Graphical Abstract

Fabrication of zeolite/polymer multilayer composite membranes for CO₂ capture: Deposition of zeolite particles on polymer supports

Kartik Ramasubramanian^a, Michael A. Severance^b, Prabir K. Dutta^b and W.S. Winston Ho^{a,c,*}

^a *William G. Lowrie Department of Chemical and Biomolecular Engineering,*

^b *Department of Chemistry and Biochemistry,*

^c *Department of Materials Science and Engineering,*

The Ohio State University, 458 CBEC Building, 151 West Woodruff Avenue,

Columbus, OH 43210-1350, USA

* Corresponding author at: The Ohio State University, 458 CBEC Building, 151 West Woodruff Avenue, Columbus, OH 43210-1350, USA. Tel.: (614) 292-9970. Fax: (614) 292-3769.

E-mail addresses: ramasubramanian.8@buckeyemail.osu.edu (K. Ramasubramanian), severance.18@buckeyemail.osu.edu (M. Severance), dutta@chemistry.ohio-state.edu (P. Dutta), ho.192@osu.edu (W.S.W. Ho).

ABSTRACT

Membranes, due to their smaller footprint and potentially lower energy consumption than the amine process, offer a promising route for post-combustion CO₂ capture. Zeolite Y based inorganic selective layers offer a favorable combination of CO₂ permeance and CO₂/N₂ selectivity, membrane properties crucial to the economics. For economic viability on large scale, we propose to use flexible and scalable polymer supports for inorganic selective layers. The work described in this paper developed a detailed protocol for depositing thin zeolite Y seed layers on polymer supports, the first step in the synthesis of a polycrystalline zeolite Y membrane. We also studied the effects of support surface morphology (pore size and surface porosity) on the quality of deposition and identified favorable supports for the deposition. Two different zeolite Y particles with nominal sizes of 200 nm and 40 nm were investigated. To obtain a complete coverage of zeolite particles on the support surface with minimum defects and in a reproducible manner, a vacuum-assisted dip-coating technique was developed. Images obtained using both digital camera and optical microscope showed the presence of color patterns on the deposited surface which suggested that the coverage was complete. Electron microscopy revealed that the particle packing was dense with some drying cracks. Layer thickness with the larger zeolite Y particles was close to 1 μm while that with the smaller particles was reduced to less than 0.5 μm. In order to reduce drying cracks for layers with smaller zeolite Y particles, thickness was reduced by lowering the dispersion concentration. Transport measurement was used as an additional technique to characterize these layers.

KEYWORDS: *zeolite Y, polymer support, CO₂ capture, hybrid membrane, multilayer composite*

1. Introduction

High performance membranes or selective barriers based on novel materials offer one of the few potential means of meeting the stringent economics of post-combustion CO₂ capture (PCC). For CO₂/N₂ separation in PCC, CO₂ permeates selectively through the membrane. In this context, it is useful to understand three quantities, CO₂ flux (J_i), CO₂ permeance (P_i) and CO₂/N₂ selectivity ($\alpha_{i/j}$) shown by Eq. (1) and Eq. (2).

$$J_i = P_i(p_f \times x_i - p_s \times y_i) \quad (1)$$

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad (2)$$

where p_f is the feed pressure, p_s the permeate or sweep pressure (if a sweep gas is used to provide driving force), x the feed side mole fraction, and y the permeate side mole fraction. High P_{CO_2} (>3000 GPU) and high α_{CO_2/N_2} (>100) selectivity are important for economic viability as pointed out by recent studies [1–3].

Membranes usually consist of a thin selective layer (~100 nm to μ m in thickness) supported on a porous and relatively thick support for mechanical stability [4-7]. Polymeric membranes are flexible and scalable in the form of hollow-fiber and spiral-wound modules having high surface area/volume ratios. Although some polymer membranes based on polar ethylene oxide groups in the backbone have demonstrated high CO₂ permeance (>2000 GPU) [2,4], their performance is usually limited by the Robeson's selectivity-permeability trade-off [8]. Inorganic membranes on the other hand can potentially provide a higher selectivity at a comparable CO₂ permeance [5,9,10] but are plagued by irreproducibility due to defects and involve the use of thick, brittle, less scalable, less compact and more expensive inorganic supports [11,12]. The support cost issues,

irreproducibility of synthesis and long synthesis times have hindered the development of inorganic membranes that barring a few examples [12], there has been minimal commercialization.

As a potential solution to the above problem and to harness the performance benefits of inorganic membranes, we studied appropriate porous polymer membranes as supports for promising zeolite-based inorganic layers. These porous membranes, generally made by phase inversion, have traditionally been used as selective layers in ultrafiltration, microfiltration and also as polymer membrane supports. Common polymers are polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile, cellulose acetate, nylon, etc. Since such supports have not yet been studied for inorganic selective layers or even inorganic particulate layers, our approach was to begin by developing a scalable method for depositing stable zeolite Y particulate layers on them with minimum defects. The specific goals of this work were as follows: (1) study and identify different support materials and support morphologies that will allow us to make defect-free zeolite Y particulate layers and (2) focus on fabricating thin zeolite Y seed layers of less than 1 μm in thickness. Subsequent growth of the seed layer into a selective polycrystalline zeolite membrane is not a part of this work. We recognize that the long times it takes for the hydrothermal synthesis of zeolites makes it incompatible with growing membranes on polymer supports, an issue we have addressed recently [13].

