DEVELOPMENT OF METAL-ORGANIC FRAMEWORK THIN FILMS AND MEMBRANES FOR LOW-ENERGY GAS SEPARATION

A Thesis

by

MICHAEL COLIN MCCARTHY

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Chemical Engineering

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Approved by:

Chair of Committee,	Hae-Kwon Jeong
Committee Members,	Daniel F. Shantz
	Tahir Cagin
	Hong-Cai Zhou
Head of Department,	Michael Pishko

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ABSTRACT

Development of Metal-Organic Framework Thin Films and Membranes for Low-Energy Gas Separation. (May 2011)

Michael Colin McCarthy, B.S., The University of California at Berkeley

Chair of Advisory Committee: Dr. Hae-Kwon Jeong

Metal-organic frameworks (MOFs) are hybrid organic-inorganic micro- or mesoporous materials that exhibit regular crystalline lattices with rigid pore structures. Chemical functionalization of the organic linkers in the structures of MOFs affords facile control over pore size and physical properties, making MOFs attractive materials for application in gas-separating membranes. A wealth of reports exist discussing the synthesis of MOF structures, however relatively few reports exist discussing MOF membranes. This disparity owes to challenges associated with fabricating films of hybrid materials, including poor substrate-film interactions, moisture sensitivity, and thermal instability. Since even nanometer scale cracks and defects can affect the performance of a membrane for gas separation, these challenges are particularly acute for MOF membranes. The focus of this work is the development of novel methods for MOF film and membrane fabrication with a view to overcoming these challenges. The specific results of this work were the development of thin films and membranes of MAMS-4 and MAMS-6 using *in situ* synthesis with modified supports and thin films of HKUST-1 using rapid thermal deposition (RTD).

To my wife.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Jeong, and my committee members, Dr. Shantz, Dr. Cagin, and Dr. Zhou for their guidance and support throughout the course of this research.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

Finally, thanks to my mother and father for their encouragement and to my wife for her patience and love.

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1. INTRODUCTION: MEMBRANES FOR GAS SEPARATION

Koros predicted in 2006 that global commodity chemical production would grow by a factor of six by 2040.[1] Koros further predicted that if the current gas separations infrastructure were simply scaled up with this demand, then by 2040 this industry alone would consume 350 quadrillion Btu per year, which is equal to 75% of the total world energy production in 2006.[1, 2] To circumvent the scale-up of contemporary energy intensive gas separations technology there is a driving need for new, low-energy technology that is capable of high-resolution separation of commercially relevant gases. Gas separation using membranes is an energetically attractive alternative to contemporary technology. The current membrane market for gas separation is dominated by polymeric membranes, but is generally limited to separation of non-condensable gases (H_2/N_2, CO_2/CH_4, N_2/air, etc.).[3] Condensable gas separations such as olefin/paraffin or butane isomer separations are an important area for membrane technology to expand into.[3] Unfortunately few membranes are capable of olefin/paraffin separation in an economically viable way and none can do so without difficulty with issues such as durability and longevity.[4] This is particularly troublesome for polymer membranes as the operating conditions these membranes are exposed to often result in membrane plasticization.[1] Polymer membranes have low production costs, exhibit high gas fluxes and mechanical flexibility, however polymer membranes also have short

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This thesis follows the style of *Langmuir*.

membrane lifetimes, low thermal and chemical stabilities and low selectivities. Robeson defined an upper bound for polymer membranes delineating a limit on their selectivity/permeability performance.[5] Although this limit has been adjusted since its inception,[6] it still indicates there is a limiting tradeoff between a polymer membrane's selectivity and permeability.

Zeolites have been investigated for application in membrane separations because of their rigid, regular pore structure and thermal and chemical stability.[7-9] Their rigid pores allow zeolite membranes to achieve gas separation with high selectivity due to the molecular sieving effect.[7, 10] The high thermal and chemical stability of these materials also makes them attractive for separation applications in industrial settings. However zeolites also have a discontinuous and limited range of available pore sizes which limits the potential separations they can be applied to. Figure 1 shows the kinetic diameters of various gases and the effective pore sizes of a few well-known zeolites. Other important challenges facing zeolite membranes are high production cost and difficult chemical tailorability. Zeolite membranes are generally much more expensive to produce than polymer membranes, approximately $\$4000/m^2$.[11]

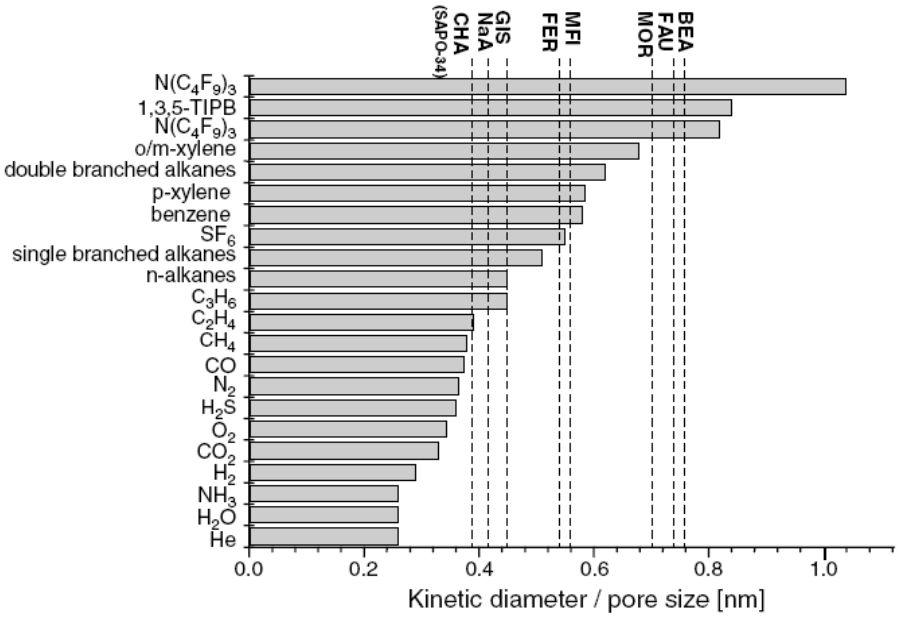

Figure 1. Comparison of effective zeolite pore sizes with kinetic diameters of common gases. Reproduced with permission.[12]

Another avenue of membrane research is focused on mixed matrix membranes. These membranes are generally polymer/inorganic composites consisting of a primary polymer phase and a secondary phase of dispersed inorganic particles. The intention for these types of membranes is to combine the advantages of the materials of both phases such as the high flux of polymer membranes and the high selectivity of the inorganic phase (e.g. zeolite phase). Unfortunately, it is very difficult to achieve a close interface between the two phases. If there is a repulsive interaction between the phases, then the interstitial space acts as a non-selective diffusion path. This creates difficulties in achieving permeability/selectivity performance greater than that of the polymer phase. Plasticization is also a danger for these kinds of membranes. In light of the challenges

for each of these membrane technologies, there is room for new materials to be applied as membranes for gas separation.

Metal-organic frameworks, a relatively new class of hybrid materials consisting of organic and inorganic moieties in crystalline lattices, have the potential to answer some of the challenges facing materials for gas-separating membranes.[13-16]

1.1 Metal-Organic Frameworks as New Membrane Materials: Promises and Challenges

Metal-organic frameworks have attracted research interest as noteworthy porous materials for over a decade. The focus of these investigations for the most part has been the discovery and characterization of new MOF structures. As illustrated in Figure 2, the number of publications discussing metal-organic frameworks has increased significantly recently. Despite this rising interest, the number of reports of MOF thin films is quite small, orders of magnitude fewer.[9, 17-34] Still fewer in number are the reports of MOF membranes for gas separation,[35-50] the first MOF membranes having been published in 2009.[36, 37]

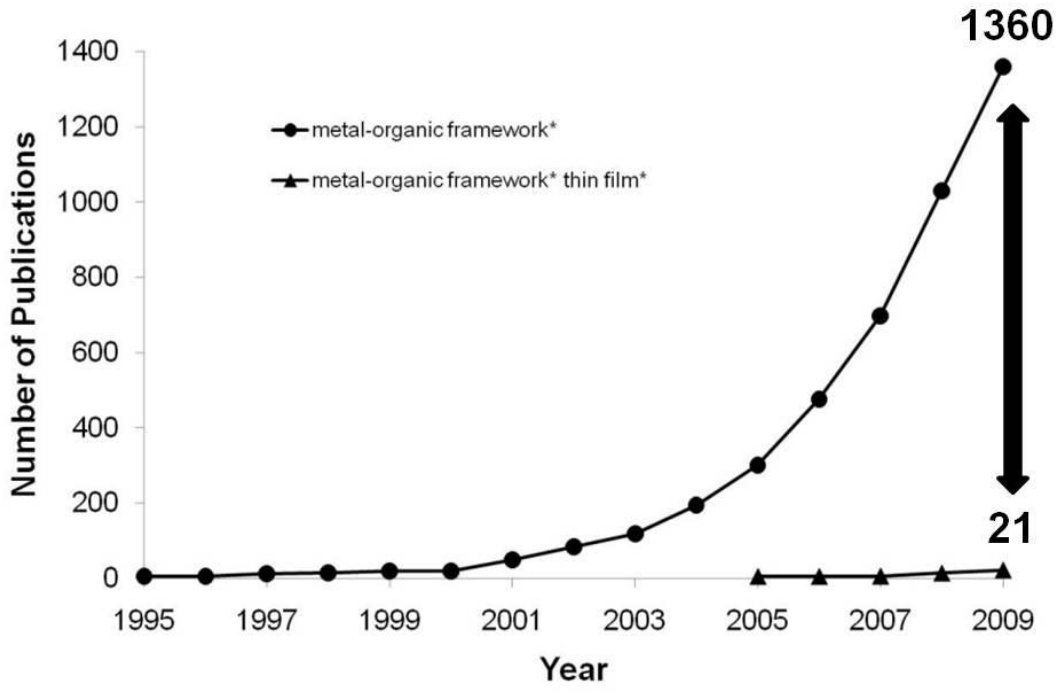

Figure 2. Publications per year containing the phrase: (●) metal-organic framework and (▲) metal-organic framework thin film. Data obtained from ISI Web of Knowledge, Thomson Reuters.

This scarcity of reports can perhaps be attributed to the challenges involved in fabricating thin films of hybrid organic-inorganic materials such as decomposition of the organic part of the material, solubility difficulties (which make solution deposition techniques unfeasible) or poor substrate wetting.[51] In particular, various MOFs have been noted for their poor interaction with native substrates such as Au(111),[18] SiO_2[19] and porous α-alumina,[27, 44, 47] necessitating a linking agent to attach these MOFs to supports for film fabrication. Although a single-crystal MOF membrane has been reported,[46] the comparatively low gas flux and difficulty in fabricating large single crystals make these impractical for industrial application.

