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Microporous Metal Organic Framework Membrane on Porous Support Using the Seeded Growth Method

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A seeded growth method is used to prepare preferentially oriented and well-intergrown films of microporous metal organic framework (MMOF) on porous α-alumina discs. A randomly oriented seed layer is deposited which leads to an oriented membrane as a result of competitive grain growth during the secondary growth process. The orientation is such that the pores are preferentially aligned along the membrane thickness and the membrane exhibits ideal selectivity for H_2/N_2 as high as 23.

1. Introduction

Metal-organic frameworks (MOFs) are a relatively new class of crystalline porous materials consisting of metal clusters connected by organic ligands. The pore size and surface properties of these materials can be tuned to a great extent with relative ease by choosing appropriate metal centers and organic ligands. This structural flexibility generated interest in these materials for applications ranging from gas storage,[1] adsorption,[2−4] catalysis,[5,6] sensors,[7,8] and so forth

MOFs are also attractive for gas separation applications as their pore size and chemistry can be tailored for specific molecular sieving needs. Despite the immense potential and wide range of separation applications, there has been little effort toward fabrication of MOF membranes. Selective nucleation and growth of MOF-5 and $Cu_3(BTC)_2$ crystals on surface modified metal substrates were studied by Fischer and co-workers.[9,10] Bein and co-workers[11,12] have reported oriented growth of MOFs (HKUST-1, MIL-53,and MIL-88) on self-assembled monolayer modified metal substrates. Use of in situ growth[13] and microwave heating[14] have also been reported to grow MOF films on porous supports. However, none of the aforementioned studies report a continuous film. In fact, until now, very few reports exist on continuous films that could be used as separation membranes. Gascon et al.[15] and Liu et al.[16] report continuous films of HKUST-1 and MOF-5, respectively, on porous alumina supports. Guo et al.[17] recently reported the $Cu_3(BTC)_2$ membrane on a copper net exhibiting a separation factor of 7 for H_2/N_2.

Microporous metal organic framework structure (referred to as MMOF hereafter), originally reported by Li and co-workers,[18,19] is built upon copper paddle-wheel and a V-shaped dicarboxylate ligand. The layered 3D structure has cage-like one-dimensional pore channels oriented along the length of the long columnar crystals. The unique shape and size of these channels enables MMOF to exhibit interesting separation properties. It has been reported to selectively adsorb smaller normal alkanes (C_1-C_4) while rejecting linear alkanes larger than C_4 and all branched alkanes.[19]

As the MMOF crystals have pore channels in only one direction, the orientation of the crystals becomes critical for membrane application. Here, we report the synthesis of continuous MMOF membranes on surface-modified porous alumina supports using a seeded growth technique.

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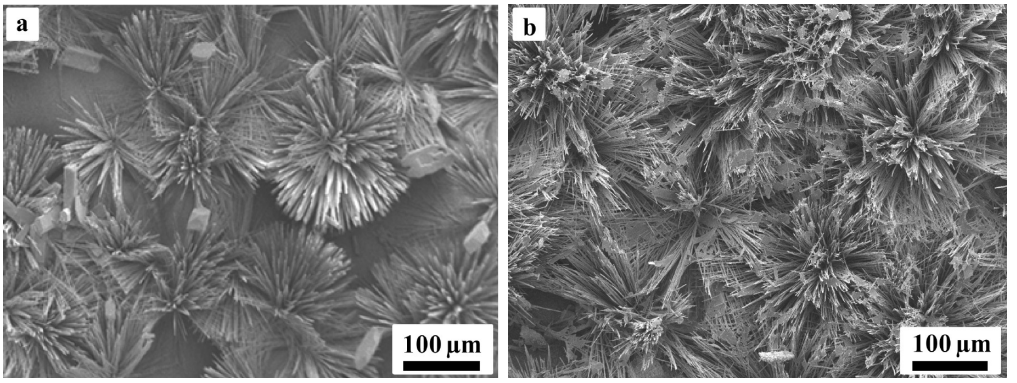

Figure 1. SEM of MMOF film grown by in situ growth at (a) 180 °C and (b) 200 °C.

