports are expensive, mechanically rigid and difficult to fabricate in large-scale production. An alternative is using polymer supports, which if successful, can use all of the advances in polymer membrane fabrication to lower cost. However, a major technical hurdle is the long time it takes to synthesize zeolites, which is incompatible with polymer membrane manufacturing methods. A second issue is that inter-particle defects appear during the zeolite growth process, no matter what the support, which leads to low performance reproducibility.[4] Multiple strategies have been proposed to fix mesoporous defects, and some of these strategies can be adapted to the zeolite polymer system.[4] There have been recent reports of synthesis of zeolite A membranes on polymer hollow fibers and examined for pervaporation applications.[21] New strategies of synthesis of ultrathin zeolite membranes is an active area of research.[30]

In this paper, we address two issues, accelerating zeolite membrane growth on polymer supports, and sealing of defects to enhance transport properties. Ultra-thin (250-300 nm) faujasite zeolite membranes on porous polyethersulfone (PES) supports has been synthesized in one hour, following the rapid crystallization synthesis procedure described previously.[31] This is amongst the thinnest faujasite membrane that has been reported in the literature. Structural characteristics of this membrane are evaluated. We have investigated the use of silicone rubber (PDMS) to heal the defects on the grown zeolite membrane. Transport properties of these membranes for CO₂/N₂ separation are explored.

2. Experimental Procedure

2.1. Chemicals

Aluminum hydroxide ($\text{Al}(\text{OH})_3$, 76.5%) was obtained from Alfa Aesar, and sodium hydroxide pellets from Fisher Scientific (NaOH , 99.0%). Ludox SM-30 colloidal silica (SiO_2 , 30%), Ludox HS-30 colloidal silica (SiO_2 , 30%), aluminum isopropoxide ($\text{Al}(\text{O}-\text{CH}(\text{CH}_3)_2)_3$, 98%) and tetramethylammonium bromide ($(\text{CH}_3)_4\text{NBr}$, TMA), 98%) were obtained from Aldrich (Milwaukee, WI, USA). Tetramethylammonium hydroxide (25% aqueous) was obtained from SACHEM Inc. All chemicals were used as received. Polyethersulfone (PES) 300kDa supports were purchased from MILLIPORE Biomax. Water was purified by a Millipore ultrapure water system.

2.2. Synthesis

Nanocrystalline Zeolite Y Seeds Nanocrystalline zeolites were synthesized by a procedure reported in the literature.[32] The gel composition was: 0.048 Na_2O : 2.40 $(\text{TMA})_2\text{O}(2\text{OH})$: 1.2 $(\text{TMA})_2\text{O}(2\text{Br})$: 4.35 SiO_2 : 1.0 Al_2O_3 : 249 H_2O (TMA^+ is tetramethylammonium). Typically, the silicon source, Ludox HS-30 (26.2 g) and TMAOH (10.46 g) were mixed in a Teflon bottle, sealed with parafilm and stirred at room temperature for 30 min. Aluminum isopropoxide (12.5) g was dissolved in 76.5 g H_2O and TMAOH (52.3 g) at 70 °C until the suspension became clear. TMABr (11.3 g) was added to the clear solution of aluminate and stirred at room temperature for 15 min. Finally, the silicon and aluminum solutions were mixed and aged at room temperature with stirring for 3 days, followed by heating at 100°C in an oil bath with stirring for 4 days. The product was isolated by dialysis and ultracentrifugation, followed by ion-exchange with 0.2 M NaCl solution for 2 hours. The ion exchanged product was washed with DI water and stored as a 1 wt% aqueous stock solution.

Zeolite Y Seed Layer Zeolite Y seed layer on PES support was prepared by vacuum dip-coating. Before dip-coating, zeolite Y stock solution was put in an ultrasonic bath for 1 hour and then diluted with DI water to the required concentration. Vacuum-assisted dip-coating involved evacuation of the PES support with zeolite seed dispersion on the top of the support for 3 seconds. The coated support was stored in a plastic sample bags.

Zeolite Y Membrane Synthesis The gel composition used for membrane growth was 8.5 Na₂O: 1 Al₂O₃: 10.9 SiO₂: 488 H₂O, (note that the previous composition reported in Reference 31 was in error by a factor of two) which was prepared by mixing 85.24 g H₂O, 2.208 g of Al(OH)₃ and 7.29 g NaOH with 13.85 g Ludox SM-30 followed by aging for 4 hours at room temperature. Then the opaque gel was moved to round bottom flask, brought to reflux, 40-45 mL of H₂O was removed from the gel during 1 hour of heating under reflux. During the next hour with the flask still under reflux, 40-45 mL H₂O was added back. The support was introduced in the flask at different stages during the synthesis, as described in results section.