2. Background and rationale

2.1. Zeolite Y as membrane material

Commonly studied physical solid adsorbents for CO_2 include different types of zeolites and activated carbons while alkali earth metal oxides, supported amines, and hydrotalcite are examples of chemisorbents [14-18]. Physical adsorbents make use of van der Waals forces between gas molecules and adsorbent surface while chemisorbents make use of a specific chemical reaction, for

instance, an acid-base type reaction in case of CO₂ and metal oxides or amines. Physical adsorbents generally show lower adsorption capacities but more favorable regeneration properties than chemisorbents. They also show acceptable to excellent adsorption and desorption kinetics. In case of post-combustion flue gas CO₂ capture, both CO₂ partial pressure (0.1 to 0.2 atm) and temperature (57 °C) are relatively low. Under these conditions, zeolites show an attractive trade-off between properties among physical adsorbents [14,15].

Zeolites are crystalline aluminosilicates with well-defined microporosity that has enabled their applications in a wide variety of fields like catalysis, detergency, and chemical sensing in addition to separations [19]. Depending upon the Si/Al ratio and the number of neutralizing cations inside the pores, zeolites can have different adsorptive properties, with the hydrophobicity increasing as the Si content increases [19,20]. The fixed pores of zeolites can also distinguish between molecules of different shapes and sizes. Traditionally, zeolites have been used in adsorption processes. Membranes are interesting from the point of view of using these materials in a continuous separation process.

Molecular permeation through a zeolite pore depends on the loading (determined by thermodynamics) in addition to the diffusion kinetics. To discuss membrane transport mechanism, it is helpful to look at permeability of component *i* as simply a product of diffusivity and sorption coefficient of that component in the membrane.

$$Permeability_i = Sorption\ coefficient_i \times Diffusivity_i \quad (3)$$

which leads to the following expression for selectivity.

$$\alpha_{ij} (Permeability_i / Permeability_j) = Adsorption\ Selectivity_{ij} \times Diffusion\ Selectivity_{ij} \quad (4)$$

$$\text{where } Adsorption\ Selectivity_{ij} = \frac{Sorption\ coefficient_i}{Sorption\ coefficient_j} \text{ and } Diffusion\ Selectivity_{ij} = \frac{Diffusivity_i}{Diffusivity_j}$$

The CO₂ and N₂ molecules are similar in their kinetic sizes at 3.3 Å and 3.6 Å, respectively [8]. Hence, pure size-sieving is not expected to yield high selectivities. In other words, the contribution of diffusion selectivity to the overall selectivity is small. However, the quadrupole moment and polarizability of the CO₂ molecule are about three times and twice those of the N₂ molecule, respectively [20,21]. Also, CO₂ is more condensable than N₂ (critical temperatures are 304.1 K for CO₂ and 126.2 K for N₂) [22]. CO₂ can therefore interact more strongly with the zeolite surface which results in adsorption and permeation CO₂/N₂ selectivities of much greater than unity in zeolites.

Faujasite (FAU) type zeolites with a low Si/Al ratio, namely, zeolite X and zeolite Y, show the highest adsorption selectivities as evidenced by several experimental and simulation studies [14,15,20]. FAU-type crystal structure has a pore size of 7.4 Å. All silica FAU-type zeolite is charge free. But in zeolite X (Si/Al < 1.5) and zeolite Y (1.5 – 3.8) [19], the presence of aluminum creates negative charges in the silicon-aluminum frameworks which are countered by metal cations in the pore space. Most common configurations contain Na⁺ as the counterion and hence are called NaX and NaY. CO₂ (compared to N₂) can interact more strongly with the micropore electric field whose strength depends on both the number and type of cations. The Si/Al ratio of NaX is less than that of NaY due to which it has more cations and demonstrates a higher CO₂/N₂ adsorption selectivity albeit with a slightly smaller pore volume than NaY. The adsorption mechanism has been explored in detail elsewhere by combining microcalorimetry measurements with molecular simulations [23].

Although interaction between CO₂ and zeolite surface increases at lower Si/Al ratios, this may cause the molecule to slow down and thus reduce the diffusivity in Eq. (3). This effect may lead to zeolite Y showing a higher CO₂ permeance than zeolite X and a better trade-off between CO₂/N₂

selectivity and CO₂ permeance. Molecular dynamics simulations have indicated that pure zeolite Y crystal permeability could be >10⁵ Barrers with a CO₂/N₂ selectivity of 100 – 200 at typical flue gas operating conditions [20]. It should be noted that this permeability is equivalent to a permeance of 10⁵ GPU for a 1-μm selective layer ($P_i = \text{Permeability}_i/l$, where l is the selective layer thickness). These values are comfortably above the Robeson upper bound for polymeric materials [8,20]. The large pores of FAU-type structure combined with the optimal Si/Al ratio are the main factors behind the expected high performance. In addition, the effect of CO₂ adsorption on the diffusion of N₂ molecules plays a role too. When CO₂ molecules adsorbed on the zeolite micropore surface preferentially diffuse along a concentration gradient by the so-called, “surface diffusion” mechanism [20,24], the pore area available for N₂ is effectively reduced.