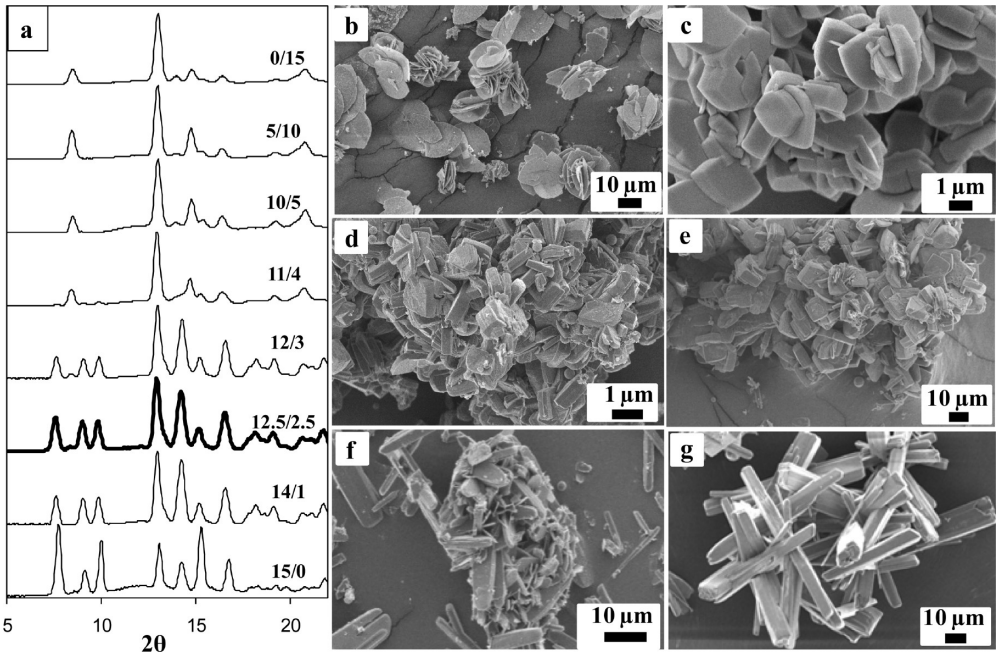

Figure 2. (a) X-ray diffraction patterns of the MMOF crystals obtained using the water−methanol ratios (v/v) shown next to the patterns (from top to bottom 0/15; 5/10; 10/5; 11/4; 12/3; 12.5/2.5; 14/1; 15/0). Diffraction pattern for the seed crystals is highlighted in bold. SEM images of the crystals at the respective solvent compositions: (b) 0/15, (c) 5/10, (d) 12/3, (e) 12.5/2.5, (f) 14/1, and (g) 15/0.

A seed layer is deposited and then grown under conditions that favor faster growth along the pore channels (*b*-crystallographic axis). The resulting membranes are well intergrown and preferentially oriented so that most of the 1-D pore channels are aligned perpendicular to the support surface.

2. Experimental Section

2.1. MMOF Powder Synthesis. All chemicals were purchased from Aldrich and used as supplied. MMOF crystals were synthesized using the procedure reported by Pan et al.[18] $Cu(NO_3)_2 \cdot 3H_2O$ (0.072 g) and 4,4′-(hexafluoroisopropylidene)-bis(benzoic acid) (0.366 g, excess) were added to DI water (15 mL), and the resulting gel was placed in a Teflon lined stainless steel autoclave followed by heating at 150 °C for 12 h. After completion of the synthesis, the blue powder was washed with dimethylformamide (DMF; 30 mL) and water (30 mL) followed by drying in air.