1.2 Chemistry and Structures of Metal-Organic Frameworks

One attractive attribute of MOFs is the ease with which they can be synthesized. Approaches to design and synthesis of these materials have been discussed in detail elsewhere.[52-56] Although the chemical steps leading to MOF formation are still debatable, there are two generally understood explanations. One explanation involves the formation of building blocks of molecules called secondary building units (SBUs) that in turn come together to form coherent structures.[19, 54, 55] Not much evidence of this synthesis route is available, though there is one report that gives X-ray absorption (EXAFS) evidence of intact trimeric iron oxide SBUs during the crystallization of MIL-89.[57]

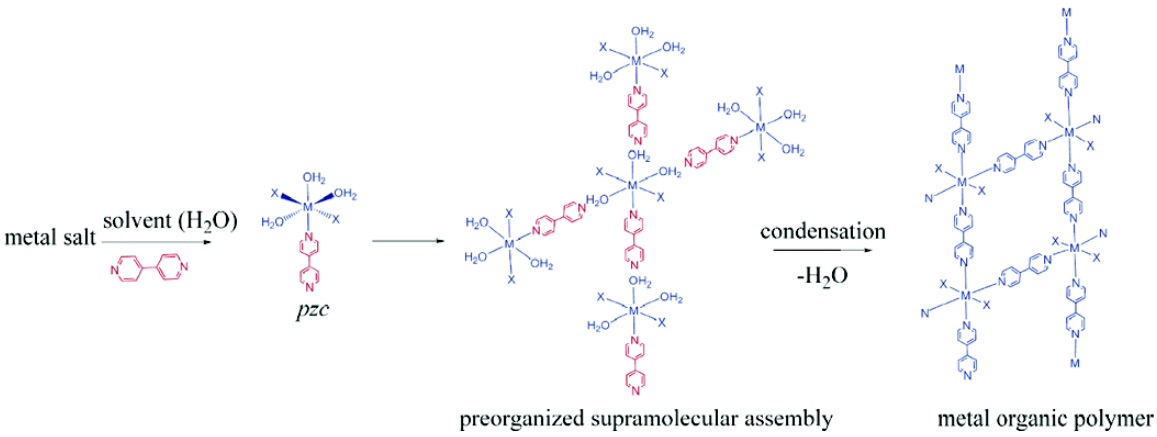

Figure 3. Proposed scheme of MOF crystal formation in solution through formation of point of zero charge (pzc) molecules and hydrolysis/condensation reactions with dissolved metal salts. Reproduced with permission.[58]

The second explanation does not include SBUs, but rather hydrolysis or condensation reactions between dissolved metal salts and organic ligands in solution (see Figure 3).[58, 59] This explanation states that first metal salts dissolve in solution and form point of zero charge (pzc) molecules. These metal complexes at their isoelectric points organize into supramolecular assemblies which then undergo condensation/hydrolysis to form crystalline structures. The bonding between metal and organic linker in the final MOF structure (whatever the actual mechanism is) is coordination bonding, which is kinetically weaker than covalent or covalent/ionic bonding such as is found in zeolites. This coordination bonding is likely the major factor contributing to many of the challenges associated with fabrication of MOF membranes.

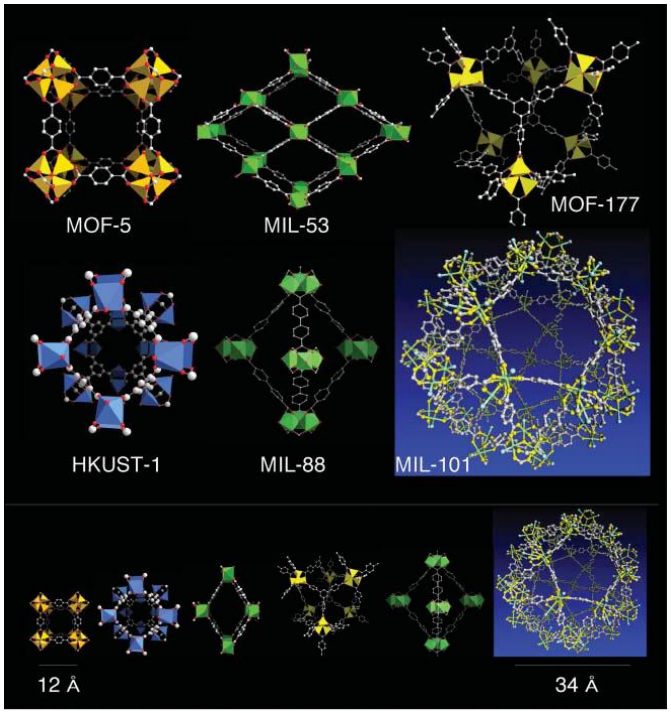

Figure 4. Various reported MOF structures. Structures are arranged according to effective pore size along the bottom. Reproduced with permission.[15]

Thousands of metal-organic framework structures have been reported to date, exhibiting properties useful for gas separation, gas storage, chemical sensors, and optical devices.[23, 33, 60, 61] Some previously reported MOF structures, including two prototypical MOFs used in pioneering MOF membrane reports (MOF-5 and HKUST-1), are illustrated in Figure 4. An important subclass of metal-organic frameworks, especially when considering gas separation applications, is zeolitic imidazolate frameworks (ZIFs). These materials, first reported in 2006 by Park et al[62] and expanded upon significantly in later reports,[16, 63] are remarkable for their particular thermal and chemical stability. ZIFs consist of metal nodes (usually zinc or cobalt) connected to imidazole (or imidazole derivative) linkers and exhibit zeolite-like structures, perhaps due to the metal-linker-metal bond angle of ~145° (close to the Si-O-Si angle found in many zeolites).[62] To date, more ZIFs have been investigated for gas separation membranes than any other kind of MOF.[35, 39, 40, 42, 43, 45, 48]

As mentioned above, coordination bonds between metal nodes and organic ligands are one of the major features of the MOF structure. Coordinate covalent bonds involve the sharing of a pair of electrons, both donated from a Lewis base (organic linkers in MOFs) to a Lewis acid (metal nodes in MOFs). These special covalent bonds are thermodynamically as stable as other covalent bonds, but are kinetically weaker. Complexes featuring coordination bonds between a metal and an organic ligand have been widely studied.[64]

1.3 Challenges Specific to MOF Membranes

Successful fabrication of metal-organic framework polycrystalline membranes of sufficient quality for gas separation is no mean feat, as evidenced by the dearth of MOF membrane reports. The relative weakness of the coordination bond (as compared to the strong covalent bonds found in zeolites) accounts for many of the challenges faced by researchers endeavoring to contribute in this particular field. Although coordination bonds are as thermodynamically stable as covalent bonds, kinetically they are not as strong. This issue has been discussed for coordination polymers (CPs).[65] As Kitigawa pointed out, coordination polymers are less stable than other porous inorganic materials due to their weaker coordination bonds. In fact, one of the major features distinguishing MOFs from CPs is the structural stability of MOFs upon evacuation of solvent molecules from the pores. Many CPs experience structure collapse upon pore activation whereas MOFs maintain permanent porosity. Despite this enhanced structural stability as compared to CPs, the nature of the coordination bond in the MOF lattice leads to numerous challenges for MOF membranes. Other porous inorganic materials that have been studied for gas-separating membranes, such as porous ceramics (alumina, zirconia, titania, etc.), dense oxides, porous metals, or zeolites do not have to contend with these same challenges.[66]

It is perhaps self-evident that not all MOFs will present the same challenges when incorporated into polycrystalline membranes for gas separation. However, a general understanding of the challenges encountered for some prototypical MOFs that

have already been reported as polycrystalline membranes will help to mitigate and overcome similar challenges in the future. The common challenges facing polycrystalline MOF membranes can be broken down into the following categories: 1) poor membrane-substrate bonding, 2) poor membrane stability, and 3) macroscopic crack formation during membrane fabrication or activation.

1.3.1 Poor substrate bonding

Various MOFs have been noted for their lack of sufficient interfacial interaction with native supports for membrane fabrication.[36, 40, 44, 45, 47] IRMOF-1, for example, was found to easily detach when synthesized on anodized aluminum oxide (AAO) supports.[25] As illustrated in Figure 5, films of IRMOF-1 grown on AAO easily break off under sonication. However IRMOF-1 films on graphite coated AAO were much more strongly bound (~80% coverage remained after an hour of sonication). Although investigations of MOF film attachment are not abundant, this study illustrates the utility of linking agents for MOF film fabrication on porous supports. Some reported techniques used to improve MOF crystal adhesion to porous supports for membrane fabrication include the use of polymer binders,[40, 47] graphite coatings,[36] silane tethers,[45, 49] reactive seeding,[50] and support modification with the precursor chemicals of the MOF of interest.[44, 48] This last technique is notable as it requires no more chemicals than are already necessary for MOF growth.

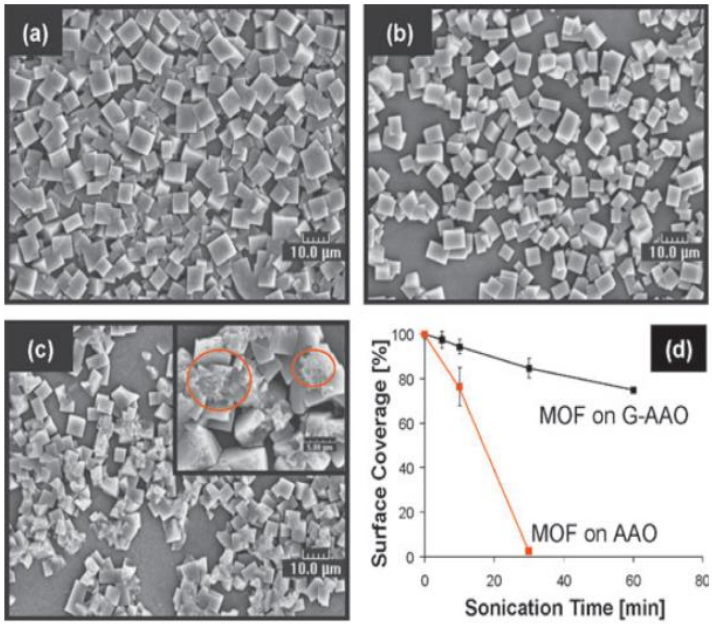

Figure 5. SEM images of IRMOF-1 films on graphite coated AAO treated under sonication for (a) 0 min, (b) 10 min, and (c) 60 min. Section (d) shows the results of a sonication time-dependent surface coverage study comparing IRMOF-1 on bare AAO to IRMOF-1 on graphite coated AAO. Reproduced with permission.[25]

1.3.2 Poor stability (in ambient conditions)

IRMOF-1 has been noted for its instability in contact with ambient humidity.[29, 67-69] Postsynthetic modification of metal-organic frameworks has been studied to improve their stability. Nguyen and Cohen [69] showed that modification of the IRMOF-3 structure with long alkyl chains showed hydrophobic behavior. Although initial MOF membrane reports have not investigated this matter, it is nonetheless a crucial issue to be addressed before MOF membranes for gas separation can be industrially applied. We have recently investigated IRMOF-3 membranes for application to CO_2 separation. IRMOF-3 is a natural choice for this application as the amine functionalized benzenedicarboxylate

linkers increase the pore affinity for CO_2.[70] Pore functionalization of this MOF has also been demonstrated, implying that membranes of this material would be useful as chemically tunable membranes.[71] To stabilize these membranes, we have found it necessary to first coat the membranes, immediately after activation, with an amphiphilic surfactant (Span-80 in this case). It was found that this coating dramatically increased the material longevity, preventing ambient moisture from attacking the MOF structure.