Experimentally, CO₂/N₂ selectivities ranging 20 – 500 at CO₂ permeances > 300 GPU have been measured for zeolite Y membranes on alumina supports [6,25]. CO₂ permeances of greater than 2000 GPU at CO₂/N₂ selectivities ~50 have been achieved using even smaller pore [10] or higher Si/Al ratio zeolites [9]. In order to make a zeolite membrane, the zeolite crystals must all be connected in a thin film of polycrystalline structure. The performance values predicted by simulations have not been achieved experimentally, in part due to the difficulties in making a defect-free and continuous polycrystalline structure. Defects can reduce the selectivity by allowing non-selective convective gas flow through them although new approaches like coating an inorganic layer with polydimethylsiloxane (PDMS) have been successful in plugging defects [26].

2.2. Zeolite membrane synthesis

Polycrystalline zeolite layers for membrane applications are generally fabricated by the deposition of a seed layer of zeolite particles or nuclei (in the nm – μm range) on a porous support followed by secondary growth of the seed layer to close the interzeolitic pores [27]. The focus of

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4 this work is to deposit the seed layer on polymeric supports, the first step in the membrane
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6 synthesis.
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8 9 *2.3. Seed layer deposition*

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11 It is imperative to obtain defect-free seed layers from stable colloidal dispersions of zeolite
12 particles. Defects in the seed layer could lead to defects in the grown membrane [7,27,28]. Also,
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14 the membrane selectivity cannot be recovered with a cover layer like a thin PDMS coating if the
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16 defect concentration is too high [26,29]. Thin seed layers would not only lead to a relatively thin
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18 grown membrane and minimize the transport resistance but also help better follow and cover the
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20 contours of a rough substrate [30], thereby reducing the possibility of flex-cracks. In addition, the
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22 thinner the layer, the smaller are the drying cracks [31]. However, the probability of producing
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24 defects due to incomplete coverage is higher during the deposition of a thinner layer. This effect is
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26 especially enhanced for rough substrates like the polymer supports used in this work.
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34 Rubbing, electrostatic deposition, electrophoretic deposition, spin-coating, and dip-coating are
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36 the techniques used by different researchers to obtain a uniform seed layer [7,31,32]. Boudreau et
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38 al. modified a silicon wafer and used electrostatic attraction to adsorb zeolite A particles (~300 nm
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40 in size) [32]. They obtained complete coverage with just one coating but the particles were not
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42 close-packed. In this process, substrates have to be modified chemically using sequential coatings
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44 with charged polymers to have opposite charge to that of zeolite particles. Not only are such
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46 processes more complicated to scale up, but they also require post-process removal of the polymer.
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48 Dip-coating is the most favorable technique for scale-up. The substrate is dipped into the coating
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50 solution vertically or at an angle and then withdrawn at a given speed. The film thickness is
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52 controlled by a balance of viscous drag with gravity or surface tension forces. On solid substrates
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54 like silicon wafers, glass and non-porous alumina, dip-coating of zeolite suspensions (in the
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absence of any polymers) has yielded only limited success in terms of achieving complete surface coverage. For example, Boudreau et al. used multiple coatings and slow withdrawal speeds to improve the coverage of zeolite particles [32]. This was largely due to the inherent poor film-forming ability of particles as compared to polymers and also the low viscosity of dilute colloids.

However, on porous substrates, dip-coating is always accompanied by not only simple film coating but also slip casting where the liquid in the coating sol is absorbed by the pores. This liquid draining helps in speedy consolidation of particles on the substrate, thereby forming a close-packed particulate layer. Coherent zeolite seed layers have been obtained on porous inorganic supports [6,7,27]. The slip-casting effect could dominate for a low viscosity coating dispersion especially in the absence of any film-forming polymer. The rate of deposition in slip casting is given by the following expression (Darcy's law) [33-35]:

$$Q = -\frac{K}{\mu} \frac{dp_l}{dz} \quad (5)$$

where p_l is the liquid pressure, Q the deposition rate or the liquid flux, K the liquid permeability through the porous media, μ the viscosity of the coating dispersion, and z the position variable in the flow direction. The liquid pressure, p_l , is influenced by the capillary suction pressure, p_c , in addition to any externally applied driving force [35].

$$p_c \propto \frac{\sigma}{d_p} \quad (6)$$

In the above relation, σ is the interfacial tension between the liquid and the substrate material, a measure of its hydrophilicity or lyophilicity, and d_p is the diameter of the pores in the substrate. It is important to note that although $p_c \propto 1/d_p$, $K \propto d_p^2$ (by the well-known Hagen-Poiseuille equation) due to which the deposition rate decreases as the pore diameter reduces. Also, p_c would reduce to zero when the substrate pores get saturated with the liquid. The ceramic supports, for

example, porous alumina used by White et al. [6] and Kuzniatsova [36], are generally thick (~2 mm) with a porosity of about 30 – 40% due to which they have a substantial unsaturated pore volume during coating. This can keep the suction pressure high and give sufficiently high deposition rates. White et al. used such alumina supports with a pore size of about 40 nm to obtain a good surface coverage of close-packed zeolite Y (80 – 200 nm in size) particles by dip-coating with a thickness of 1.6 μm for the seed layer [6]. Fig. 1 shows the top surface of that layer.