2.2. Films by in Situ Growth. Homemade porous α-alumina supports[20] were used as the support for in situ growth of the membranes. One side of the support was polished using 600 grit paper to obtain a smoother surface for the membrane growth. The synthesis gel, prepared using the procedure for MMOF described in section 2.1, was placed in a Teflon lined stainless steel autoclave. The polished alumina support was placed vertically in the autoclave with the help of a Teflon holder.[21] Several synthesis temperatures were investigated. The resulting films were washed with DMF and water followed by drying at 100 °C.

2.3. Seeded Growth of the Membrane. MMOF membranes on porous supports were prepared through a modified seeded growth procedure. The growth procedure is described in detail below.

2.3.1. Surface Modification of the Alumina Support. The polished α-alumina support surfaces were modified using polyethyleneimine (PEI) based on the expectation for enhanced attachment of seeds via H-bonding. The PEI deposit was formed by dip-coating in a PEI−water solution (1:30 w/w) followed by drying. The process was repeated twice to enhance coverage of the support.

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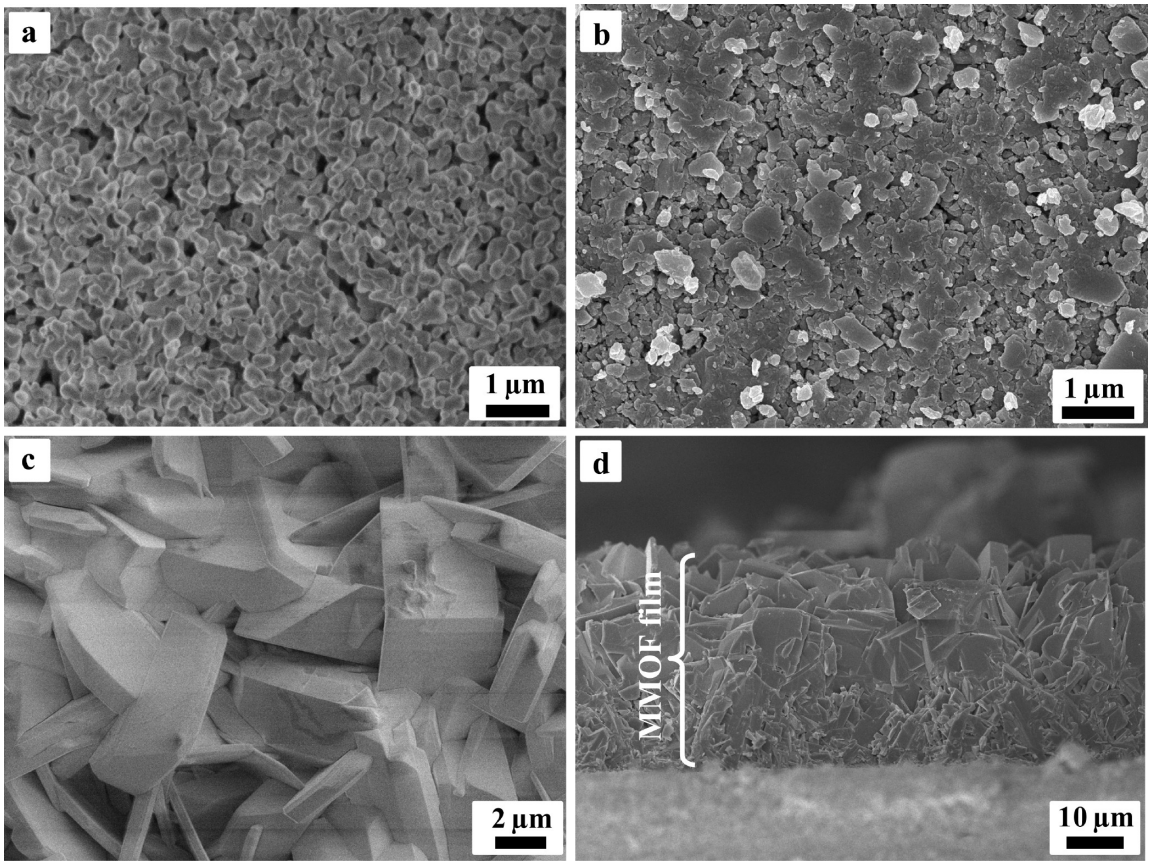

Figure 3. SEM images at different stages of MMOF membrane growth: (a) α-alumina support, (b) seed layer, (c) membrane (top view), and (d) membrane (cross-section view).