1.3.3 Crack formation during fabrication

Macroscopic or microscopic cracks in polycrystalline films can form for a number of reasons and will likely ruin a membrane's performance for gas separation.[10] Crystalline materials such as zeolites are mechanically very hard, but tend to crack rather than deform under stress such as a polymer would. MOFs, also being crystalline, are mechanically brittle. Consequently when using MOFs for polycrystalline gas-separating membranes, methods used for the prevention of cracks is a subject of some importance.

Cracks in MOF membranes have been observed to form due to mechanical stresses induced while cooling membranes after synthesis at elevated temperature.[44] HKUST-1,[44] ZIF-69,[43] and IRMOF-1[36, 37] membranes were all reported to require slow (natural) cooling after synthesis rather than quenching (as is common after synthesis of zeolite membranes). The effect of cooling rate on HKUST-1 membranes is quite dramatic as seen in Figure 6. The reasons for crack formation in films that were rapidly cooled can perhaps be explained by the mismatch in thermal expansion between MOF film and porous supports. Although no MOF membrane report to date has given specific evidence of this (by measuring and comparing thermal expansion coefficients of film

and support), several have mentioned natural cooling for long times as part of the membrane synthesis (sometimes for as long as 30 hours).[36, 37, 43, 44]

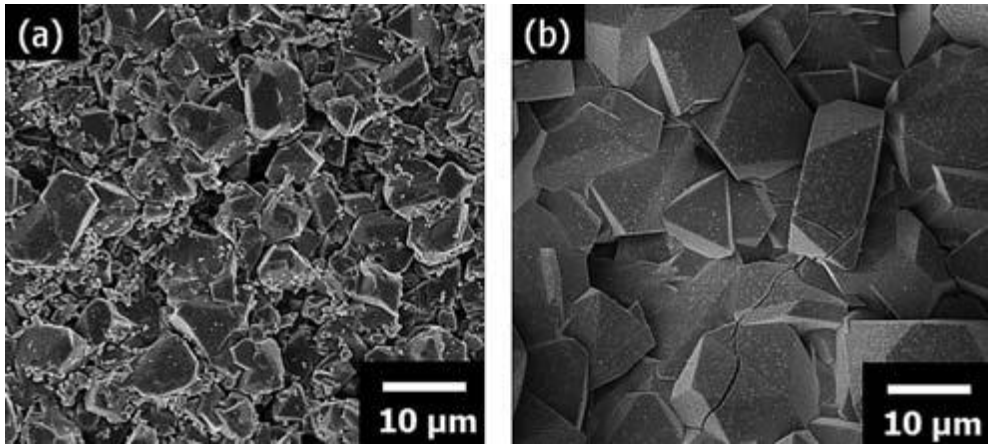

Figure 6. SEM images of HKUST-1 membranes we reported which illustrate the difference in rapid cooling (a) and slower cooling (b) of films after synthesis. Reproduced with permission.[44]

Drying of MOF membranes after synthesis can also result in crack formation. Capillary stresses in drying films are caused by surface tension at the solid/liquid interface in film pores during drying and by vapor-pressure differences at the liquid-gas interface in different film pores, as described by the Kelvin equation. The vapor pressure at the liquid/gas interface is inversely proportional to the radius of curvature of the surface. Thus, as the film dries and the drying front of liquid moves into the film pores, any non-uniformity in the pore structure (such as grain boundaries or film defects) will lead to asymmetric stress in the film due to the differences in vapor pressure in adjacent pores. One method we have found for reducing capillary stresses in MOF membranes is by decreasing the drying rate (slowly drying the newly fabricated

membrane in nearly saturated conditions).[44] Another method we have found for decreasing capillary stress is by introducing a surfactant to the film surface before drying. A surfactant serves to decrease solid/liquid surface tension and thereby decrease capillary stress.

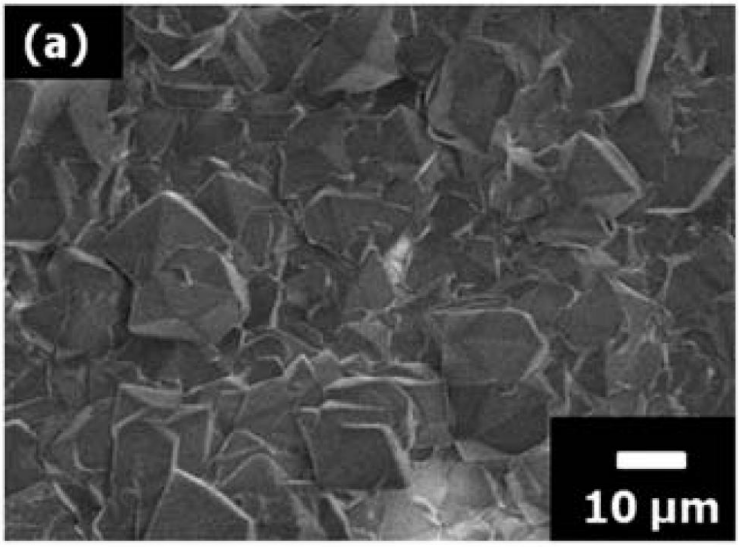

Figure 7. SEM image of HKUST-1 membrane after both slow cooling and slow drying in nearly saturated conditions. Reproduced with permission.[44]

1.4 MOF Membrane Fabrication Techniques

The study of MOF membranes for gas separation is as yet a fledgling field with only fifteen reports to date. The first MOF membranes were reported in 2009 by the Lai and Jeong groups.[36, 37] These were polycrystalline IRMOF-1 membranes and exhibited Knudsen diffusion. Although Knudsen selectivity is unsurprising considering the large pore size of IRMOF-1 (14.5 Å) [36] these reports demonstrated the feasibility of

fabricating MOF membranes for gas separation. The absence of macroscopic cracks in both of these reports was demonstrated by pressure dependent gas permeation measurements. Polycrystalline membranes of only 9 different MOFs have been reported: IRMOF-1, HKUST-1, MMOF, ZIF-7, ZIF-8, ZIF-22, ZIF-69, ZIF-90 and MIL-53. In general, fabrication of thin films of crystalline materials follows one of two approaches: *in situ* growth (sections 3a - 3c) and secondary or seeded growth (sections 3d – 3f). *In situ* growth here refers to a film fabrication method in which the substrate is immersed in the growth solution without any crystals previously attached to the surface; nucleation, growth and intergrowth of crystals on the substrate all happen during the same fabrication step. Secondary or seeded growth refers to film growth from pre-attached seed crystals. Although not as simple as *in situ* growth, secondary growth has been noted to allow better control over microstructure in polycrystalline films.[72-74]

The strategy for film fabrication used in the initial MOF film investigations involved chemically bonding MOF crystals to the substrate.[18-20, 22] This was accomplished by chemical functionalization of the substrate surface prior to film growth with alkanethiol self assembled monolayers (SAMs) which were terminated by either carboxylate or hydroxyl groups. The presence of those same functional groups on the organic linker of the MOF of interest led to dense (and often oriented) MOF crystal growth on the substrate surface. Many different MOF film synthesis techniques have been reported to date but will not be discussed here (the interested reader should direct their attention to a recent review by Zacher et al).[9]

1.4.1 In Situ Growth – Unmodified Supports

As mentioned above, fabrication of membranes of metal-organic frameworks is complicated by the fact that there is usually no strong interfacial bonding between MOFs and the native substrates of interest (which for MOF membranes are typically α-Al_2O_3 or TiO_2). Consequently, not many MOF membranes have been reported that were synthesized without some kind of pretreatment to the porous support. Liu and coworkers were able to grow membranes of IRMOF-1[37] and ZIF-69[43] on α-alumina without substrate modification. Bux et al. grew membranes of ZIF-8 on bare titania using microwave irradiation.[39] Although these authors did not discuss the nature of the bonding of their membranes with the substrate, the use of unmodified supports suggests that the membranes are only physically bound (i.e. it appears that the attachment of these membranes to the substrate is not by the formation of chemical bonds).

1.4.2 In Situ Growth – Modified Supports

Support modification, as mentioned previously, is an effective strategy for improving MOF-support interaction for membrane fabrication. Although many of the reported methods are rather laborious,[45] we have recently reported a simple method for substrate modification that yields well-attached polycrystalline MOF membranes.[48] This method, demonstrated for ZIF-8 membranes and ZIF-7 films, is based on covalent linkage of imidazole ligands to supports via an Al – N bond.[48] As illustrated in Figure 8, supports were thermally modified by rapid evaporation of a solution of the organic linker (2-methylimidazole in methanol for ZIF-8 or benzimidazole in methanol for ZIF-7) on the surface of hot α-alumina (~200 °C). The solvent evaporates quickly, leaving organic

linkers covalently attached to the α-alumina surface, as evidenced by N 1s XPS data (see Figure 8).

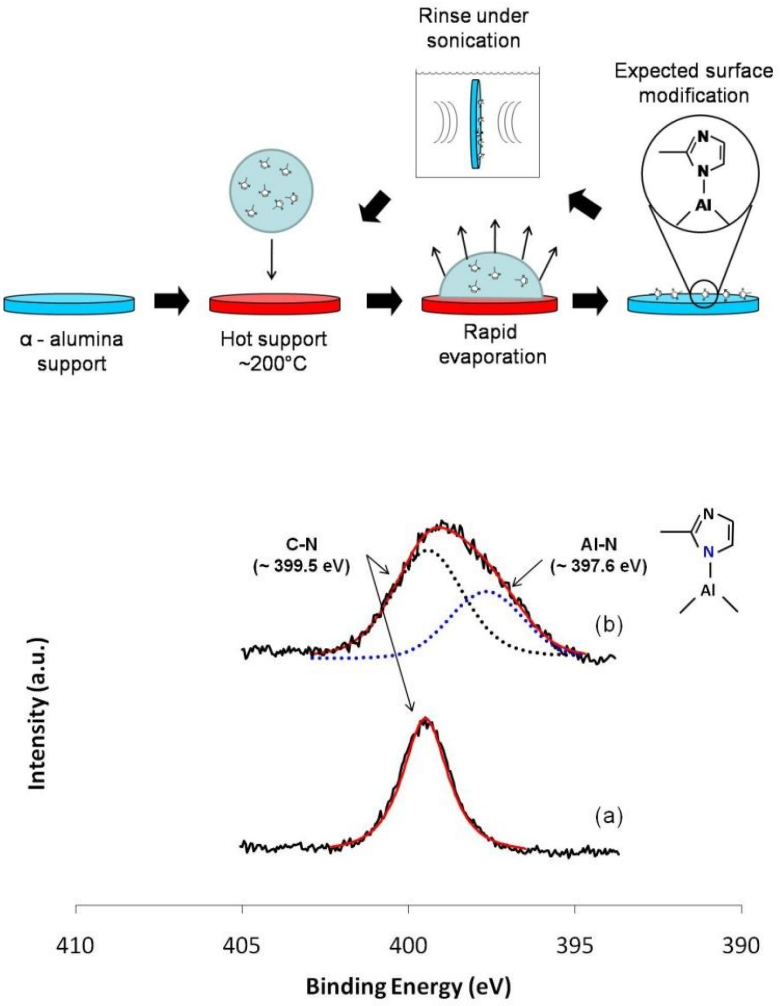

Figure 8. Preparation procedure for thermal modification of α-alumina with 2-meth ylimidazole (*top*). N 1s XPS spectra of α-alumina supports modified with 2-methylimidazole (a) at 25°C (a) and (b) at 200 °C (*bottom*). Reproduced with permission.[48]