PDMS coating Zeolite membranes were spin coated with 3.5 wt% polydimethylsiloxane (PDMS) monomer solution. PDMS monomer solution was prepared by adding PDMS monomer, crosslinker and catalyst in the ratio of 100:1:0.5 to heptane. For spin coating of PDMS onto a zeolite membrane, the membrane was first taped on the flat plate of the spin coater and PDMS monomer dispersion was added to cover the whole membrane. Spinning process consisted of 2000 rpm spin for 5 s and then 4000 rpm spin for 1 min. After spin coating, the membranes were kept at room temperature overnight for crosslinking of the PDMS.

2.3. Characterization

X-Ray Diffraction A Bruker D8 X-Ray Diffractometer using CuK α ($\lambda=1.5405$ Å) radiation was used to characterize the phase composition of zeolite membranes.

Size and zeta potential Size and zeta potential of nanocrystalline zeolite Y was characterized with Malvern Zetasizer.

Optical Microscope Surface morphology of membrane samples were studied with OLYMPUS PME3 optical microscope.

Scanning Electron Microscopy Membrane samples were taped on a SEM holder with conductive carbon paste and gold coated at 40 mA for 20 s. Electron beams with 30kV voltage and 41pA current were typically used. A FEI Helios Nanolab 600 Dual Beam Focused Ion Beam/Scanning Electron Microscope (FIB/SEM) was employed for cross sectional measurements.

Mechanical Tape Test Scotch tape was pushed onto the surface of membrane and then peeled off. The peeled tape and membrane were analyzed by SEM to study the mechanical stability of top layer of membrane.

Leak Test A leak test was used to investigate the defects in the membrane samples.[33] The membrane was placed in the middle of a glass cell with one side filled with ethanol and the other side filled with Rhodamine 6G (10^{-4} M) in ethanol. By detecting the fluorescence of solution in cuvette over time, the dye leak through the membrane was studied. This test was done using a fluorimeter, Fluorolog from HORIBA.

Gas Transport Measurement A gas separation setup was constructed. Feed gas and sweep gas compositions were controlled with a flow box and mass flow controllers from SIERRA Instruments Inc. Feed gas was introduced on the zeolite side of membrane and sweep gas on the support side of membrane. Concentrations of permeate and retentate gas compositions were investigated with a SRI 310C gas chromatograph equipped with a Hysep D column, and TCD detector.

3. Results

3.1. Zeolite Membrane Synthesis

3.1.1. Zeolite Seed Deposition

Polyethersulfone (PES) with a 300 kDa molecular weight cut off was used as the support. Figure 1A shows a top-view SEM of the support, with ~77 nm average pore size and ~15% porosity. Zeolite Y nanocrystals were used for seeding, and based on the morphology shown in Figure 1B, the size of the particles was between ~ 30-40 nm. The coating of the seed on the PES support was carried out by applying vacuum on the back side of the PES support. The pH of the seed dispersion was varied as 2, 7 and 12 and the deposition was carried out with a seed loading of 0.09 wt%.

Figure 2 shows the zeta potential - pH titration curve for the zeolite seed dispersion along with the corresponding top-view SEM for the seeded samples deposited on PES. The zeta potential was negative (~ -55 mV) at pH ~12, and tended towards more positive values with decreasing pH. At pH 7, the zeta potential was -45 mV and at pH 2, it was -5 mV. From the SEM micrographs, it is clear that the optimum packaging of crystals on the PES

surface occurs at $\text{pH} \geq 7$. Thus, for all subsequent studies, vacuum-assisted seed deposition was carried with the nanozeolite dispersion at $\text{pH} \sim 7$.

The amount of seed in the suspension was varied from 0.001 to 0.09 wt%, and from the top-view SEM, shown in Figure 1S (Supplementary Section), it was determined that the uniform packing of the zeolite nanocrystals was obtained at 0.09 wt%. Since our goal was to synthesize as thin membranes as possible, higher seed concentrations were not examined. With lower seed concentrations, the pores in the PES became visible.