2.3.2. Seed Synthesis and Layer Formation by Manual Assembly. The MMOF synthesis procedure described by Pan et al.[18] was modified to obtain isotropic particles. A solvent mixture consisting of methanol and water (1:5 v/v) was used for solvothermal growth. $Cu(NO_3)_2 \cdot 3H_2O$ (0.072 g) and 4,4′-(hexafluoroisopropylidene)-bis(benzoic acid) (0.366 g, excess) were added to the methanol−water solvent mixture (15 mL), and solvothermal growth was carried out at 150 °C for 12 h. The crystals obtained after the solvothermal growth were crushed into submicrometer sized crystals. Seed layers of these particles were deposited by the manual assembly method of Lee et al.[22] on PEI coated supports.

2.3.3. Secondary Growth. Secondary growth was done using the same gel composition used for seed crystal synthesis. The seeded support was vertically placed in a Teflon lined steel autoclave containing the synthesis gel and heated in an oven at 150 °C for 12 h. The resulting membrane was washed with DMF and water and dried under vacuum at 150 °C.

2.4. Characterization of Membrane. SEM images were taken using a JEOL 6500 operated at 1.5 kV. X-ray diffraction patterns were collected using a Bruker-AXS D-5005, and pole figure analysis was conducted using a Philips X'pert diffractometer using Cu Kα (λ = 1.5406 Å) radiation.

Single gas permeation measurements were carried out with the feed side maintained at 1 atm and the permeate side under vacuum. Permeate side pressure was being monitored using a pressure transducer and was continuously recorded in a computer. The permeation setup is described in detail elsewhere.[23]

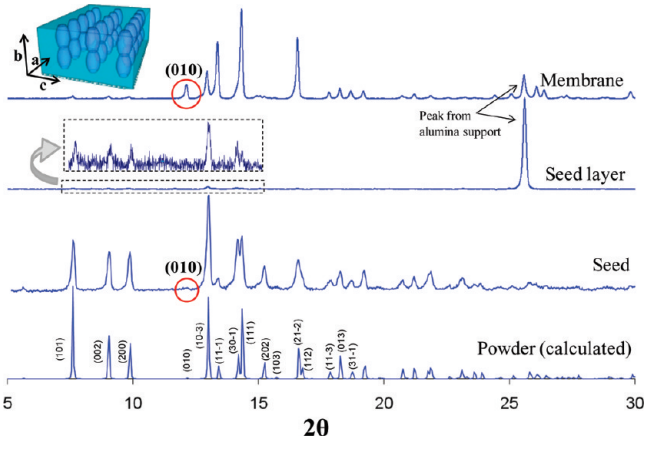

Figure 4. XRD patterns of MMOF powder (calculated), seeds, deposited seed layer, and the membrane. A part of the seed layer pattern has been enlarged for illustration purposes. The (010) peak is highlighted by the circle.

3. Results and Discussion

3.1. In Situ Growth. SEM images of the MMOF crystals grown on an alumina support using in situ growth are shown in Figure 1. At 150 °C, almost no crystal growth was observed at the support surface (result not shown here). However, at higher temperatures (180 and 200 °C), we observed growth of crystals from the support surface. As shown in Figure 1a,b, the nucleation density at the support surface was not enough to provide a continuous film. Furthermore, the synthesis condition favors growth