The XPS data also confirms that high temperature (200 ºC) is necessary for covalent bonding between the organic linker and the surface as supports modified at

room temperature did not have any XPS peaks characteristic of Al – N bonding. Solvothermal growth of supports modified in this way was found to yield ZIF-8 membranes half as thick as those reported previously (see Figure 9).[39] These membranes exhibit preferential permeation of small gas molecules with selectivities far in excess of Knudsen selectivity. It is interesting to note though, that unlike molecular sieving observed in zeolite membranes, ZIF membranes have not been observed to exhibit sharp permeance cutoffs. This is understood as a result of the flexible nature of organic ligands in the ZIF structure.[39]

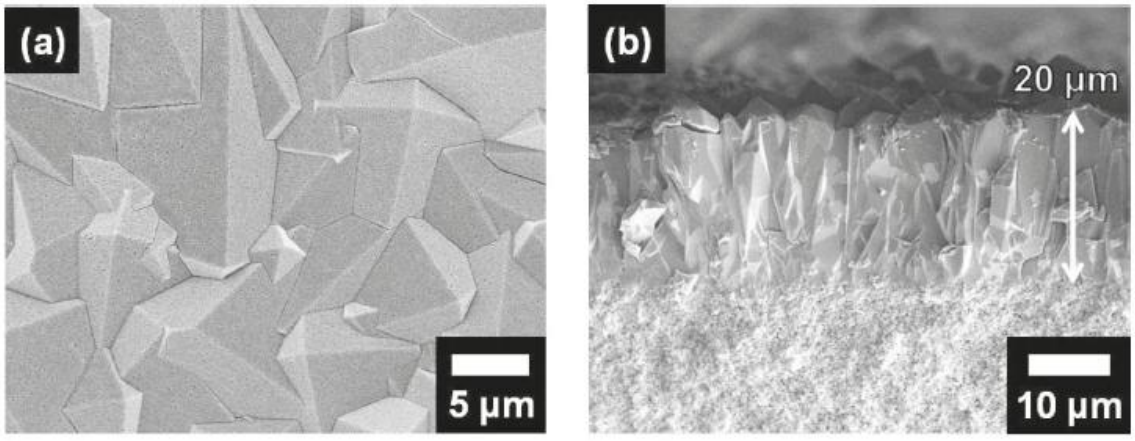

Figure 9. Top-down (a) and side-view (b) SEM images of ZIF-8 membranes fabricated using thermal deposition of imidazolate linkers on porous supports. Reproduced with permission.[48]

Li et al reported oriented ZIF-7 membranes fabricated on porous α-alumina.[35] Supports were modified by manually depositing a mixture of polyethyleneimine (PEI), $ZnCl_2$, and benzimidazole (bIM) in DMF on the α-alumina surface. The orientation

sharpening observed in this report is explained according to the Van der Drift growth model (also referred to as *evolutionary selection*).[75] This model states that crystals with fast-growing facets oriented vertically with respect to the support eventually overgrow crystals of other orientations during synthesis, yielding a preferentially oriented film.

Lastly, membranes of ZIF-22 [45] and ZIF-90 [49] have been fabricated on porous supports modified with 3-aminopropyltriethoxysilane. The silane tethers induce nucleation and growth of the ZIFs on the supports as illustrated in Figure 10.

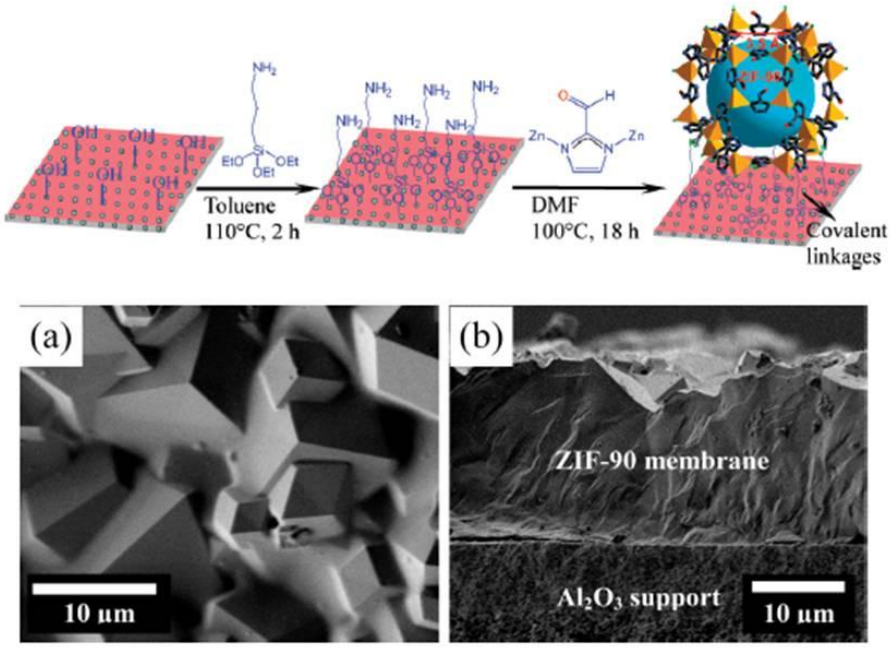

Figure 10. Illustration of ZIF-90 preparation scheme using APTES tethers via an imine condensation reaction (*top*). (a) Top-down and (b) side-view SEM images of ZIF-90 membrane on porous supports. Reproduced with permission.[49]

1.4.3 In Situ Growth – Secondary Metal Source

Some groups have used alternate metal sources to anchor MOF films.[21, 38] As mentioned above, MOF synthesis involves coordination bonding between organic and inorganic moieties in solution creating the hybrid organic-inorganic framework. In this approach, the support structure for the membrane itself contains the same metal in the framework of the MOF of interest. Guo et al. reported an HKUST-1 membrane grown on an oxidized copper mesh.[38] It should be noted that this membrane is essentially free-standing and is likely to have problems with mechanical stability.

1.4.4 Seeded (Secondary) Growth

Secondary growth is a film growth approach commonly used for zeolite membranes.[73, 74, 76] This method involves first seeding the support with seed crystals of the material of interest followed by hydrothermal or solvothermal growth. Secondary growth decouples the nucleation and growth steps for polycrystalline membrane fabrication. This allows for better control over film microstructure (density of grain boundaries, film thickness, orientation, etc.) by controlling the relevant properties of the seed crystal layer such as seed crystal size, thickness and orientation. By having pre-attached seed crystals on the support, secondary growth also allows film growth to be somewhat substrate independent. For zeolite films, seed attachment to porous supports does not present any difficulty; simple calcination of seed crystals on the surface of porous supports leads to a condensation reaction between surface hydroxyl groups and the zeolite seeds become covalently bound. For MOF crystals this approach is not viable

as MOFs cannot withstand such high temperatures. Consequently other methods for seed attachment to supports have to be pursued for MOF membrane fabrication.

Manual deposition following the method reported by Lee et al. for zeolite crystals is a simple method for attaching crystal seeds to a substrate,[77] but the reports of MOF membranes seeded in this way required the use of a polymer binder to attach seed crystals to the support.

We recently reported a novel secondary growth technique for MOF membranes which circumvents the problem of MOF crystal thermal instability and does not require foreign binders. This technique, termed thermal seeding, was demonstrated for HKUST-1 membranes.[44] Thermal seeding consists of dropping HKUST-1 crystal seed solution onto hot (200 °C) porous α-alumina supports followed by rinsing under gentle sonication (see Figure 11). This process is repeated to insure sufficient coating of seed crystals. Solvothermal growth of supports seeded in this way result in continuous, crack-free, well intergrown membranes of HKUST-1. Separation performance of these membranes are comparable to those previously reported by Guo et al.[38, 44] It was observed that HKUST-1 seed crystals alone in solution during thermal seeding do not remain attached after sonication. Only when seeded in the presence of HKUST-1 precursor chemicals do the seed crystals adhere to the support. This indicates that crystals of HKUST-1 do not interact attractively with porous α-alumina and there is the need for linking chemicals. This method for MOF crystal seeding has the potential to be applied to other MOFs.

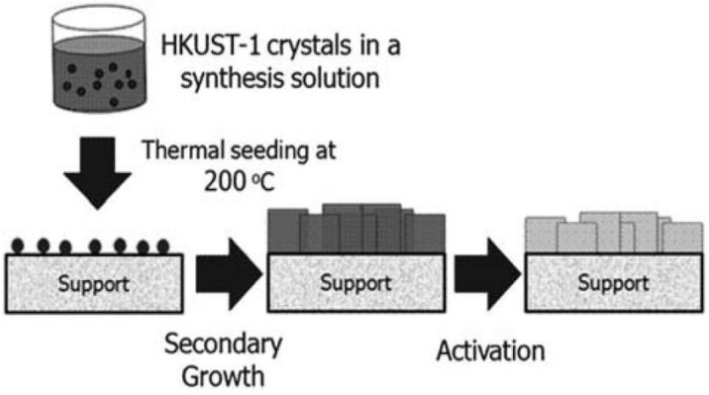

Figure 11: Illustration of HKUST-1 membrane fabrication using thermal seeding and secondary growth. Reproduced with permission.[44]

Ranjan and Tsapatsis reported a membrane of a microporous MOF using secondary growth in 2009 (see Figure 12).[47] The seeds were deposited by manually rubbing the crystals onto PEI coated α-alumina. According to the report, in situ growth did not yield membrane quality films. Their results showed *b*-out-of-plane orientation in their membrane, demonstrated using the crystallographic preferential orientation (CPO) indexing method and pole figure analysis. Although the seeds used for secondary growth were randomly oriented, the investigators attributed the membrane orientation to faster crystal growth in the *b*-direction. The effective pore size of this MOF is 3.2 – 3.5 Å.[78, 79]