Polymer supports, on the other hand, are different in morphology from the ceramic supports. They are generally produced as a two-layer composite structure with the polymer of interest supported on a porous fabric. The total thickness is about 100 – 300 μm and the total bulk pore volume is small due to the small thickness. This could reduce the slip casting effect due to pore saturation during the coating process.

A similar issue was tackled by Pan et al. for coating thin-walled ceramic hollow fibers with alumina particles [37]. They used evacuation to increase the suction and form a continuous layer in a cross-flow filtration set-up. Huang et al. obtained a uniform layer of zeolite A seed particles (500 – 1500 nm) on alumina supports using vacuum-assisted dip coating [38].

The role of the colloidal dispersion is important in this regard in addition to the deposition process. The more stable the dispersion is, the lesser is the number of aggregates and consequently, a more close-packed and dense particulate layer could be formed. This means that there is minimal subsequent particle rearrangement and shrinkage due to which less cracking occurs [31,35,36]. Ultrasonication is the usual method for dispersing the zeolite particles in water.

3. Experimental

3.1. Materials

The nanoporous PSf support (thickness of 160 μm including a non-woven polyester fabric backing) was kindly provided by NL Chemical Technology, Inc. (Mount Prospect, IL). Biomax PES ultrafiltration membranes (thickness of 270 – 330 μm including a non-woven fabric) of different molecular weight cut-offs, namely 30 kDa (kilo-Daltons), 50 kDa, 100 kDa, 300 kDa and 1000 kDa, were kindly provided by EMD Millipore (Billerica, MA). Sterlitech PES (free-standing) microfiltration support with a nominal pore size of 30 nm and thickness of 50 μm was purchased from Sterlitech Corporation (Kent, WA). The actual pore size is different from the nominal pore size and has been shown in Table 1. All these supports were also characterized by scanning electron microscopy to obtain a more accurate picture of their surface morphology. PDMS was kindly provided by Wacker Silicones, Inc. (München, Germany) as a viscous liquid product with a trade name Dehesive[®] 944. The corresponding crosslinker (Wacker[®] Crosslinker V 24) and catalyst (Wacker[®] Catalyst OL) were also provided. Zeolite Y particles of roughly two sizes, 200 nm and 40 nm, were synthesized. The procedures used to prepare and characterize these particles are detailed in the recent dissertation work conducted at The Ohio State University [39] and in the related publication [40]. The synthesis of smaller zeolite particles of roughly 40 nm size was based on prior work by Holmberg et al. [41]. The aforementioned sizes are used to refer to the two different particle types in this study. More accurate average particle diameters and intensity averaged particle size distributions of zeolite dispersions were determined by dynamic light scattering using a Malvern Zetasizer Nano system (see Fig. 2a). The correlation functions measured were averaged over 45 accumulations of 10 sec scans collected at a backscattering angle of 273°. The method of cumulants was used to obtain an average particle size. The non-negative nonlinear least squares method was used to invert the intensity correlation functions to particle size distributions. Average zeta potentials were measured by electrophoretic light scattering.

Electrophoretic mobility measurements were converted to zeta potentials according to the Henry equation at the Smoluchowski limit. The average particle sizes were 214 ± 1 nm and 40.0 ± 0.1 nm while the zeta potentials were -56 ± 4 mV and -44 ± 2 mV, respectively, for the submicron zeolite and nanozeolite. Transmission electron micrographs (TEM) were collected using a Tecnai F20 field emission 200 kV S/TEM system. TEM image of the nanozeolite, in Fig. 2b, shows well-formed particles with size range 20 – 50 nm. The surface areas of the 200 nm and 40 nm particles were measured as $635 \text{ m}^2/\text{g}$ and $475 \text{ m}^2/\text{g}$, respectively, as nanozeolite Y is reported to have a lower surface area than bulk zeolite due to crystallinity difference [39].

3.2. Lab-scale deposition

Dispersions of different zeolite Y concentrations were prepared in water. Dispersions of 200 nm particles were ultrasonicated at room temperature for around 90 minutes whereas those of 40 nm particles were ultrasonicated for around 40 minutes. The water in the ultrasonication bath was changed intermittently (every 15 minutes) to prevent a temperature rise. The coating of the dispersion onto a polymer support is described in the following paragraph. Millipore PES supports as obtained had glycerol in the pores which was removed using water washing followed by dipping in isopropanol (IPA), before deposition. Each washing/dipping step was done for at least 30 minutes. After the deposition, the seed layers were dried overnight at room temperature prior to further characterization or PDMS coating for transport measurements. The layers with 40 nm zeolite particles were dried at 70% relative humidity at room temperature.