3.1.2. Adapting rapid synthesis method to membrane growth

Figure 3 is a schematic of the synthesis apparatus and the procedure for rapid growth of zeolite Y.[31] After aging the gel for 4 hours, the gel was loaded into a round bottomed flask with a condenser. During the first hour of reflux at $\sim 100^\circ\text{C}$, about 40-45 ml of the water is removed from the flask into the dripper. The concentrated gel left behind in the flask is referred to as the 60 min-gel, and was isolated from the reaction medium and used for coating of the PES support. We have reported that this 60 min-gel is heavily nucleated, and upon readdition of the water back (under reflux condition), high quality faujasite crystals are formed within an hour.[31] Eight different membrane growth experiments were carried out, as outlined in Table 1. The first set of experiments were carried out with the free standing seeded PES membranes introduced into the reactor. Curling of the support was noted during the membrane synthesis process. Second set of experiments were carried out with the seeded support placed in a sample holder. This holder, shown in Figure 2S held the PES support flat during the hydrothermal synthesis. The distance between the frame and the bottom is 3 mm, which prevented the PES support

from rolling up but did not hold the membrane too tightly. The sample holder accommodated membranes of size 2.3 cm x 4.1 cm. The observations below regarding the growth were noted with both the free standing and PES support held in the sample holder.

Bare PES support (M1, M2) The 60 min-gel was used as a coating on the PES supports, either by itself (M1) or with a physical mixture with the seeds (M2). The coating was applied on the PES support using a knife casting method. Both M1 and M2 were introduced into the reactor by interrupting the reaction after the dehydration step and the reaction continued by dripping the water back under reflux conditions for an hour, and the samples isolated. Figure 4 AB shows a top view SEM of M1 and M2, and there is no evidence of formation of a zeolite membrane.

Seeded PES support Six experiments were done with the seeded support using the pH 7, 0.09 wt% dispersion, shown in Figure 2. For four of these, 60 min-gel (M3, M4) or a 60 min-gel plus seed (M5, M6) was knife cast on the seeded support. Two of these (M3, M5) were introduced into the reactor right from the start with the aged gel, and for one hour the water was withdrawn from the reaction and then during the second hour, the water was added back, all under reflux conditions. Figure 4 CE shows the SEM of M3, M5, and membrane formation is incomplete. With the other two supports (M4, M6), they were introduced into the reactor after the 1-hour dehydration step, and while water was added back, the reflux continued for an hour, after which the samples were withdrawn. With both these samples (Figure 4 DF), the SEM shows that a membrane-like layer is formed on the support.

The final two experiments were done only with the seeded support introduced into the reactor from start (M7), and after 1-hour of dehydration (M8). For M7, the process was continued for two hours, one hour for removal of water and the second hour, the water was added back. For M8, the process took one hour, with the water being added back during the hour, while under reflux. Figure 4 GH shows the SEM micrographs. With M7, the membrane layer is not uniform, and the pores of the PES support were evident. Thus, there were three cases M4, M6 and M8 that appeared to have a membrane layer on the PES support. We focused on the M8 membrane grown with the flat holder in this paper, since it did not require the extra step of knife casting of the gel, and its characteristics are detailed below.

3.2. Characteristics of M8 membrane

3.2.1. Morphology

Optical micrographs provide a convenient way to estimate if there is growth on the PES support. Figure 3S (ABC) shows the optical micrographs of the bare, seeded support and M8, respectively. The continuous color patterns on the seeded support and M8 are indicative of uniform deposition. Black dots shown in all 3 images are defects inherent to the PES support. As shown in Figure 3S (D), M8 exhibits the characteristics (111) peak of faujasite at $2\theta = 6.4^\circ$, which is typically the most intense reflection of the faujasite framework. The other reflections were not intense enough to be observed.

Figure 5ABC shows the cross-section SEM of a PES support, a seeded support and the M8 membrane. The seed layer is $\sim 250\text{-}300$ nm thick, and some of the nanozeolite seed

crystals penetrate into the PES layer. With M8, there is clear densification of the seed layer into a continuous membrane, and the thickness is ~ 250-300 nm.

3.2.2. Mechanical Properties

Leak Test Using the cell shown in Figure 4S, the migration of the dye Rhodamine 6G across the membrane was compared for bare PES support, seeded support and M8. The driving force for the migration is the concentration gradient of the dye, 10^{-4} M at the initial stage of the experiment. The dye is sufficiently large that it cannot penetrate through the 7.4 Å windows of the faujasite supercage, and would have to diffuse through the defects. Figure 5S shows the fluorescence measured on the support side of the membrane as a function of time. For the bare PES and the seeded support, the dye leaked through after the first two minutes, as measured by the fluorescence on the opposite side of the support. In case of M8, the dye leakage was prevented over 10 minutes, indicating that there are fewer mesopore defects on M8.