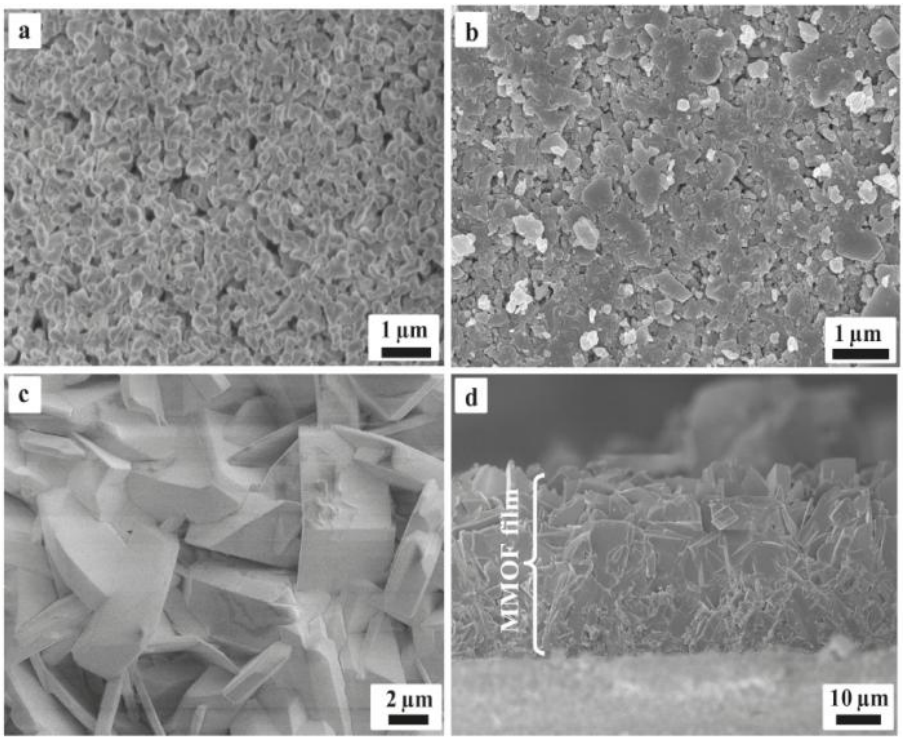

Figure 12. Bare α-alumina support (a), seeded support (b), top-down image of MMOF membrane (c), and side view of MMOF membrane (d). Reproduced with permission.[47]

Li et al. also used this approach to synthesize membranes of ZIF-7.[40] Poor interaction between seed crystals and the substrate surface necessitated the use of polymer binder. Although use of a polymer binder attached seed crystals to the support surface, the seed crystals are not directly attached to the substrate. This means that seed attachment strength is only as good as the polymer attachment strength and one would expect that membranes fabricated in this way are only physically attached to the support surface.

In one of the earliest MOF membrane reports, our group reported a membrane of IRMOF-1 produced by secondary growth using a seed layer that was deposited using

microwave induced thermal deposition (MITD). Fast microwave seeding resulted in a dense, randomly oriented seed layer on α-alumina thinly coated with graphite. This was immersed in MOF-5 growth solution and produced well intergrown MOF-5 membranes. A thicker graphite layer was also used for MITD and resulted in oriented MOF-5 crystals attached to the surface (see Figure 13). When this oriented seed layer was grown solvothermally, it produced dense, highly oriented MOF-5 films. This is the first report of an oriented MOF membrane. Unfortunately, the mechanical instability of these films (readily peeling off) made gas permeation measurement impossible.

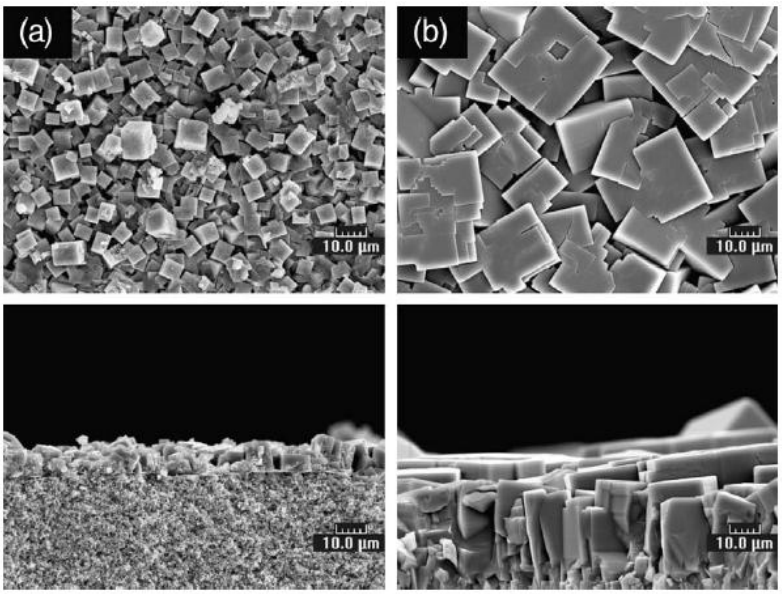

Figure 13. SEM images of the oriented IRMOF-1 seed layer (a) and the oriented membrane after secondary growth (b). Reproduced with permission.[36]

1.5 Gas Separation Performance of MOF Membranes

Two reported MOFs exhibit ideal selectivity values that are consistent with Knudsen diffusion (MOF-5 and ZIF-69).[36, 37, 43] Membranes of ZIF-7, ZIF-8, and ZIF-22 exhibit molecular sieving, preferentially allowing higher permeation of small gases over larger molecules.[39, 40, 45] Gas permeation results for the microporous MOF (MMOF) investigated by Ranjan et al. showed an ideal selectivity of 23 for H_2/N_2.[47] Low fluxes were also reported for this membrane and ascribed to the randomly oriented seed layer impeding gas diffusion. ZIF-8 has a reported aperture diameter of 3.4 Å.[16, 62] This aperture diameter leads one to expect that ZIF-8 membranes would be capable of good hydrogen/methane separation. Binary mixture permeation data confirms this expectation; the membrane's H2/CH4 separation factor at room temperature and pressure was 11.2. As pointed out by the author, however, the membrane's hydrogen flux is about half of that obtained by zeolite membranes with similar selectivity. This was attributed to the fact that the membrane is quite thick (~40 μm). HKUST-1 membranes exhibit lower H2/CH4 separation than expected. It was speculated that this was due to the slower-diffusing and faster-sorbing methane blocking the faster-diffusing and slower-sorbing hydrogen.

2. MOF THIN FILMS AND MEMBRANES

As discussed previously, MOF membrane fabrication is a challenging task due to poor substrate-MOF interaction in general and easy crack formation. To address these challenges, several techniques have been developed such as thermal modification of supports with metals or ligands for *in situ* synthesis. Here these techniques have been demonstrated using a specific sub-class of MOFs called Mesh-Adjustable Molecular Sieves or MAMS.

2.1 Mesh-Adjustable Molecular Sieve Thin Films and Membranes

Mesh adjustable molecular sieves (MAMS) are a new subclass of metal-organic frameworks which exhibit temperature tunable molecular gates within their pores.[80, 81] These gates afford control over the gases absorbed into the material by discriminating based on molecular size; a property that is of particular interest for membrane-based gas separation. A membrane capable of continuously adjusting its pore size would be applicable not only for separation of very similar gases (i.e. olefin/paraffin or butane isomers) but would be useful for its market flexibility (a single membrane could be used to achieve separation of many different gas mixtures). Another important feature of MAMS is that although the molecular gates within the structure open and close with temperature, the lattice constants remain unchanged. This means that, unlike previously

reported titanosilicate molecular sieves,[82] the MAMS unit cell is unaffected by the molecular gating effect.[81]

2.1.1 Project Materials and Initial Results

The specific materials used for this study are MAMS-4 and MAMS-6, developed by the Zhou research group in the Department of Chemistry at Texas A&M University. The molecular structures of MAMS-4 and MAMS-6 consist of metal clusters (copper paddlewheels) connected in a rigid hexagonal lattice by organic ligands. Our initial attempts to fabricate MAMS films on supports followed previously demonstrated techniques such as those described in section 1. These techniques included *in situ* growth on bare supports, spin coating, dip coating and manual deposition on a variety of substrates such as bare silicon, PEI coated silicon, anodized aluminum oxide, porous aluminum oxide, bare glass and glass coated with a hydrophobic silane molecule (polytetrafluoroethylene). Following the failure of each of these, two new methods were developed based on thermal seeding, a secondary growth technique developed in our group and discussed in detail in section 1.5.4. As illustrated in Figure 14 the methods developed here, referred to as thermal modification, consist of pre-attachment of either the appropriate metal (copper for MAMS-4 and -6) or the organic linker (4'-*tert*-butylbiphenyl-3,5-dicarboxylic acid (BBPDC) for MAMS-4 or 5-(1,3-dioxo-3a,4-dihydro-1*H*-isoindol-2(*3H*,7*H*,7a*H*)-yl)cyclohexane-1,3-dicarboxylic acid (ICHDC) for MAMS-6) to the support prior to solvothermal synthesis. We have also applied the ligand-modification variant of this method to membranes of ZIF-8 [48] as discussed in section 1.5.2.

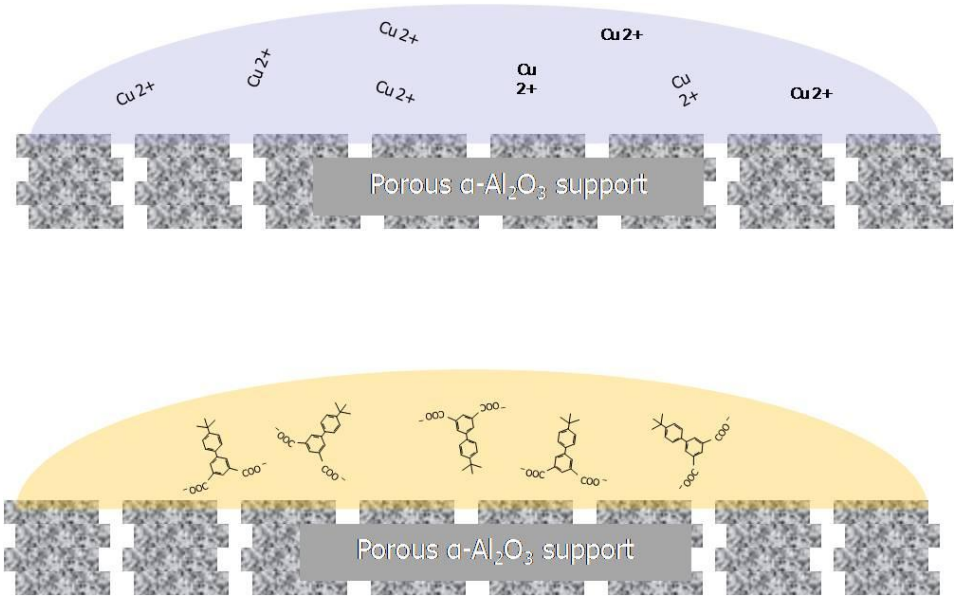

Figure 14. Illustration of support modification techniques: (*upper*) copper modification of porous supports and (*lower*) ligand modification of supports.

2.1.2 Experimental Methods- Thermal Modification of Supports with Copper

Porous α-Al_2O_3 supports are prepared following a method reported by the Tsapatsis group.[73] Supports are then heated to the appropriate temperature (150°C for copper modification) in a convection oven. The same copper solution is used for both MAMS-4 and MAMS-6 membranes. To prepare the copper solution, combine 15 ml of ethanol, 15 ml of DI water and 15g $Cu(NO_3)_2$*$2.5H_2O$ in a small nalgene bottle. Stir the solution until copper is dissolved and solution is deep blue (concentration = 500 mg/mL). The copper solution is quickly deposited drop by drop using a disposable polypropylene dropper until the support surface is coated (~300 – 500 µL total). The copper solution is allowed to evaporate at 150°C (~3 min). Coated supports are then removed from the oven and carefully sonicated in DI water for ~10 sec to remove

loosely bound copper (contact with the sonicator surface should be avoided to prevent sample damage). Modified supports are then allowed to dry in the oven at 150°C (~5 min).

