



Synthesis and stability of zeolitic imidazolate framework-68 membranes



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ABSTRACT

Large pore zeolitic imidazolate framework (ZIF) membranes offer potential for separation of gases with different adsorption affinity on ZIF crystals and separation of liquid molecules by molecular sieving. In this work continuous, highly crystalline, largely *c*-oriented ZIF-68 membranes were reproducibly synthesized on macroporous zinc oxide supports by the reactive seeding method. The membranes were roughly 50 microns thick and the single component gas permeance measurements obtained adhered to Knudsen diffusion, indicating the presence of limited nonselective defects. The membranes were found to be highly stable at room temperature and ambient conditions, although immersion in water at room temperature and 100 °C caused irreparable damage to the ZIF-68 crystallinity. Immersion in organic solvents did not render the crystallinity notably altered. A prolonged *p*-xylene pervaporation run indicated that ZIF-68 membranes were susceptible to fouling, by showing an approximately 55% decrease in *p*-xylene pervaporation flux from when the membrane was fresh to the second data point tested at 4 h. The extent of fouling equilibrated after 4 h on-stream and the pervaporation flux remained constant throughout the remainder of testing. The membrane crystallinity was not degraded by *p*-xylene pervaporation.

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1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are a subset of metal–organic frameworks (MOFs) that are gaining substantial interest. ZIFs, much like MOFs, are characterized by highly crystalline, microporous structures constructed from three-dimensionally repeating arrays of tetrahedrally coordinated metallic ions connected by rigid organic ligands [1–3]. The distinguishing feature of ZIFs is the use of imidazole linkers which create bond angles, that when coordinated with inorganic constituents, mimic those of the bonds intrinsically created between silicon and oxygen atoms in the formation of zeolites. To this end, it is possible to synthesize ZIFs in any number of topological conformations previously only found in aluminosilicate zeolites while still retaining the customizability of metal–organic frameworks [1–4]. The duality of the organic and inorganic components, coupled with the self-assembling nature of the crystals renders them highly amenable to rational design. Through altering synthesis conditions, organic linkers and metallic ions, it is conceivable that a ZIF material can be tailored to address with better acuity established zeolite applications, such as membrane reactor processes and gas and liquid separations [4–6].

Of the known ZIF materials, there have been many synthesized and studied in crystalline form, while a few have been mainly relegated to theoretical research methods and fewer still have been synthesized and studied as continuous membranes. There are currently reports on no more than a handful of ZIF membranes; most notably are ZIF-7 [7], ZIF-8 [8–14], ZIF-22 [15], ZIF-69 [16,17], ZIF-71 [18], ZIF-78 [19,20], ZIF-90 [21,22] and ZIF-95 [23]. All of which are characterized by smaller pore openings, with pore sizes ranging from 2.9 Å for ZIF-7 and ZIF-22 to 4.4 Å for ZIF-69 [2]. Given the relative saturation of smaller-pore ZIF membrane materials being studied, it would be advantageous to begin exploring membrane synthesis of larger-pore ZIF materials. While the characteristic desirability of ZIFs would remain intact, larger-pore ZIF membranes would allow for a different set of potential gas and liquid separation applications to be explored. These applications include separation of gas molecules with perm-selectivity determined by the adsorption properties, such as those offered by the large pore FAU type zeolite membranes and large liquid molecules by molecular sieving [24]. It is in this regard, the interest in studying ZIF-68 in membrane form has emerged. ZIF-68, a ZIF material characterized by a 7.4 Å pore diameter and 10.5 Å cage diameter, has been lauded for its crystalline integrity in harsh conditions, as well as its predicted preferential adsorption of CO₂, and could serve well as a stable membrane for gas and liquid separation processes [2,24].

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To synthesize continuous ZIF-68 membranes a novel reactive seeding approach was utilized. Reactive seeding is a membrane synthesis method that has been reported for MIL-53 [25], MIL-96 [26] and ZIF-71 [18] which centralizes around a surface modification step wherein the seeds are created from an in situ solvothermal reaction between the imidazole linkers and the inorganic support itself. In this manner an intimately adhered and homogeneous seeds layer can be directly created from the support itself, and following secondary growth, a defect free membrane layer can be obtained. The objective of this work is to reproducibly synthesize continuous and defect-free ZIF-68 membranes by the reactive seeding method, and to study the stability of ZIF-68 membranes to help determine for which potential applications this larger-pore ZIF material is suited.

2. Experimental

2.1. Zinc oxide supports

ZIF-68 synthesis via reactive seeding was carried out using homemade zinc oxide supports. To prepare the supports, 8 g of a 3 wt% solution of polyvinyl alcohol (Sigma Aldrich, PVA, 99+%) in deionized water was added to 76 g of zinc oxide powder (Sigma Aldrich, ZnO, 99.9+%) and intimately mixed. Once mixed, 3.2 g of the powder was placed in the support mold and pressed in a Carver hydraulic pellet press to an applied load of roughly 12,500 lb for a minute. The green bodies were sintered for 5 h at 570 °C to produce the disks with the diameter of 22 mm, thickness of 2 mm, and normal pore size of ca. 100 nm. The sintered supports (one side) were then gently polished using 800 and 1200 grit sandpaper, rinsed in deionized water and ethanol for 15 min under ultrasonic agitation, and dried at 100 °C for 3 h.