Tape Test A test of the mechanical stability of the seeded support and M8 was compared by pressing down a Scotch tape on the membrane surface and then peeling it off. Figure 6 shows the SEM micrographs before and after the test. The surface of the seed layer is destroyed (Figure 6B), including some damage to the underlying PES support. However, M8 appeared to remain intact, as seen in Figure 6D, and the tape test could be repeated 10 times without any damage to the membrane, as determined by SEM.

3.3. Transport Measurements with M8

Table 2 compares the transport data of a bare PES support, seeded support and M8. All transport measurements were done at room temperature. Even with M8, there is no selectivity of CO₂ over N₂, indicating that there are intercrystalline defects through which the gas molecules can pass.

We coated the surface of the bare support, seeded support and M8 with a thin film of PDMS by spin coating. The strategy was that the monomers would penetrate into the intercrystalline defects and then upon polymer formation, the defects would be sealed. Figure 7 shows the cross-section data, indicating that a thin 150 nm layer of PDMS covers the entire zeolite membrane. Table 2 shows that CO₂/N₂ selectivity of M8 is dramatically improved with a selectivity of ~72.3, while still maintaining high CO₂ permeance (~789.0 GPU).

Figure 8 compares the transport properties of M8 with changes in feed gas composition, and temperature. As seen in Figure 8A, for M8, with increasing CO₂ concentration, the N₂ permeance decreases, whereas the CO₂ permeance increases, with the overall selectivity exhibiting an increase with CO₂ concentration. Figure 8B shows that with increasing temperature (25-57°C), both CO₂ and N₂ permeance increase, but the latter is more pronounced and the overall selectivity decreases.

3.4. Reproducibility of membranes

Eighty M8 membranes with PDMS coating were fabricated and their transport properties examined. Figure 9 shows the data for all eighty M8 membranes tested. There are three sets of data in Figure 9. The red circles correspond to membranes samples (51 in

number) that were prepared by placing the seeded self-standing PES support in the flask used for membrane growth. Even with PDMS coating, the data were consistently poor, with CO₂/N₂ separation factors less than 10. The second group of membranes (blue diamonds, 17 in number) were placed in the flat sample holder (Figure 2S) during membrane growth. After growth, the membrane was removed from the holder, washed, dried and coated with PDMS. There was significant improvement with 35% of the samples showing CO₂/N₂ selectivity greater than 20. For the third set of samples (black squares, 12 in number), the membranes were grown in the holder, and considerable caution was exercised to keep the membrane flat during washing, drying, PDMS coating and mounting into the transport cell. The improvement was marked. In the insert of Figure 9, the performance of these 12 membranes is explicitly presented. The mean permeance was 839 GPU with a standard deviation of 527 GPU, and the CO₂/N₂ selectivity means was 44 with the same standard deviation. The covariance was negative, indicating that the permeance and selectivity exhibit an inverse dependence, as evident from the figure. It is relevant to note that 83% of the membranes exhibited CO₂/N₂ separation factor of > 30.

To account for the large variation in the transport data between the three sets of membranes, electron microscopy was carried out. For the first set of membranes (red circles), which were free standing and found to curl during the synthesis, there was extensive cracking, as shown in Figure 6S. PDMS layer is incapable of healing these defects. In Figure 10B, we show the optical micrograph of a membrane that was handled with care and maintained in a flat position. There are no obvious cracks, and the membrane appears uniform. The membrane was wrapped around a tube of 1.5 inch diameter, as

shown in Figure 10A. Upon examining the optical micrograph, extensive striations are noted in Figure 10C, and as the SEM in Figure 10D shows, deep cracks of 1 μm are apparent through the entire membrane. Thus, if precautions are taken to keep the membranes flat during all manipulations, including recovery from the reactor, washing, drying, mounting in the transport cell, the transport data of a significant fraction of these membranes were satisfactory. As is evident from the insert of Figure 9, with 10 of 12 samples, the permeance varied between 200-2000 GPU and CO_2/N_2 separation factors between 30 and 110.

4. Discussion

There are several review articles that describe in detail the various strategies used to synthesize zeolite membranes.[2,4,6,9] The secondary growth method being examined in the present study is by far the most popular method. Adapting the previous reported rapid zeolite growth[31] to zeolite membrane synthesis on polymer supports, as reported in this paper, has led to several novel observations regarding synthesis parameters, transport properties and membrane performance reproducibility, and is the focus of this discussion.