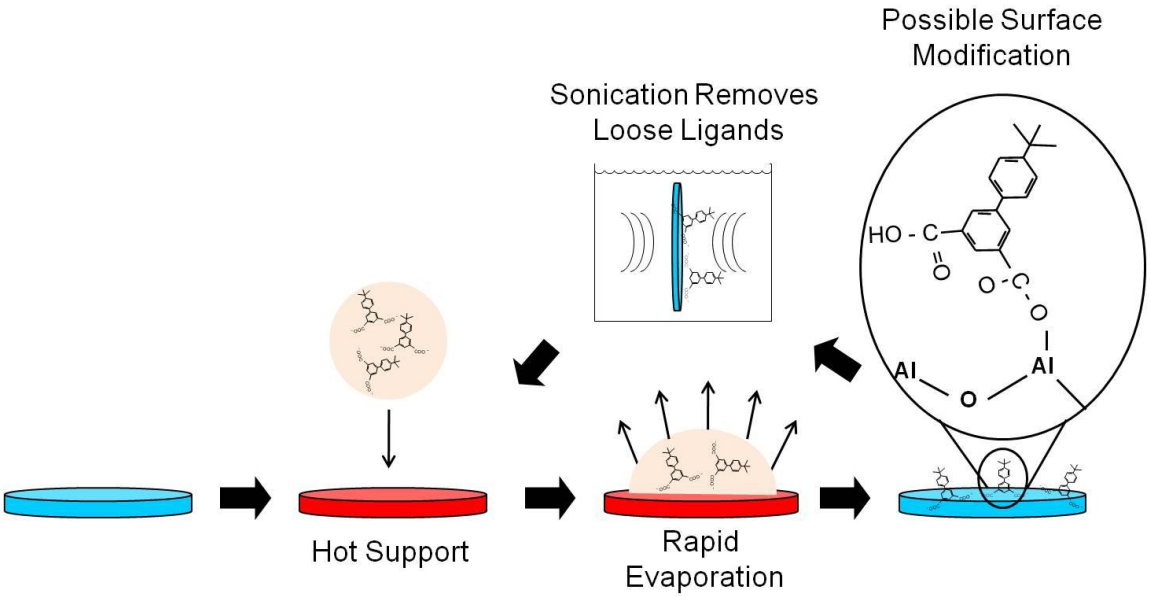

Figure 15. Schematic illustrating the thermal modification process.

2.1.3 Experimental Methods- Thermal Modification of Supports with Ligands

The procedure for modifying supports with organic ligands is illustrated in Figure 15. Porous α-Al_2O_3 supports are prepared following a method reported by the Tsapatsis group.[73] The process of support modification with organic ligands is illustrated in Figure 15. Supports are first heated to the appropriate temperature (180°C for ligand modification) in a convection oven. To prepare the ligand solution, combine 30 ml of dimethylacetamide (DMA) and 300 mg ligand (ICHDC for MAMS-6, provided by the

Zhou research group) in a small nalgene bottle. Stir the solution until the ligands are dissolved and solution is light brown (concentration = 10 mg/mL). The ligand solution is quickly deposited drop by drop on the hot support using a disposable polypropylene dropper until the support surface is coated (~300 – 500 μL total). The ligand solution is allowed to evaporate at 180°C (~10 min). Coated supports are then removed from the oven and carefully sonicated in DMA for ~10 sec to remove loosely bound particles (contact with the sonicator surface should be avoided to prevent sample damage). Seeded supports are then allowed to dry and reheat in the oven at 180°C (~10 min). The process is repeated until the supports are well coated, typically 6 times.

2.1.4 Experimental Methods- Solvothermal Synthesis

MAMS membranes are synthesized using solvothermal growth. MAMS-4 growth solution is prepared by dissolving 0.67g $Cu(NO_3)_2$*$2.5H_2O$ and 0.333g BBPDC separately in 25 mL of DMF. Solutions are combined prior to synthesis. MAMS-6 growth solution is prepared by first preparing 50 mL DMA/H2O (2:1 by vol) solvent solution. Following this, 0.4g $Cu(NO_3)_2$*$2.5H_2O$ and 0.267g ICHDC are dissolved separetly in 25 mL solvent solution. Solutions are combined prior to synthesis.

The following procedure applies to both MAMS-4 and MAMS-6. Modified supports are loaded vertically into custom Teflon holders and immersed in the appropriate growth solution (typically a glass jar is sufficient due to the low solvent vapor pressure). The tightly closed jar is then placed in an oven at 85°C for 24 hours. After growth, it is important to allow the newly grown membranes to cool slowly to

prevent cracking. Typically, glass jars are removed from the oven and left to cool in a hood overnight.

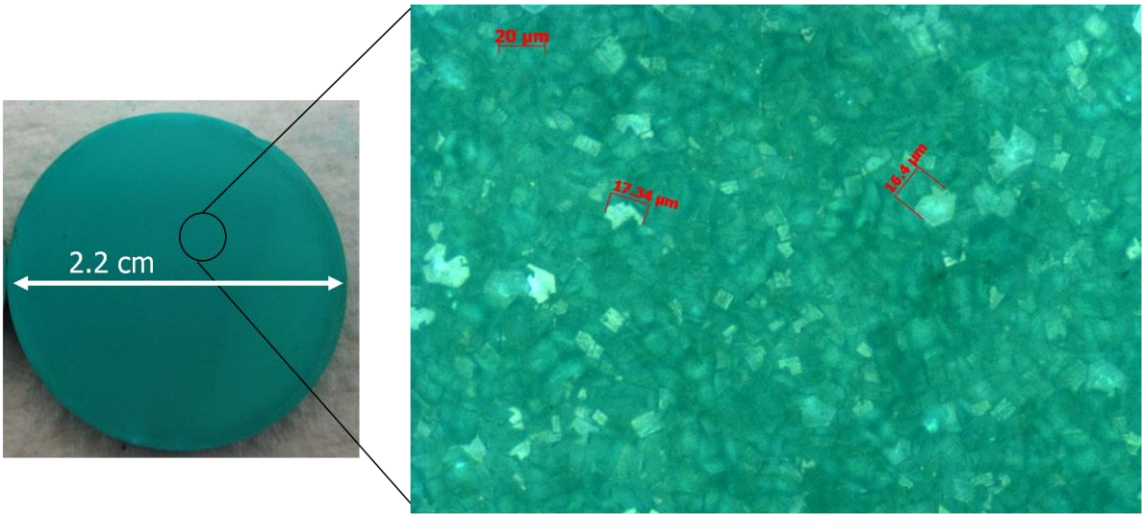

Figure 16. A typical well-intergrown membrane of MAMS-6 after solvothermal growth of copper-modified supports.

2.1.5 Results and Discussion

Initial gas permeation testing of MAMS membranes focused on measuring the permeance of single gases through the membranes at varying feed pressures using the time-lag method. The purpose of these trans-membrane pressure drop permeation tests is to determine if there are performance-hampering cracks or defects present in our polycrystalline membranes. If significant cracks or defects are present in a membrane, then permeance would be a strong function of feed pressure which is characteristic of viscous flow of the gas.[36, 37] Figure 17 shows the result of initial trans-membrane pressure tests of MAMS membranes from copper-modified supports. We took the slope of another MOF membrane we recently reported as our goal;[48] on this scale it is 0.00001.

As seen in Figure 17, the slope of the permeance vs. feed pressure line indicates the presence of significant cracks or defects in the MAMS-6 membranes.

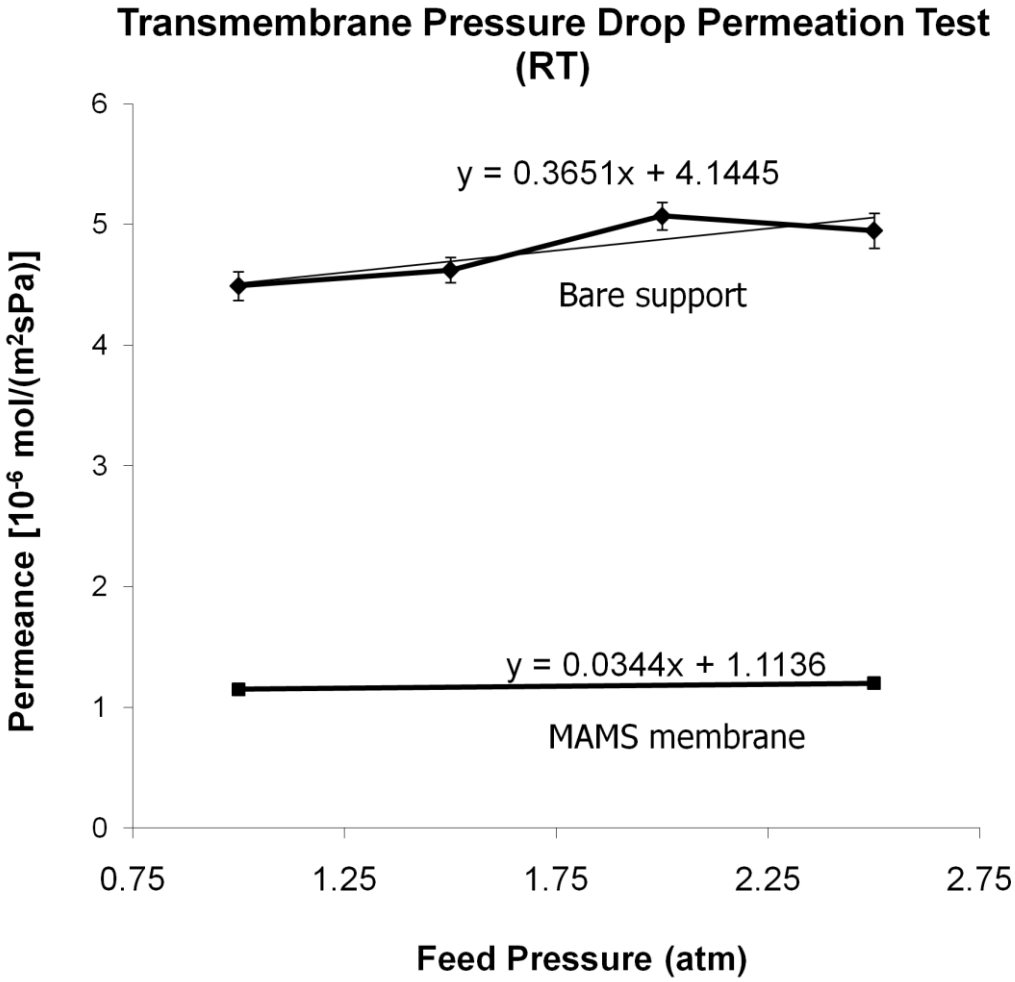

Figure 17. Trans-membrane pressure drop permeation test for a typical MAMS membrane grown from a copper modified support (H_2 at 1 bar and 2.5 bar).