2.2. ZIF-68 seed layer synthesis

To create the seeds synthesis solution, 0.25 mmol each of 2-nitroimidazole (Bosche Scientific, nIm, +98%) and benzimidazole (Sigma Aldrich, bIm, 99%) were added to 30 mL of dimethylformamide (Alfa Aesar, DMF, +98%) and thoroughly stirred until all precursors were dissolved. The solution was then added to a Teflon lined autoclave containing a cleaned and dried ZnO support suspended polished side down. Due to the nature of reactive seeding, all exposed surfaces of the ZnO support are susceptible to the growth of ZIF-68 seeds. To avoid complications due to seed and membrane growth on both sides of the ZnO support, an unreactive alumina support was placed flush to the unpolished side of the ZnO support to serve as a hindrance to seed growth. Once both supports were in place in the solution, the autoclave was sealed shut and left to react in an oven at 120 °C for 8 h. At the end of 8 h, the autoclave was allowed to return to room temperature naturally. Once cooled, the seeded support was removed and gently cleaned with a cotton ball wet in DMF to remove any unreacted imidazole precursors. The membrane was then soaked for three hours in DMF and dried for 3 h under vacuum.

2.3. ZIF-68 secondary growth

Once the support containing the ZIF-68 seeds layer was washed and dried, secondary growth began. The secondary growth step differed from the synthesis of the seeds layer mainly as it incorporated the addition of a zinc source, as the free surface zincs were largely depleted in the seeds layer creation. To prepare the secondary growth solution, 1 mmol of each precursor, bIm, nIm and zinc nitrate hexahydrate (Sigma Aldrich, $\text{Zn}(\text{NO}_2)_3 \cdot 6\text{H}_2\text{O}$, 98+%) were measured out. The zinc nitrate hexahydrate was added to 10 mL

of DMF and stirred thoroughly until completely dissolved. Concurrently, the imidazole precursors were added to a separate vial containing 20 mL of DMF and were also allowed to stir until completely dissolved. After the precursors were completely dissolved in their respective solutions, the 10 mL of DMF in which the zinc source was dissolved was added dropwise to the still-stirring solution of imidazole precursors in 20 mL of DMF. Once the mixtures were both completely combined and thoroughly stirred, the solution was poured into a Teflon lined autoclave wherein the seeded support was suspended horizontally, with the seeded side down. As with before, an unreactive alumina support was placed flush with the unpolished side of the support. The autoclave was then sealed shut and placed in an oven at 120 °C for 8 h and allowed to return to room temperature naturally. Once the autoclave was cooled, the membrane was removed, washed thoroughly in DMF and brushed gently with a cotton ball to remove any unreacted precursors. The membrane was then immersed in methanol overnight to allow for solvent exchange and dried under vacuum at ambient temperature.

2.4. Characterization of ZIF-68 crystals and membranes

The crystallinity of the ZIF-68 membranes was determined through X-ray diffraction (XRD) on a Panalytical X'Pert Pro X-ray Diffractometer at 40 kV and 40 mA at a scan speed of 5°/min using Cu K α radiation. Further characterization of ZIF-68 membranes included permeation measurements using a simple permeation set up as described previously [27]. The permeation testing using helium, nitrogen, oxygen and carbon dioxide was carried out following thorough membrane activation. The ZIF-68 membrane was held under vacuum in an oven at 100 °C for 5 h to remove trapped impurities within the pores, and following activation the membrane was placed in a stainless steel permeation cell, with the ZIF-68 layer on the feed side, and sealed on both sides with Viton O-rings. Following permeance measurements, ZIF-68 membranes were further characterized through pervaporation, as it allows for further insight into the membrane continuity and quality. Pervaporation was carried out as shown in previous works [27]. Prior to pervaporation, the membrane was activated under vacuum at 100 °C for 5 h, then immediately transported to a stainless steel pervaporation cell, where it was sealed securely on both sides by chemical resistant O-rings.

The final step was to carry out the destructive characterization of these membranes using a scanning electron microscope (SEM). Micrographs of ZIF-68 membranes were obtained using a Philips FEI XL-30 scanning electron microscope set at a 12 kV accelerating voltage. The membranes were sputtered thoroughly with a coating of Pd-Au prior to imaging to decrease the likelihood of surface charging during imaging.

2.5. ZIF-68 stability tests

To test the stability of ZIF-68 membranes in atmospheric conditions, the structure of the as-synthesized ZIF-68 membranes were first examined by XRD, then the membranes were placed in a petri dish (loosely covered) in the air and left undisturbed for 12 months. At the end of the 12 months the crystal structure was analyzed again to determine any alterations to crystallinity.

Much in the same manner, testing the stability of ZIF-68 in water, hexane, *p*-xylene and DMF at room temperature began with obtaining an initial XRD pattern for a fresh ZIF-68 membrane. The membranes were then each placed in a vial containing 50 mL of the relevant liquid, capped and left undisturbed for the entirety of the week. Upon removal and drying, their crystal structures were analyzed again. The boiling water stability testing was carried out in a similar manner, with the exception of the testing apparatus. The

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