Some of the initial experiments on polymer supports were performed using dip-coating. The dispersion sol was spread evenly on the substrate attached to a glass plate in a horizontal position after which it was allowed to stand in a vertical position, thereby draining all the liquid solution of the dispersion. Later, in order to avoid saturating the relatively thin polymer supports during dip-

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4 coating, a vacuum dip-coating apparatus was set up. A circular holder shown in Fig. 3 was
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6 designed and fabricated, the tube end of which was connected to a Duoseal 1405 liquid ring
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8 vacuum pump. The substrate to be coated was taped onto a fixed flat porous metal plate supported
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10 on the holder. The top surface of the substrate was then dipped tangentially (as in crossflow
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12 filtration) into the coating dispersion for a couple of seconds and then taken out. The vacuum in
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14 addition to assisting the layer formation helped to keep the support flat during the coating process.
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16 A bypass was used to control the downstream vacuum, if needed. When the bypass was
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18 completely closed, the downstream pressure went down to about 3 inch Hg. All the results
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20 discussed in Section 4 were obtained using these conditions.
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26 In the last step during fabrication and also for transport characterization, the membrane was
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28 spin-coated with a PDMS solution using a WS-650 spin-coater from Laurell Technologies.
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30 PDMS, obtained from Wacker Silicones, Dehesive[®] 944 was a 30 – 40% solution in an organic
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32 solvent. PDMS solution for the coating was prepared by dissolving 2.5 g of Dehesive[®] 944 in 16.2
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34 g of heptane. The corresponding crosslinker and catalyst were then added in the ratio 100 : 1 : 0.5
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36 (PDMS : Crosslinker : Catalyst) by weight. The coating procedure used was as follows: PDMS
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38 solution was spread evenly on the stationary substrate. After the spreading, the spinning speed was
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40 increased to 1000 rpm and maintained for 10 sec after which it was increased to 3500 rpm for a
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42 minute. The coated membrane was dried in the hood for 30 minutes after which it was cured at
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44 100 °C for 30 minutes. This same procedure was used to PDMS-coat different substrates. For the
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46 more viscous PDMS solution preparation, about 3.9 g of Dehesive[®] 944 was dissolved in 9.3 g of
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48 heptane. The spin-coating speed was increased to 5000 rpm instead of 3500 rpm, and the solution
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50 was spread on an already rotating substrate at 2000 rpm.
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4 It is important to note that the above PDMS coating step generates a covering PDMS layer
5 along with causing PDMS to infiltrate the zeolite interparticulate pores. To minimize/eliminate
6 infiltration of the PDMS solution into the zeolite layer (with ~40 nm particles), water was evenly
7 spread onto the surface followed by spinning at 1000 rpm for 10 sec and then at 3000 rpm for 5
8 sec. This was repeated five or six times after which the PDMS was coated and cured by the usual
9 procedure. For comparison, we made coatings on bare Millipore PES 300 kDa. For PDMS
10 coating on the bare PES support, the glycerol in the pores was removed after the PDMS curing by
11 overnight immersion in IPA.
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14 3.3. *Imaging by scanning electron microscopy*

15 For SEM, both PSf and PES supports were immersed in IPA overnight at room temperature
16 before sample preparation. The Sterlitech support was used as received. The samples were gold-
17 coated before imaging. The cross-sectional imaging was done using a Focused Ion Beam (FIB)
18 with SEM (FEI Helios Nanolab 600 Dual Beam FIB/SEM). The top surface images were analyzed
19 using the Clemex Image Analysis software to estimate the surface porosities and mean pore sizes
20 reported in Table 1.
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23 3.4. *Transport characterization*

24 The gas permeation set-up described in our previous work [42,43] was used to test the PDMS-
25 coated zeolite particulate layers. Most of the measurements were performed under dry conditions.
26 All permeance measurements had a $\pm 1.5\%$ standard error due to the fluctuations in GC peak areas
27 obtained at steady state. For wet gas measurements, the feed-side humidifying vessel was filled
28 with water upto a volume of 60% of the total volume. The feed gas was then bubbled through it.
29 For low selectivity (CO_2/N_2) and high permeances reported in this paper, the counterdiffusion of
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Ar sweep gas through the membrane can be significant. This was taken into account for membrane performance evaluation.

The tests were conducted using a small rectangular cell (area: 2.71 cm²). The feed and permeate/sweep flows were countercurrent relative to each other, and the log-mean partial pressure driving force was used to calculate the permeances. The test temperature was 57 °C, and feed and sweep pressures were 1 atm each. The feed gas consisting of 25% CO₂ and 75% N₂ (on dry basis) was used for these tests. High sweep flow of around 300 cc/min was used for these tests to eliminate any sweep side mass transfer resistance at high permeances. The feed gas flow was approximately 60 cc/min.

4. Results and discussion

4.1. Identification of polymer supports

The inherent hydrophilicity of the common ceramic support, alumina, is much more than that of PSf and PES, which are the two most widely used polymeric ultrafiltration and microfiltration membrane materials [44,45]. The first dip-coating experiments were performed using the PSf support (surface pore size = ~9 nm and surface porosity = ~7%). Although the pore size and porosity were considerably lower than those of alumina support [6,36], we were interested in using this support due to its ease of availability. The surface morphology of the support is shown in Fig. 4a.

The top surface of the seed layer on the PSf support is shown in Fig. 4b. It should be noted that vacuum was not used for this experiment. The larger zeolite Y particles (~200 nm) were used at a dispersion concentration of about 0.5 wt%. The zeolite particles did not form a coherent layer. Instead, they formed loose aggregates and settled randomly on the support surface. The small pore size (as well as porosity) of PSf support and the resultant viscous resistance to the liquid draining

through the support could result in an insufficient slip-casting or draining effect by reducing K in Eq. (5).