4.1. Optimal conditions for membrane Growth

There were eight different synthesis strategies, three of which resulted in continuous zeolite membrane formation. The steps involved in the rapid zeolite synthesis, shown in Figure 3, are relevant for understanding membrane formation. An aged gel of composition 8.5 Na_2O : 1 Al_2O_3 : 10.90 SiO_2 : 488 H_2O was put through two stages in a reflux apparatus. During stage I, half of the water was removed during reflux over the period of one hour,

and in stage II, this water was added back during the course of an hour. This process led to rapid crystallization of zeolite Y powder, with the crystallization of zeolite speeded up by a factor of four as compared to a conventional hydrothermal synthesis using the same composition.[31] We have reported that at end of stage I, the gel that is present is amorphous, but extensively nucleated.[31] This gel, referred to as the 60 - min gel was isolated and used as a reactant for membrane formation.

In order to successfully grow a zeolite membrane, it was essential to start with a seeded PES support. Because PES membrane is hydrophobic, vacuum had to be applied on the back of PES membrane to help zeolite seed deposition. Neutral to basic pH was found to produce uniform seed cover layers <300 nm thick, as shown in Figure 2, consistent with previous studies.[34,35]

As Table 1 and Figure 4 show, M1 and M2 grown with only the 60 min-gel and 60-min gel mixed with seed did not form a membrane. All trials with seeded membranes with and without 60-min gel coating (M3, M5, M7) when introduced into the reactor system at the beginning of the synthesis (before Stage I starts) did not form membranes. The three M4, M6, M8 that formed continuous membranes were all introduced at the end of stage I, and were subjected only to stage II protocol. Since M8 with only the seed and without any coating of the 60-min gel formed a zeolite membrane, there was no need of the 60 - min gel as an intermediate reactant for membrane growth. Thus, the conclusion is that seeded support and growth during the stage II process are essential for continuous membrane formation.

Size of the zeolite seeds are ~30-40 nm, and some fraction of these crystals penetrate into the PES support, as evident from the cross-section SEM in Figure 5B. These interpenetrated crystals along with the surface seeds grow during the stage II phase, and this intergrown layer within the membrane is important for anchoring the top membrane layer. This explains why unseeded supports such as M1 and M2 do not form membranes. The gel coating in M1 and M2 fall off during the synthesis. All attempts with different surface treatments (M3, M5, M7) introduced in the beginning of the reaction also do not result in continuous membrane, just the formation of crystals on the PES support surface. Introduction after stage II is important for successful membrane growth (M4, M6, M8), since the highly supersaturated solutions present in the heavily nucleated reaction medium after stage I help rapid growth of zeolite in the spaces between the seed crystals, resulting in membrane growth within an hour. The M8 strategy is optimum since it does not require coating with the 60-min gel and was the focus of further characterization and transport measurements. Figure 11 is a schematic representation of the proposed growth mechanism, with Figure 11A indicating seed layer deposition within and on top of the PES support. Once placed in the supersaturated solution of the growth medium, the seeds grow into a membrane with penetration into the PES support (Figure 11 BC).

4.2. Properties of M8 membranes

The formation of a uniform deposition on the PES support is evident from the optical micrograph in Figure 3S(C), and X-ray diffraction confirms that faujasite framework (Figure 3S (D)) is being formed. The cross-section SEM image in Figure 5C suggests that the zeolite membrane on the PES support is 250-300 nm thick. In addition,

there is growth within the porous support, arising from the penetration of seeds and subsequent growth. The infiltration into the support is essential for providing mechanical rigidity, as shown in the tape test of Figure 6.

A membrane preparation procedure in which the synthesis mixture is infiltrated into the pores of a porous α – Al_2O_3 support by manipulation of gel viscosity followed by hydrothermal growth with a clear solution for 24h has been reported.[35] With these long growth times, zeolite crystallization in the large pores of the alumina support was noted, which adversely affected the transport properties.

