



Organic solvent pervaporation properties of MOF-5 membranes



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ABSTRACT

Membranes made of microporous metal–organic frameworks (MOFs) with pore sizes larger than zeolites, such as MOF-5, offer potential for separation of large molecules in liquid phase. However, MOF-5 exhibits severe degradation upon contact with atmospheric levels of moisture. The objective of this work is to determine material stability of MOF-5 membranes during pervaporation of organic solvents. High quality MOF-5 membranes about 10 μm in thickness were prepared by the secondary growth method using ball-milled MOF-5 seed crystals. On-stream *p*-xylene pervaporation test of the as-synthesized MOF-5 membrane shows the *p*-xylene flux declines and levels off at a steady-state value about 70% of the original value for fresh-membrane after 16 h on the stream. The *p*-xylene flux cannot be restored to the original value, suggesting permanent fouling of the MOF-5 membrane upon exposure to *p*-xylene stream. Subsequent characterization indicated there was no structural or microstructural degradation that occurred, and evidence of retained xylene isomers in the MOF-5 structure was found using Fourier transform infrared spectroscopy. Nevertheless, the fouled MOF-5 membranes exhibit stable pervaporation fluxes for organic molecules with sizes smaller than the aperture of the MOF-5 cage, and exclude organic molecules with sizes larger than MOF-5 aperture. The results show that the MOF-5 membranes, after a permanent reduction in permeation flux by initial exposure to xylene stream, are stable in organic solvent and can be used for separation of liquid organic molecules based on the molecular sieving effects.

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1. Introduction

In recent years, hybrid materials known as metal–organic frameworks (MOFs) have begun garnering a sizeable amount of attention in the research community. The highly crystalline, microporous materials consist of metal oxide tetrahedra constructed into repeating arrays by rigid organic linkers [1]. The interest in studying MOFs stems from the extensive variability inherent to the nature of the material itself; through altering synthesis conditions, metallic constituents or organic ligand functionality it is feasible to tailor a MOF to meet the needs of any number of material design issues [1,2].

The focus of this study is on MOF-5, the first successfully synthesized MOF [1]. MOF-5 is known for its large pore size (8 Å) and aperture sizes (12 and 15 Å) and attributes its highly-crystalline cubic structure to a network of zinc oxide tetrahedra rigidly connected by terephthalic acid organic linkers [1–6]. It is this combination of pore size and functionality of the organic ligands that render MOF-5 particularly attractive. Since Yaghi and coworkers [1] first reported the synthesis of MOF-5 in 1999, it has become one of the most widely studied MOFs for its potential use in hydrogen storage, CO₂ sequestration, and a wide array of separation

processes [6–11]. Roughly a decade after MOF-5 first gained notoriety; the first successful MOF-5 membrane was synthesized by Lai and coworkers [10]. Along with the first successful synthesis of the MOF-5 membrane, and the subsequent synthesis of thinner, more continuous membranes by Zhao et al. [11] entirely new research possibilities were emerging for MOF-5. There is, however, a substantial drawback that could potentially limit the practicality of the use of MOF-5 in many applications.

MOF-5 has shown a rather crippling aversion to small amounts of atmospheric moisture that ultimately results in irreversible destruction of the structure. Kaye et al. [12] reported a systematic degradation of MOF-5, monitored by obtaining XRD patterns at different time intervals. The XRD patterns began showing a significant phase shift that began after only 10 min in air, and ultimately rendered the porous material a solid with the chemical formula C₂₄H₂₂O₁₈Zn₄ after a 24 h period [12]. The mechanism of this extreme degradation was researched by Huang et al. [13] who noticed that water rather insidiously replaced portions of the BDC ligand and fully ingratiated itself into the structure, leading to hydrolysis of Zn atoms from adjacent Zn₄O tetrahedra. The effect is not limited to just water vapor, as further reports tout the ability of any polar, hydrogen-containing molecule to alter the structure of MOF-5 by secondarily bonding to the zinc–oxygen tetrahedra causing a collapse or shift of the structure [14]. This premise is further substantiated by Saha and Deng [15] who showed a structural

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degradation of MOF-5 tangibly via measuring a substantial surface area reduction from 2449 to 10 m²/g following exposure to ammonia.

By virtue of the widely reported instability of MOF-5 in humid atmospheric conditions, the potential to utilize MOF-5 membranes for applications in which the contact with atmosphere is negated, such as pervaporation, is gaining interest. Pervaporation through smaller pore MOF membranes such as ZIF-8 and ZIF-71, where ZIF, a specific type of MOF, stands for zeolitic imidazolate framework, has given initial indication of the interesting and sometimes unpredictable nature of pervaporation through MOFs. ZIF-8, with a pore size of only 3.4 Å, would most likely exhibit a sharp cut off that would exclude aromatic molecules larger than the pore size; however Diestel et al. [16] found that this was not the case. During pervaporation experiments using benzene and *n*-hexane, probing molecules with effective diameters that exceed the pore size of ZIF-8 by twenty to forty percent, significant fluxes of approximately 0.6×10^{-4} and 14×10^{-4} mol/m²s mol, respectively, were reported [16]. Only when pervaporation using a binary solution of *n*-hexane and mesitylene, a molecule with a kinetic diameter just over 2.5 times the size of the ZIF-8 pores, did ZIF-8 behave as a molecular sieve [16]. As the concentration of mesitylene increased, it hindered the flux of *n*-hexane through the membrane, as the bulky molecule was unable to pass [16]. Another study on a small-pore MOF, ZIF-71, reported successful separation of organic–inorganic and organic–organic solvents [17]. Dong and Lin [17] found ZIF-71 to show good permselectivity for dimethyl carbonate (DMC) over methanol despite DMC having a larger kinetic diameter than methanol. This was attributed by the hydrophobicity of ZIF-71, and its preference to the weaker polarity of the DMC molecules [17].