Sterlitech PES support was then used for a similar experiment. This support had a larger pore size and surface porosity (pore size = ~ 100 nm and porosity = $\sim 14\%$) than the PSf support. The top surface of the coating is shown in Fig. 5. It can be seen clearly that the surface coverage was better than on the PSf support. Also, the particles were more closely packed in this case. This could be attributed to the greater deposition rate on the Sterlitech support due to the larger pore size and porosity (larger K in Eq. (5)). Although the particle packing was better than that on PSf support, it was not as tightly packed as in the case of alumina support (Fig. 1). This was likely due to the saturation of support pores as indicated in Section 2.3. This support thickness was only about $50\text{ }\mu\text{m}$ as opposed to the alumina support which was about $2 - 3$ mm in thickness. In order to obtain a better deposition at this point, we set up the vacuum dip-coating apparatus. We identified three commercial PES supports for this purpose. The top surfaces of all these supports are shown in Fig. 6. The image analysis results are shown in Table 1. As indicated by these results, all these supports including the Sterlitech support had a larger pore size and surface porosity than the PSf support. The slightly greater hydrophilicity of PES vs. PSf could help in the deposition too (greater σ and consequently greater p_c in Eq. (6)). The deposition experiments with these supports are described in the following sections.

4.2. Seed layer deposition by vacuum dip-coating

For the 200 nm zeolite Y particles, we used the Sterlitech PES and Millipore 1000 kDa PES supports (Table 1). Fig. 7 shows an example of the coating on the Sterlitech PES support. The coating showed a color pattern throughout the surface due to an optical opalescence effect, which is typical of thin uniform layers [46]. Fig. 8 shows the images of the top surface and cross-section

of the sample obtained by SEM. These colors were also seen for a similar coating on Millipore 1000 kDa PES support. Fig. 9 shows an optical microscopic image of the same. The dark spots or patches on the background are macroscopic defects or non-uniformities of the support.

The top view in Fig. 8 shows a fairly close packing of zeolite Y particles similar to that seen in Fig. 1. The cross-sectional view obtained using FIB etching and SEM shows a thickness of about 1 μm or less. Fig. 10 shows a similar deposition performed on the PSf support. As it can be seen, the surface coverage was not very good despite the use of vacuum. These results showed that, if the pore size (as well as surface porosity) was too small, it was difficult to obtain enough suction even with vacuum.

We were also interested in depositing the polymer supports with smaller zeolite particles to obtain a relatively smaller interparticulate pore size. This is more favorable for subsequent growth to fill these pores or even from the point of view of using these layers as porous substrates or intermediate layers. For this, we carried out experiments on Millipore PES 1000 kDa and Millipore PES 300 kDa supports. The Sterlitech support could not reproducibly form a layer with the smaller particles due to its large pore size.

We started with a deposition of about 0.58 wt% dispersion of ~ 40 nm zeolite particles on Millipore 1000 kDa support. The top surface obtained was full of cracks and is shown in Fig. 11. We then reduced the concentration of the dispersion to about 0.19 wt%. The optical microscopic images of the resultant coatings on both Millipore 1000 kDa and 300 kDa supports are shown in Fig. 12 and Fig. 13, respectively. It can be clearly seen that the size of cracks drastically reduced at the lower concentration (and consequently, lower thickness). They can be observed only when viewed carefully. The cracks in such layers usually originate during initial consolidation and drying. It is known that these cracks increase in width with thickness [31]. Also, these cracks

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4 seem to appear more for the smaller particles due to the larger drying stresses associated with
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6 smaller spaces between the particles.
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9 Fig. 14 shows the depositions with about 0.19 wt% dispersion on these supports as seen using a
10 digital camera. As discussed before, the color patterns show the presence of a continuous zeolite
11 layer from a macroscopic view [46]. But they do not explain enough about the quality of the layer
12 as shown by the previously discussed images.
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19 We then attempted to make the layer thinner by diluting the dispersion to about 0.1 wt%. Fig.
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21 15 shows the top-surface SEM image of the seed layer deposited with about 0.1 wt% dispersion on
22 Millipore 300 kDa. With this concentration, it was not possible to get a good coverage of ~40 nm
23 particles on Millipore 1000 kDa support which had a higher number of large pores (>200 nm) than
24 the 300 kDa support. On Millipore 300 kDa support, the dilution resulted in a thinner layer with
25 much fewer cracks having an average width of less than 100 nm or so. A layer thickness of less
26 than 400 nm or so was confirmed by cross-sectional SEM using FIB as shown in Fig. 15(c). Such
27 a thin seed layer is highly desirable for the high permeance zeolite Y membrane and also for use as
28 a substrate or intermediate layer.
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41 We performed some adhesion check experiments for these particles using a scotch tape test. In
42 this test, the scotch tape was flattened evenly on the top surface (zeolite) and then ripped off.
43 From the force used to remove the tape and the residue left on the tape, conclusions could be
44 drawn about the quality of the adhesion between the top surface and the layer beneath. The results
45 could be classified qualitatively. For the 40 nm particles on Millipore 300 kDa support, the
46 adhesion was good. But for the 200 nm particles, the adhesion was poor. This could be explained
47 by the fact that the smaller particles could come into a much more intimate contact with each other
48 as well as with the substrate layer, compared to the larger particles. This can be further attributed
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to (1) the larger contact area of the smaller particles and (2) the plausibility that the 40 nm particles could enter the substrate pores to a greater extent than the 200 nm particles.