Even though dye leaking test in Figure 5S (C) indicates that the intercrystalline porosity is being reduced upon membrane formation, the gas transport measurements in Table 2 indicates that there are still defects within the membrane. The permeance of both CO_2 and N_2 decrease as the PES support is covered with zeolite seeds and upon M8 growth, yet the CO_2/N_2 selectivity remains unchanged at 1.2 for all three samples. The separation factor of as-synthesized M8 ($\alpha \approx 1.2$) is comparable to previous studies with defective zeolite Y membranes.[36]

4.3. Fixing Defects

The presence of intercrystalline defects in zeolite membranes is well known, and many strategies have been proposed to heal such defects.[12,17,33,37–44] Among limitations of zeolite membrane scale-up, poor reproducibility in fabrication is often the main drawback.[4] The reason for low reproducibility is defects on zeolite membrane. Several strategies have been reported to eliminate defects. Longer synthesis times and

multiple growth steps has been used to minimize inter-particle defects, but from a manufacturing perspective, such treatments may be inefficient.[17][37] Another method involves adding positively charged molecules to the growing zeolite layer, which facilitates the transport of anionic species into the defects and helps in the intergrowth of the zeolite crystallites resulting in denser zeolite grown membrane.[12,38–40] Chemical vapor deposition within the defects has been shown to reduce defects. In one such study, intercrystalline region was filled by silica formed via a counter diffusion reaction between tetraethylorthosilicate and ozone introduced from opposite sides of the membrane.[41–43] Defects have also been healed in zeolite membrane with nonpermeable polyfurfuryl alcohol.[42] Defect healing of mordenite membranes by grafting polymers on the surface and subsequent use for pervaporation studies has been reported.[43] Deposition of photoresist on membrane followed by irradiation and washing off the exposed part has been shown to reduce defects.[33,44]

The separation factor for the seeded and zeolite (M8) membrane was close to 1.2, which is near the Knudsen factor (0.8) indicating significant mesoporosity. Coating of PDMS, commonly used as sealing material, has been reported to seal defects on porous polymeric materials, as well as zeolite membranes.[36,45] PDMS was chosen in the present study to fix the mesoporous defects on M8-type zeolite membranes. PDMS can be polymerized after spin coating of monomer, cross-linker and catalyst on membrane.[45,36] Small monomer molecules can penetrate into the defects, and after cross-linking, polymerized PDMS can block the defects. The PDMS cross-sectional size, based on tetramethylsilane, is 0.8 nm and will not penetrate into zeolite cages.

4.4. Transport Studies

Figure 7B shows a ~150-200 nm PDMS layer on the M8 membrane. A 150 nm layer of PDMS has been estimated to provide a permeance reduction for CO₂ of < 1%. [36] However, if PDMS penetrates into the supporting membrane layers through macro/meso defects, then the permeance will decrease significantly. Thus, with both bare PES support and a seeded PES support coated with PDMS, there is a significant drop in permeance (Table 2) and CO₂/N₂ selectivity of < 20. The CO₂/N₂ separation factor for pure PDMS is reported to be around ~10 at room temperature. [46] With a PDMS layer on M8, the defect density was significantly decreased, leading to an improvement of CO₂/N₂ selectivity from 1.2 to 72 (Table 2), with CO₂ permeance of 789.0. Thus, we conclude that the zeolite membrane is responsible for the improved selectivity.

The feed gas compositional study shown in Figure 8A also indicates that the gas separation is occurring via the zeolite pores. The separation factor based on pure gas permeance for M8 is 45.2, and increases with CO₂ content in the feed to a final value of 95.1 for a 1:4 N₂:CO₂ mixture. This indicates that the separation mechanism of M8 membrane involves selective adsorption of CO₂ within the zeolite cages, which blocks the permeance of N₂. Preferential adsorption and diffusion of CO₂ in the zeolite pores stems from its higher quadrupole moment. This trend in selectivity is consistent with previous studies on zeolite membranes on alumina supports. [16]

Using the formula [23]

$$P = \frac{D}{\delta RT}$$

Where P is the permeance, D the diffusivity, δ the membrane thickness, we calculate D to be $2 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, comparable to previous studies on zeolite Y membranes.[23]

With increasing temperature (Figure 8B), CO_2 and N_2 permeance increases, but the increase in N_2 permeance outpaces that of CO_2 , decreasing the overall selectivity. This trend is consistent with previous studies of zeolite Y on alumina membranes in the temperature range that we are examining ($25 - 57^\circ\text{C}$).[17,23] The increase in permeance with temperature primarily arises from increased surface diffusivity. The decrease in selectivity with temperature is caused by the reduced adsorption of CO_2 on the zeolite framework, promoting enhanced transport of N_2 .

M8 membranes reported in this study were only dried under ambient conditions, so have considerable amounts of water in the zeolite. It has been pointed out that such highly structured water can be advantageous for gas separations.[39] The presence of water can increase CO_2 flux and selectivity, due to CO_2 dissolution in a water-like film.