Virtually all reports of MOF pervaporation behavior is of smaller pore MOFs, with limited research into the pervaporation behavior of larger pore membranes, such as MOF-5. Previously, Zhao et al. [11] reported xylene isomer and large probing molecule pervaporation as a means of deducing the quality of the MOF-5 membranes; however sustained stability upon exposure to organic solvents has not been investigated [11]. Because of the large pore size of MOF-5, MOF-5 membranes offer potential for liquid phase separation of organic molecules. The focus of the work presented herein is to determine the ability of MOF-5 membranes to withstand immersion in organic solvents while maintaining structural stability, which may allow for the novel properties of this membrane to be utilized for organic separation without the risk of degradation in humid atmosphere.

2. Experimental

2.1. Synthesis of MOF-5 seeds and suspension

MOF-5 powders were synthesized via solvothermal synthesis as reported previously [11,18]. Given amounts of zinc nitrate hexahydrate (Zn(NO₃)₆ · 6H₂O, 1.664 g, 99%, Sigma Aldrich) and terephthalic acid (BDC, 0.352 g, 99+%, Acros Organics) were added to a vial containing 2,2-dimethylformamide (DMF, 40 mL, 99.8+%, Alfa Aesar) that had been previously degassed for 60 min in argon. Once the precursors were fully dissolved, the vial was capped and immersed in an oil bath held at 403 K for 3 h. After removal from the oil bath, the vial, now containing macroscopic, colorless crystals, was allowed to naturally return to room temperature. Once cooled, the solvent was decanted and the crystals were washed three times with DMF in order to remove any unreacted precursors. After the final washing, the crystals were immersed in chloroform, held at 343 K for 3 days to allow for solvent exchange to occur and dried under vacuum overnight at 323 K. The resultant crystals were

quite large, between 20 and 40 μm, and using N₂ porosimetry with a Micromeritics' ASAP 2020 machine, were found to have a surface area of 646.46 m²/g. Due to the large crystal size, further mechanical processing was necessary to reduce the size of the crystals to that needed for creating a suspension for membrane synthesis.

In previous work the powders were ground by a mortar and pestle to reduce the particle size [11]. In this work, the powders were ball milled in a Teflon container, the MOF-5 crystals were immersed in 50 mL of chloroform and the grinding media, in this case alumina balls, were added at a ball to powder mass ratio of 25:1. The container was then sealed and securely placed in an Across International PQ-N04 Planetary Ball Mill set to 150 rpm for 24 h. An rpm of 150 was chosen because it is high enough to ensure an adequate reduction in crystal size, while preserving the nanoscopic crystalline structure. After ball milling, the seeds were dried under vacuum overnight to remove any excess chloroform. The ball milled seeds, now between 1 and 3 μm in sizes, were added at a concentration of 2 wt% to DMF and ultrasonically agitated for 4 h to create a stable MOF-5 suspension.

2.2. MOF-5 membrane synthesis

Once a stable MOF-5 suspension was obtained, the membrane synthesis via dipcoating and secondary growth proceeded. Macroporous α-Al₂O₃ supports were synthesized in-house, from a 10:1 ratio of alumina powders (A16, Alcoa) to distilled water by the press-sintering method. After being intimately ground, 2.1 g of the mixture was used to form pellets, using a Carver pellet press slowly raised to 20,000 lb for 5 min. The supports were then sintered and polished with progressively finer grit sandpaper (#500, #800 and #1200). Once well-polished, the supports were placed, polished side up, in a solution of ethanol and distilled water and ultrasonically agitated for 15 min to remove any debris that may remain from polishing. The supports, once dried at 373 K for 12 h, were then ready for use in dipcoating. To dipcoat, the supports were immersed, polished side down, in the MOF-5 suspension for 5 s, then removed and left to dry at 323 K for 24 h. This process was repeated three times to achieve a thorough covering of the seed layers.

Following MOF-5 seed deposition, secondary growth was carried out to achieve a continuous membrane. As with MOF-5 crystal synthesis, a given amount of zinc nitrate hexahydrate (0.416 g) and BDC (0.88 g) are mixed with 40 mL of degassed DMF in a sealable vial. The solution was then stirred vigorously to allow for the precursors to completely dissolve while a given amount of *N*-ethyl-diisopropylamine (EDIA, 0.069 g, +99.5%, Acros Organic) was slowly added drop-wise. The EDIA was incorporated to allow less competition between ligands and available metal sites [11]. Once thoroughly stirred, two seeded supports, held vertically by Teflon holders, were placed in the solution. The vial was then tightly capped and placed in an oil bath heated to 303 K for 3 h. After 3 h, the vial was removed from the oil bath and left to cool. Upon returning to room temperature, the membranes were removed and washed three times with DMF to remove any unreacted precursors. The membranes were then placed in chloroform for 2 days to allow for solvent exchange and, following solvent exchange, were dried overnight under vacuum.

2.3. MOF-5 membrane characterization

Using the membrane synthesis method outlined, multiple membranes were synthesized concurrently under the same processing conditions. This created theoretically identical MOF-5 membranes, which allowed for destructive characterization using scanning electron microscopy to illuminate membrane microstructure prior to any pervaporation stability testing. The membrane

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