As seen in Figure 18, the presence of both cracks and pinhole defects in our membranes was confirmed. The most prevalent cracks observed in our samples are in the a-b plane of each crystal; this is not surprising as there are no covalent bonds

between adjacent layers in the MAMS structure and fracture is most likely to happen where the structure is weakest.

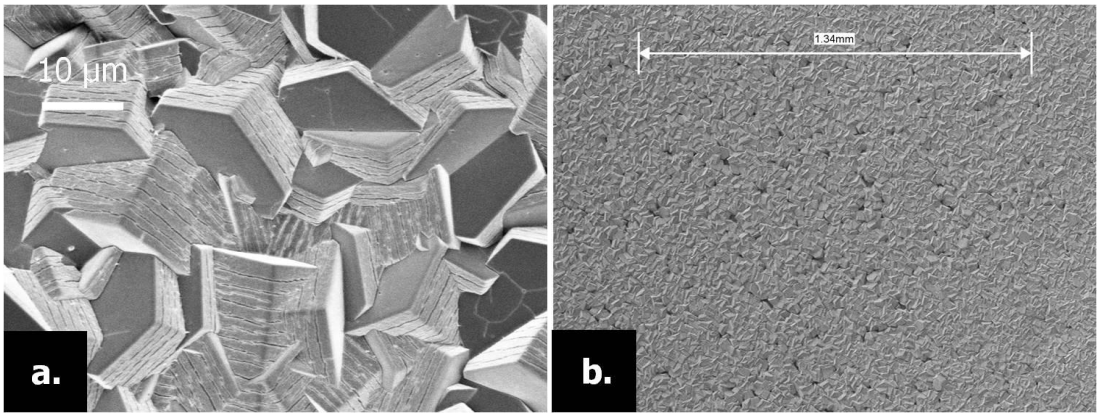

Figure 18. Top-down FE-SEM image of a typical MAMS-6 membrane showing cracks in the membrane (a). Top-down FE-SEM image of a large area of a typical MAMS-6 membrane showing pinhole defects (b).

According to our experience with other MOFs, the method used to dry MOF membranes after synthesis can be a significant factor in causing film fracture.[44] We hypothesized that the capillary stress induced in our films during the drying process was the root cause of the cracks we observed. To combat this problem, we adopted a novel strategy to reduce the surface tension during drying as illustrated in Figure 19. Immediately after solvothermal synthesis, MAMS-6 membranes were immersed in a solution containing an amphiphilic surfactant for 1 day. From our experience with other MOF membranes we chose a 10 wt% solution of Span-80 in methanol. We expected that the surfactant would associate itself with the surface of our films in solution and serve to decrease surface tension at the solid/liquid interface during drying.

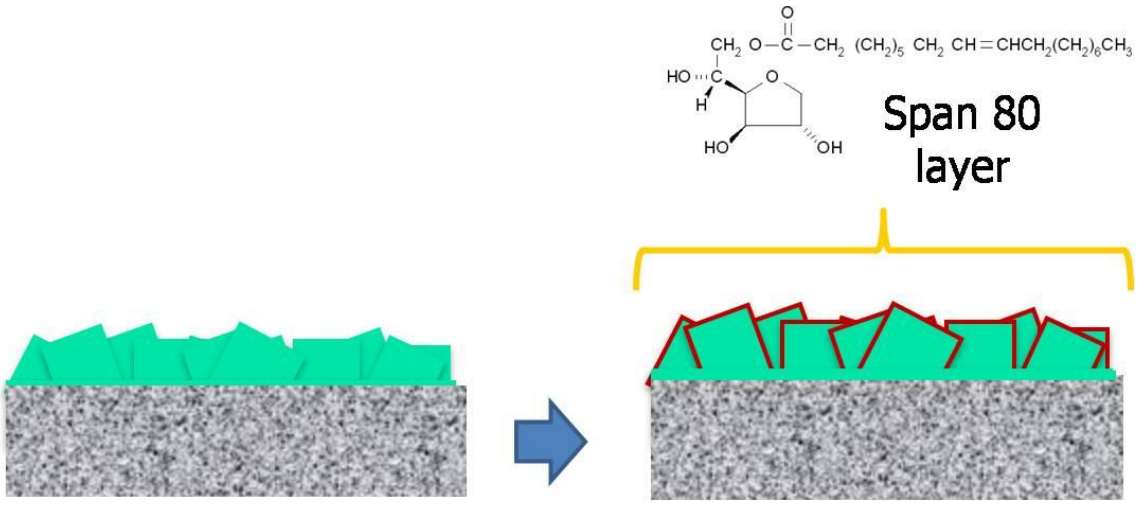

Figure 19. Illustration of our approach to reducing surface tension in our MAMS films during the drying step after fabrication.

Figure 20 shows the resulting MAMS-6 membrane after drying using a Span-80 coating. The density of cracks has been drastically reduced. This result confirms our hypothesis that crack formation during drying is a central concern for MOF membranes. Figure 21 shows the cross section of these membranes. Membranes grown from either copper or ligand modified supports have similar film microstructure and are 15-22 μm thick.

MAMS-6 membranes that were dried using a surfactant coating were subsequently subjected to the trans-membrane pressure drop permeation tests and compared to our previous results (see Figure 22). As Figure 22 shows, the permeance-feed pressure slope of our MAMS-6 membranes improved by an order of magnitude.

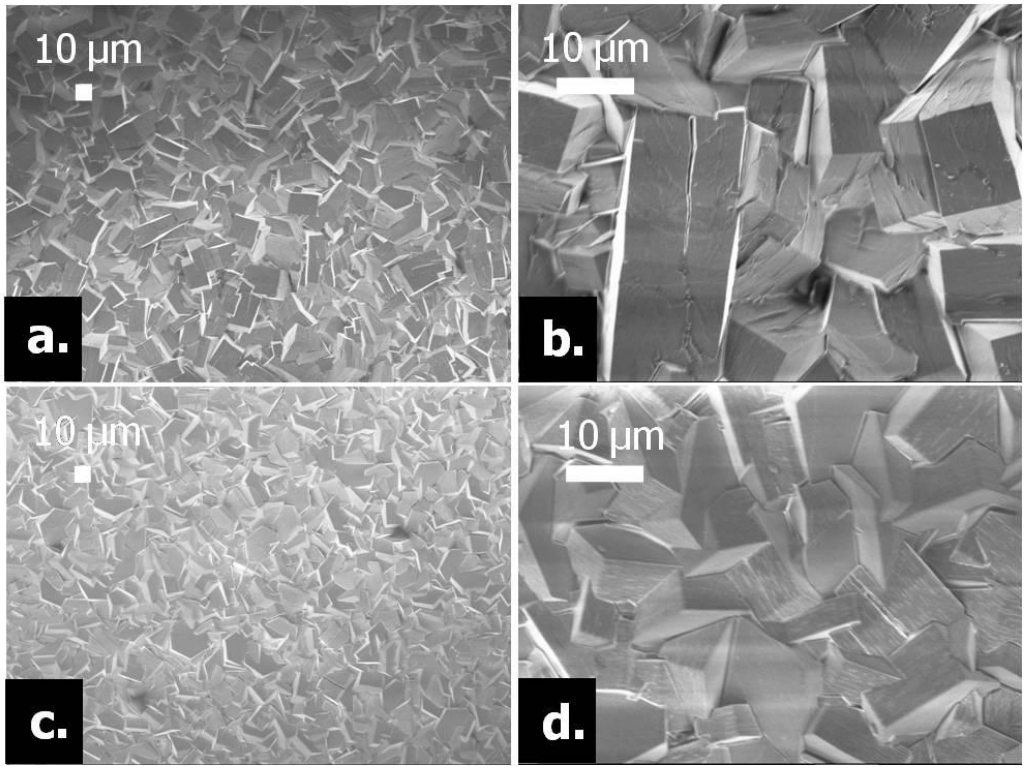

Figure 20. Top-down FE-SEM images of a crack-free MAMS-6 membrane grown from a copper-modified support and dried using a Span-80 coating (a), (b). Top-down FE-SEM images of a crack-free MAMS-6 membrane grown from a ligand-modified support and dried using a Span-80 coating (c), (d).

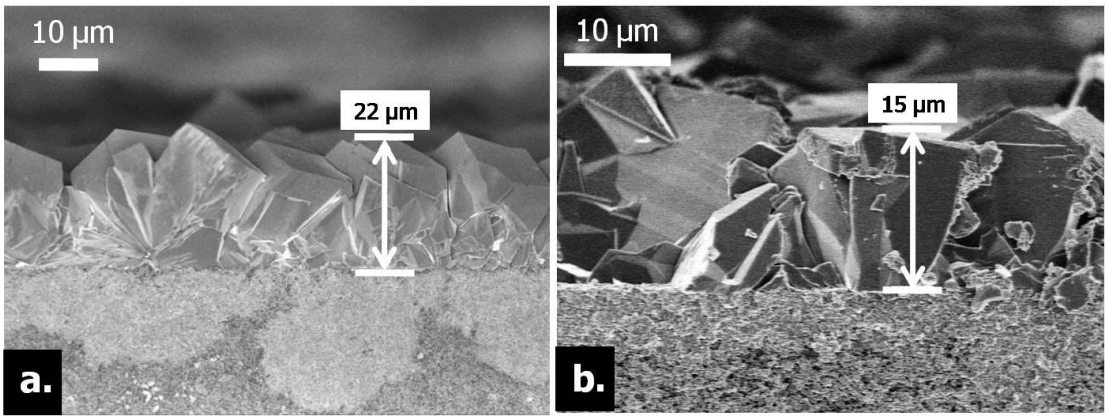

Figure 21. Cross-section FE-SEM images of a crack-free MAMS-6 membrane grown from a copper-modified support and dried using a Span-80 coating (a). Cross-section FE-SEM images of a crack-free MAMS-6 membrane grown from a ligand-modified support and dried using a Span-80 coating (b).