4.5. Reproducibility of Membrane Performance

Eighty membranes were made following the procedure for M8 and their transport properties were examined. The CO_2 permeance as well as the CO_2/N_2 selectivity are plotted in Figure 9. It is clear that there is a wide variation in performance, depending on the handling of the samples. For membranes synthesized as free-standing membranes, the transport properties are very poor (red circles). Figure 6S shows the SEM of such a membrane, with extensive cracks, that are not suitable as functioning membranes even with a coating of PDMS. These cracks can be several microns wide and the PDMS cover layer

does fill these cracks and the membrane performance is similar to PDMS on the bare support. These cracks rip through the zeolite layer and the PES support. The best transport data were obtained with membranes that were kept in a flat configuration throughout the synthesis and mounting process (Figure 9, black squares). As is seen in Figure 10, such membranes will also show cracks if there is flexing of the support. We propose that the cracking is extensive because the zeolite layer also grows within the PES support. The rigidity of the inorganic membrane and the elasticity of the PES support are mismatched giving rise to the cracks.

However, with careful manipulation of the membrane, high quality transport data is obtained. The issue of reproducible manufacture of zeolite membranes on conventional alumina supports has been addressed.[4]

4.6. Comparison to Studies in the Literature

In Table 3, we compare the performance of one of the crack-free M8 membrane (one of the 12 samples represented as black squares marked with the dotted red circle in Figure 9) with literature reports of zeolite Y on alumina supports. Though all these studies were done in the same temperature range, these comparisons should be taken with caution, since the experimental parameters are not the same for (e.g. flow rate, sweep gas, pressure) all these experiments.

All of the zeolite membranes in Table 3 were synthesized on α -alumina supports at 90-100 °C for 12 hours to several days. Zeolite Y membranes can be grown on the inner and outer surface of tubes. Typically for zeolite membrane grown on outer surface,

thickness was 10 μm and it has 289 GPU CO_2 permeance and 50 CO_2/N_2 selectivity.[23]

While, for inner surface zeolite membrane, thickness was lower, 5 μm and CO_2 permeance and CO_2/N_2 selectivity were 4477 GPU and 32, respectively.[25] Seike et al. reported zeolite Y membrane synthesized on stainless steel plates formed by electrophoretic deposition of zeolite Y crystals followed by heat treatment. This membrane has CO_2 permeance of 1600 GPU and CO_2/N_2 selectivity of 20.[28] Other researchers have also reported zeolite membranes for CO_2/N_2 separation. The separation factors for CO_2/N_2 vary between 5 and 50.[17,28,29,35] We have reported on zeolite membranes grown on porous α -alumina disks. With 8 hour synthesis, 2 μm thick zeolite Y membrane with CO_2/N_2 selectivity higher than 550 and CO_2 permeance of 12 was observed. With longer synthesis time of 7 days, the high CO_2/N_2 selectivity was maintained and CO_2 permeance increased to 290.[16] A more recent study concluded that such zeolite membranes could have nanoscale defects, which were assisting in the separation process.[47] Performance wise, the present M8 membranes are comparable in permeance and separation factors to the literature. Of the 12 membranes, 10 had selectivity factors greater than 30, but there still needs to be improvement in the reproducible fabrication of these membranes. The major advantage of the M8 membrane is that it is grown on a polymer support within a very short time period (1 hour) and also is the thinnest membrane ($\sim 300\text{ nm}$) among reported zeolite membranes. Polymer membranes are typically grown on a large scale via a continuous preparation process using a casting machine. [48,49] The short time of zeolite synthesis reported in this study makes it feasible to grow the zeolite membrane on the PES polymer support, while it is being slowly drawn through the continuous casting machine containing a reactive aluminosilicate gel at elevated temperature, with the final composite being

maintained in a flat configuration as compared to a spiral wound module. Our current research is focused on accomplishing this goal.

5. Conclusion

A 300 nm zeolite membrane has been synthesized on polymer support within one hour and the composite membrane shows comparable CO₂/N₂ separation property with reported zeolite membranes on alumina supports. Synthesis process takes only 1 hour, making it feasible to synchronize polymer fabrication with zeolite membrane growth. The zeolite/polymer membrane will crack if it is subjected to bending motion. Thus, for the practical application of this family of membranes in gas separations, they need to be maintained in a flat configuration [50] during manufacture and use.