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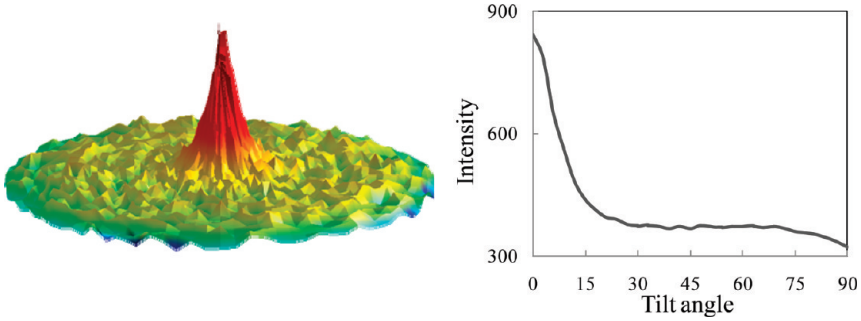

Figure 5. (010) pole figure of a MMOF membrane.

along the length of the crystals and hence the intercrystalline gaps could not be filled by the small in-plane growth.

3.2. Seeded Growth of Membrane. MMOF synthesis described by Pan et al.[18] results in long columnar crystals with the one-dimensional pore channels aligned along their length. These particles are not suited for seed layer formation as the resulting film will have pores oriented parallel to the support surface. Various organic solvents (e.g., methanol, ethanol, acetone, DMF) were investigated as crystal shape modifiers to achieve a more favorable morphology for seed crystals. A methanol−water solvent mixture for solvothermal growth was found suitable to obtain particles with lower aspect ratio. XRD patterns and SEM images of MMOF crystals synthesized at various solvent compositions are shown in Figure 2. As the methanol content in the solvent mixture is increased, columnar particles gradually change to less anisotropic particles. However, along with morphology change, there is change in crystal structure as shown by XRD. A methanol−water composition of 1:5 (v/v) was selected for synthesis of seeds since, at this solvent composition, isotropic particles were obtained while retaining the original crystal structure. The XRD pattern and morphology of the seeds synthesized at this condition are shown in Figure 2a,e.

Submicrometer sized seeds were attached to the modified support surface using the manual assembly process.[22] SEM images of the bare alumina support and the seed layer are shown in Figure 3a,b, respectively. Although the coverage on the support surface is almost complete, the seeds are not closely packed because of the nonuniform shape and size of the particles. The secondary growth was carried out at 150 °C for 12 h resulting in a blue colored intergrown MMOF film. SEM investigation across the entire film revealed a continuous crack free membrane. The cross-section image of the film shows a thickness of about 20 μm (Figure 3d).

X-ray diffraction (XRD) patterns were collected after seed layer deposition and secondary growth and are shown in Figure 4. By comparing the calculated powder pattern and the seed's diffraction pattern it is evident that there is no change in the original framework structure. Furthermore, a comparison of the XRD pattern of the seed layer with the calculated powder pattern suggests absence of any preferred orientation.

To get an estimation of the orientation of the membrane, the crystallographic preferential orientation (CPO) indexing method[24,25] was used. The CPO index, obtained using the (010) and (200) reflections, is approximately 100 indicating a strong "*b*" out of plane orientation. Similarly, the CPO index using (010) and (002) reflections is ~80.

Pole figure analysis was used to further study the preferred orientation of the membrane. Figure 5 shows the (010) pole figure of the MMOF membrane. It has maximum intensity at 0° tilt angle indicating that most of (010) planes in the membrane are parallel to the support surface. The symmetric nature of the peak indicates no preferred in-plane orientation. As expected, misoriented grains in the membrane give the off-peak intensity, which is invariant of the tilt angle.