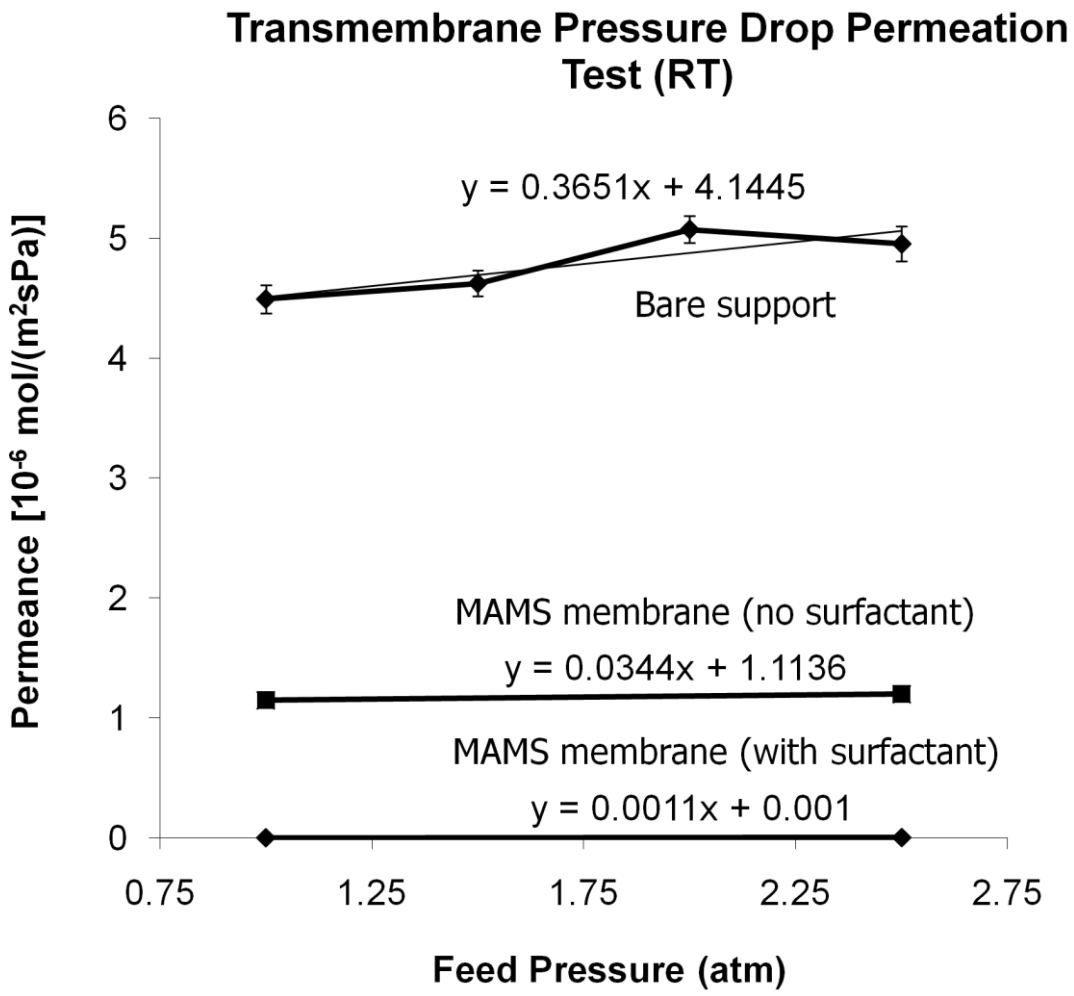

Figure 22. Trans-membrane pressure drop permeation test for MAMS membranes grown from copper-modified supports dried with and without the aid of a surfactant (H_2 at 1 bar and 2.5 bar).

2.2 Rapid Thermal Deposition of Metal-Organic Framework Thin Films

As discussed in section 1.5, polycrystalline MOF film fabrication typically follows one of two general approaches: *in situ* growth or secondary growth. Both of these approaches to MOF film fabrication feature solvothermal synthesis, typically at elevated temperature (~100 – 200°C) and constant pressure for an extended period of

time (~8 – 48 hrs). Synthesis is usually carried out using Teflon-lined steel autoclaves and is inherently a batch process. This approach to MOF film fabrication follows established approaches to zeolite membrane fabrication on porous supports. However, we have found that for metal-organic framework film fabrication, this traditional approach is unnecessary. The process of MOF synthesis has been referred to as inorganic self-assembly, similar to polymerization. Due to this ease of assembly, we have found that MOF films can be rapidly synthesized directly on porous supports without the need for extended solvothermal synthesis.

2.2.1 Initial Results of RTD with HKUST-1 Films

HKUST-1 is a well-known MOF that has been used in studies of MOF films and membranes in a number of reports.[27, 38, 44] The structure consists of copper nodes connected by trimesic acid (benzene-1,3,5-tricarboxylic acid). Films of HKUST-1 were fabricated using two variants of RTD. In the first variant, the growth solution [83] was simply dropped on hot supports and allowed to evaporate, leaving crystals of HKUST-1 agglomerated on the surface. As can be seen in Figure 22, HKUST-1 crystals do not appear to be well intergrown under SEM. This is likely a result of rapid crystal nucleation on the hot support surface.

In the second approach, bare supports were allowed to soak in the growth solution for approximately 30 minutes. Following this soaking, supports were simply placed in an oven at 180°C for ~10 minutes. As can be seen in Figure 23, HKUST-1 crystals now appear to be well intergrown on the support surface. Gas permeation properties of these films remain to be confirmed.

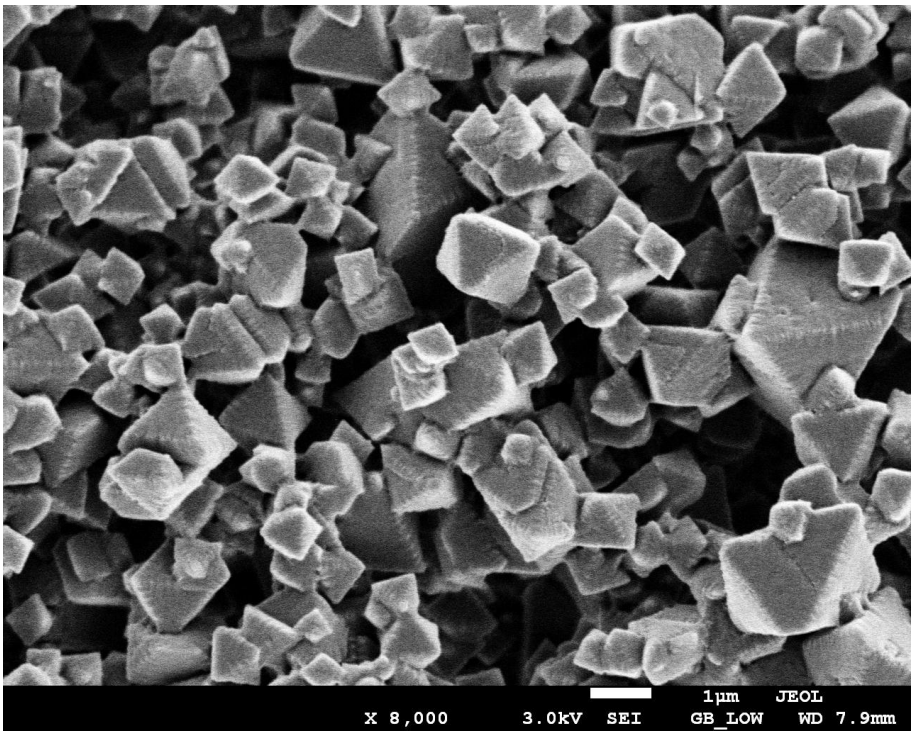

Figure 23. HKUST-1 film fabricated using RTD (solution dropping variant).

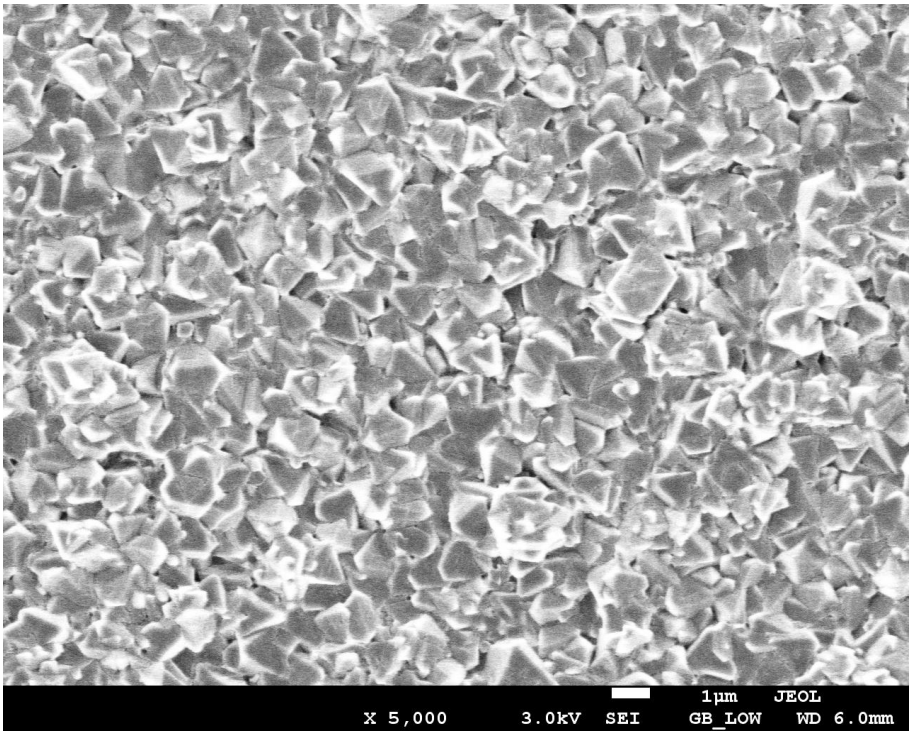

Figure 24. HKUST-1 film fabricated using RTD (support soaking variant).

3. SUMMARY AND CONCLUSIONS

3.1 Summary

We have developed three new fabrication methods for metal-organic framework film and membrane synthesis. The first of these methods (thermal modification of supports using metals or ligands) have been demonstrated with members of a new class of MOF materials called Mesh Adjustable Molecular Sieves, specifically MAMS-4 and MAMS-6. The last method we have developed, rapid thermal deposition, has been demonstrated using HKUST-1 as a typical MOF. Although MOF membranes that are effective for gas separation have not been demonstrated with this method yet, the paradigm shift in MOF film synthesis techniques that this method represents easily justifies further research in this direction.

3.2 Conclusions

There is much room left for exploration of MOF membranes as indicated by the orders of magnitude difference between the number of reports of MOF structures and that of MOF films and membranes (see Figure 2). It is important to note that half the reports of MOF membranes to date have been short communications briefly discussing membrane synthesis and performance. [38, 40, 42, 45, 46, 84] Thus there is not only room for work to be done in exploring new MOFs, but there is room for more detailed

investigations discussing important topics for polycrystalline membranes such as microstructure control, effect of grain boundaries on separation properties, and defect and crack removal. There is also room for exploration of MOFs with other interesting properties such as the enantioselective pores exhibited by POST-1.[85] Different MOFs exhibiting pores with handedness have been reported, but none have been explored for membranes or thin films.[86, 87] A MOF membrane with enantioselective pores could possibly be used for high resolution separation of racemic mixtures, providing an alternative to methods such as chiral column chromatography. Though progress is being made in this field of research, many avenues of study for MOF membranes have yet to be explored.

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VITA

Michael Colin McCarthy received his Bachelor of Science degree in chemical engineering from The University of California at Berkeley in 2004. He entered the Master of Science degree program in the Artie McFerrin Department of Chemical Engineering at Texas A&M University in September 2007 and completed his degree in May 2011.

Mr. McCarthy can be reached through the Department of Chemical Engineering at Texas A&M University, 3122 TAMU, College Station, TX 77845. His email address is mcolinmccarthy@neo.tamu.edu.