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This manuscript is based on the PhD thesis of Bo Wang, who did the bulk of the work. The paper was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Tables

Table 1. Secondary growth strategies of sample M1-M8 on PES 300 kDa support

Sample Code	Support	Knife Casting Material	Secondary Growth Starts
M1	Bare PES	Gel	After Dehydration
M2	Bare PES	Gel/Seed	After Dehydration
M3	Seed on PES	Gel	Before Dehydration
M4	Seed on PES	Gel	After Dehydration
M5	Seed on PES	Gel/Seed	Before Dehydration
M6	Seed on PES	Gel/Seed	After Dehydration
M7	Seed on PES	No Coating	Before Dehydration
M8	Seed on PES	No Coating	After Dehydration

Table 2. Transport Measurement Results of M8 Related Membranes

Sample Name	CO ₂ Permeance /GPU	N ₂ Permeance /GPU	CO ₂ /N ₂ Selectivity
PES only	3675.4	3118.1	1.2
Seed/PES	2990.2	2514.4	1.2
M8	1497.5	1273.5	1.2
PDMS/PES	383.6	22.8	16.8
PDMS/Seed/PES	810.1	52.4	15.5
PDMS/M8	789.0	10.9	72.3

Table 3. Comparison of Published zeolite membranes for CO₂/N₂ separations and in this study

Ref	Membrane support	Membrane thickness / μm	Synthesis Condition	Temperature / $^{\circ}\text{C}$	CO ₂ Permeance /GPU	CO ₂ Selectivity
[23]	α -alumina tube	10	90 $^{\circ}\text{C}$,24h	30	289	50
[24]	α -alumina tube	10	90 $^{\circ}\text{C}$,24h	40	836	45
[14]	α -alumina tube	10	90 $^{\circ}\text{C}$,24h	35	3880	30
[25]	α -alumina tube	5	90 $^{\circ}\text{C}$,24h	35	4477	32
[27]	α -alumina tube	3	90 $^{\circ}\text{C}$,24h	35	3283	37
[17]	α -alumina disk	4	90 $^{\circ}\text{C}$,12h	50	116	20
[35]	α -alumina tube	10	85 $^{\circ}\text{C}$,24h	50	1039	5.7
[26]	α -alumina tube	3	90 $^{\circ}\text{C}$,24h	35	2567	19
[28]	from SS plate	60	80 $^{\circ}\text{C}$,30h	25	1612	20
[29]	α -alumina disk	50	100 $^{\circ}\text{C}$, days	25	448	54
[16]	α -alumina disk	2	90 $^{\circ}\text{C}$,8h	30	12	>550
[16]	α -alumina disk	0.6	100 $^{\circ}\text{C}$,7d	30	290	503
Our	PES membrane	0.3	100 $^{\circ}\text{C}$,1h	25	789.0	72.3

*1 GPU = 3.35×10^{-10} mol / (m²·s·Pa)

FIGURE CAPTIONS

Figure 1. (A) SEM of PES support and (B) TEM of nano zeolite Y particles

Figure 2. Zeta potential – pH titration curve of nano zeolite Y particles and SEM of their deposition on PES support

Figure 3. (A) Reactor of zeolite membrane and (B) Schematic of secondary growth procedure of M7 & M8

Figure 4. SEM of A)M1, B)M2, C)M3, D)M4, E)M5, F)M6, G)M7, and H) M8 as defined in Table 1

Figure 5. Cross-section SEM of (A) bare PES support, (B) nano zeolite deposition on PES support and (C) zeolite membrane, M8

Figure 6. SEM of zeolite seed layer (A) before and (B) after tape test and zeolite membrane (C) before and (D) after tape test

Figure 7. Side-view SEM of (A) zeolite membrane and (B) PDMS coated zeolite membrane

Figure 8. Separation property of PDMS/M8 membrane with (A) feed gas composition and (B) temperature change (the red arrows point to the CO₂/N₂ selectivity)

Figure 9. Separation characteristics of PDMS/M8 membranes (red circle-free standing membrane during growth, blue diamond-membrane held in flat holder during growth, black squares-membrane held flat during growth and in all subsequent handling steps). The membrane with the red dotted circle was used to obtain the data in Figure 8. Insert in the figure is a detailed plot of the transport data of the 12 samples (black squares) that were

held flat in all steps, with the value indicating the number of membranes that had the particular transport characteristics.

Figure 10. (A) Bendability study diagram, optical microscope of PDMS/M8 membrane (B) before and (C) after bending and (D) SEM of cracks created in bending

Figure 11. Schematic illustration of (A) seed deposition layer, (B) membrane growth and (C) zeolite membrane in secondary growth

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