The preferred orientation is attributed to faster growth along the *b*-direction during the secondary growth on the randomly oriented seeds. This situation is analogous to the well established case of *c*-oriented columnar MFI membranes formed by secondary growth of randomly oriented seeds.[26]

3.3. Gas Permeation Results. The MMOF membranes were tested in a single gas permeation setup using H_2, He, CO_2, N_2, and *n*- and *i*-butane. The permeation results at various temperatures are summarized in Figure 6. As shown in Figure 6a, the membrane exhibits a moderate selectivity for H_2 over N_2 and CO_2. The ideal selectivity of H_2/N_2 is around 23 at 190 °C. This is three times higher than the previously reported selectivity[17] in MOF membranes. However, the permeances are low compared to those obtained for other molecular sieve membranes like zeolites.[27] Gas permeation experiments using bare alumina support and PEI coated support were conducted to ensure that the PEI coating on the support does not act as a barrier. Gas permeance was not affected by the PEI coating. The low gas flux through these membranes is probably due to the misoriented seed layer which in effect results in blocking of the 1-D straight pore channels in the membrane. Blocking of the channels can further be aided by less oriented grains in the membrane resulting from the

(24) CPO is calculated from peak intensities for the appropriate reflections. CPO $=[(I_{010}/I_{hkl})_m-(I_{010}/I_{hkl})_p]/(I_{010}/I_{hkl})_p$ where "m" refers to membrane and "p" refers to powder samples.
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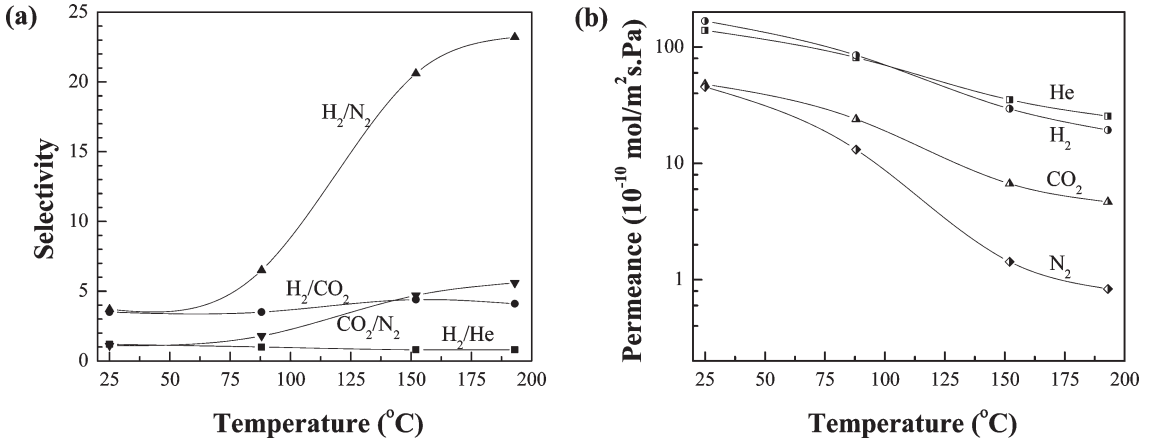

Figure 6. Gas permeation results: (a) ideal selectivity for various gas mixtures and (b) permeance values for different gases.

randomly oriented seed layer. Interestingly, as shown in Figure 6b, with the increase in the temperature, permeance values of all gases decrease with strong deviation from the expected reduction for the Knudsen diffusion. Our intention was to use these membranes for separation of *n*- and *i*-butane based on the adsorption results presented by Pan et al.[19] However, very low fluxes and low *n*-/*i*-butane selectivity were obtained, pointing again to pore blocking by the randomly oriented seed layer. Future work will focus on improving the microstructure of these films following the strategy developed for zeolite films.[28]

4. Conclusion

Continuous MMOF membranes on porous α-alumina supports were synthesized using the seeded growth method where isotropic seeds were used for randomly oriented seed layer deposition. XRD and pole figure analysis confirmed the preferred (010) orientation of the film after secondary growth. Gas separation study on this membrane shows moderate ideal selectivity for H_2/N_2. The permeance values are relatively low and decrease further with increasing temperature. Several aspects of these membranes, such as thickness and orientation, need to be further investigated to improve their performance.

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