4.3. *Transport measurements*

The seed layer formed by zeolite particles has interparticulate pores or voids. There are two types of such voids in hexagonal close packing of perfectly spherical particles: tetrahedral and octahedral holes. If the particle diameter is 40 nm, the interparticulate tetrahedral void size is <10 nm (diameter of the largest sphere the void can hold) while the octahedral hole is about 16 nm in diameter [47]. Thus, these interparticulate gaps are too big to offer any gas separation. In order to obtain a selective zeolite membrane, the interparticulate pores need to be closed or plugged via zeolite growth. Although obtaining a purely zeolite-based selective layer was out of the scope of this work, we covered the seed layer with PDMS to plug these pores and characterized the layers through transport measurements. Fig. 16 shows these results. The zeolite Y seed layers were obtained as shown in Fig. 8 and Fig. 15 and described in Section 3.2. The selectivity of all the PDMS-coated zeolite membranes was close to 9. Although low, it was significantly higher than that of PDMS which varied between ~3.5 and ~5.5 at 57 °C (see ‘PDMS/Millipore 300 kDa’ points in Fig. 16). The preferential adsorption of CO₂ vs. N₂ at the interface between zeolite and PDMS phases may increase the CO₂ loading vs. that of N₂ in the mixed matrix compared to pure PDMS selective layer [48]. Although the CO₂/N₂ selectivity increased, CO₂ permeances of these membranes were much lower than that of pure PDMS membrane.

Zeolite Y is a microporous particle with a high crystal CO₂ permeability (>10⁵ Barrers) predicted by molecular dynamics simulations [20]. This permeability is equivalent to a permeance of 100000 GPU for a 1-μm membrane. Although this permeance has not been verified experimentally, we can reasonably assume that the microporous zeolite Y phase has a CO₂

permeability of 3000 Barrers, same as that of PDMS at 57 °C, for an order-of-magnitude analysis. The thickness of the zeolite particulate layer from Fig. 8 is about 1 μm . With the assumption that the PDMS has infiltrated to fill all the interparticulate pores in this layer, the thickness of the mixed matrix layer should be about 1 μm . The CO_2 permeance for the mixed layer should therefore be at least 3000 GPU. The spin-coating process creates a covering PDMS layer. By assuming a CO_2 permeance of 2500 GPU for a covering PDMS layer on the zeolites (see ‘PDMS/Millipore 300 kDa’ points in Fig. 16), the CO_2 permeance for the composite membrane can be estimated as about 1400 GPU by a resistances-in-series model.

Since the CO_2 permeances observed in this work were considerably lower than the above estimate, it is important to examine the possible non-idealities existed in the system. PDMS chains might block the micropores of zeolite Y to gas molecules. This meant that only the external surface area of the particles might be available for adsorption. These blocking effects might reduce permeabilities by a factor of 2 or more in high zeolite content zeolite X – PDMS mixed matrix compared to pure PDMS [48]. Other factors such as pre-adsorbed H_2O molecules or intercrystalline transport resistances might also contribute to lowering the permeance of zeolite micropores [14,20]. The lower than expected permeance might also indicate that the infiltration of PDMS into the underlying porous substrate (PES) was significant.

Samples were also prepared by filling the zeolite layer with water (see ‘water filled’ points in Fig. 16) and then coating with PDMS as described in Section 3.2. In these cases, the zeolite-coated Millipore 300 kDa gave a high CO_2 permeance (between 2700 to 4000 GPU) similar to or better than PDMS on bare Millipore 300 kDa (close to 2500 GPU). The better result was presumably due to two factors: (1) the smaller pore size and higher porosity of the particulate zeolite layer compared to those of Millipore 300 kDa could reduce the effect of infiltration into the

substrate and (2) the less spreading resistance for the PDMS on the zeolite layer, i.e., the resistance in the PDMS layer to find the pore in order to transport through the porous substrate underneath was lower on the zeolite layer than that on the Millipore 300 kDa substrate [49]. However, transport modeling and more experiments are required to understand the difference between the two scenarios (whether zeolite layer is present or not). Similarly, more samples will need to be analyzed to average out the variation in CO₂ permeance (2700 to 4000 GPU) obtained for different samples with PDMS coated on the water-filled zeolite layer. Nevertheless, the effect of filling the zeolite layer with water before PDMS coating is pretty clear from the results shown in Fig. 16. The CO₂ permeance is much higher and the CO₂/N₂ selectivity is considerably lower for samples with water filling compared to samples with no water filling of zeolite interparticulate pores. This can be explained by the hypothesis that water filling of these pores will reduce the PDMS solution infiltration into them. That would reduce the mixed-matrix effect and consequently the selectivity while decreasing the mass transfer resistance and increasing the permeance.

An attempt was also made to reduce infiltration of PDMS solution by making it more viscous (see ‘PDMS/ZY-200 nm’ points in Fig. 16). But, the CO₂ permeance further reduced to about 215 GPU (viscous PDMS solution) from about 330 GPU (usual PDMS solution) with the selectivity increasing marginally from 8.5 (usual PDMS solution) to 9 (viscous PDMS solution). Although the higher viscosity of the PDMS solution should reduce its infiltration into the zeolite layer, it also makes the covering layer significantly thicker, increasing the overall mass transfer resistance.

5. Conclusions

This paper describes the laboratory development of a scalable method for depositing defect-free zeolite layers on commonly used polymer supports. We developed a vacuum dip-coating technique to obtain <1 µm thick coatings of zeolite particles on these supports. Favorable polymer

support surface morphologies that could allow for a successful deposition were identified. The effects of coating dispersion concentration and particle size on the dried layer thickness and quality were studied, and the suitable dispersion concentration and particle size were identified. The relation between layer thickness and crack formation was also explored. Smaller particles were found to be more prone to cracking than larger particles at the same thickness. But, the smaller particles were used advantageously to reduce the layer thickness and the interparticulate pore size. Also, smaller particles showed better adhesion with the underlying substrate.

The seed layers can be used to grow polycrystalline zeolite layers or used as substrates for polymer membranes. By filling the interparticulate pores with a suitable polymer, a mixed matrix membrane with high inorganic loading (60% or more by volume) can also be fabricated as demonstrated using PDMS and zeolite Y in this work.

This work could also be adapted to other separations that use inorganic membranes as selective layers and applications such as ultrafiltration and nanofiltration. It can potentially improve the economics of inorganic membrane fabrication for a wide range of applications.

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Nomenclature

d = diameter (m)

J = steady-state flux (mole/m²/s)

K = permeability of the porous media (m²)

l = selective layer thickness

P = mixed-gas permeance (GPU, 1 GPU = 10⁻⁶ cm³ (STP)/cm²/s/cm-Hg; 3000 GPU = 10⁻⁶ mole/m²/s/Pa = 10⁻¹ mole/m²/s/bar).

p = pressure (bar)

Q = liquid flux (m³/m²/s)

x = mole fraction on the feed side

y = mole fraction on the permeate or sweep side

z = position variable in the direction of flow through support (m)

Greek Letters

α = membrane selectivity

μ = coating liquid viscosity (Pa•s)

σ = interfacial tension between coating liquid and substrate material (N/m)

Subscripts

c capillary suction

f feed side

i, j species

l liquid

p pore

s sweep or permeate side

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Table 1. Surface morphology of the different supports used for zeolite deposition. These numbers were obtained through the analysis of SEM images in Fig. 4a and Fig. 6.

Support	Mean pore size; Largest pore size (nm)	Surface Porosity (%)
Sterlitech PES	~96; 810	~14.4
Millipore 1000 kDa PES	~57; 683	~17.1
Millipore 300 kDa PES	~62; 385	~15.4
PSf	~9; 35	~6.9

Figures

Fig. 1. The top surface view (SEM) of the Zeolite Y seed layer in Ref. 6.

Fig. 2. (a) Zeolite particle size distributions obtained by dynamic light scattering and (b) TEM image of nanozeolite.

Fig. 3. Schematic of the vacuum-assisted dip-coating set-up.

Fig. 4. Zeolite Y dip-coating (0.5 wt% dispersion in water, ~200 nm particles) onto PSf support. (a) Bare PSf support and (b) Resultant zeolite coating on PSf.

Fig. 5. Zeolite Y dip-coating (0.5 wt% dispersion in water, ~200 nm particles) onto Sterlitech PES support.

Fig. 6. Top surface views (SEM) of commercial PES supports used for zeolite Y coating. (a) Millipore 300 kDa PES, (b) Millipore 1000 kDa PES, and (c) Sterlitech PES.

Fig. 7. Zeolite Y vacuum dip-coating (0.5 wt% dispersion in water, ~200 nm particles) onto Sterlitech PES support. (a) Bare support and (b) Resultant zeolite coating on the support.

Fig. 8. Zeolite Y vacuum dip-coating (0.5 wt% dispersion in water, ~200 nm particles) onto Sterlitech PES support. (a) Top view (SEM image) and (b) Cross-section (FIB-SEM image).

Fig. 9. Optical microscopic image of zeolite Y vacuum dip-coating (0.5 wt% dispersion in water, ~200 nm particles) onto Millipore PES 1000 kDa support.

Fig. 10. Zeolite Y vacuum dip-coating (0.5 wt% dispersion in water, ~200 nm particles) on PSf support.

Fig. 11. Optical microscopic image of zeolite Y vacuum dip-coating (0.58 wt% dispersion in water, ~40 nm particles) onto Millipore PES 1000 kDa support.

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Fig. 14. Zeolite Y vacuum dip-coating (0.19 wt% dispersion in water, ~40 nm particles) onto Millipore supports. (a) Coating on Millipore 1000 kDa and (b) Coating on Millipore 300 kDa.

Fig. 15. Zeolite Y vacuum dip-coating (0.1 wt% dispersion in water, ~40 nm particles) onto Millipore 300 kDa support. (a) Top view of the zeolite layer under lower magnification, (b) Top view of the zeolite layer under higher magnification, and (c) Cross-section.

Fig. 16. Transport characterization of PDMS-coated zeolite seed layers (polymer-supported) and PDMS-coated polymer supports.

¹ 0.58 wt% zeolite Y dispersion.

² Feed gas was humidified in these experiments.

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(b)

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(a)

(b)

(c)

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(b)

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(a)

(b)

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