UNDERSTANDING AND CONTROLLING METAL ORGANIC FRAMEWORK CRYSTALLIZATION FOR THIN FILM FABRICATION

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ABSTRACT

Metal organic frameworks (MOFs) are a promising class of materials that have seen an exponential growth in research interest in the past few decades. Composed of transition metal nodes with organic linkers, these crystalline, highly porous, and chemically versatile structures show significant promise in applications ranging from drug delivery, data storage, separations, sensing and catalysis. Many of these applications require MOFs to be configured as a thin film for better transport characteristics and to act as a selective barrier between two mediums. In terms of film quality, properties such as grain size, coverage, polycrystallinity, orientation, and thickness must be controlled to optimize thin film performance for a given application. Current fabrication technologies often see a tradeoff between controllability and scalability, where the highest quality films require time-consuming, low-area, and complicated fabrication techniques. This relationship motivates the need to develop a scalable, large area, and rapid fabrication technique capable of producing high quality MOF thin films. The work put forth in this dissertation is an effort to couple MOF crystallization to a thin film deposition technique called solution shearing to fabricate high quality thin films on a seconds to minutes time scale.

In Chapter 2, two methods for thin film fabrication are developed where MOF growth is decoupled from the film fabrication process. MOF morphology and coating parameters were varied to determine effect on thin film properties. Films were characterized using x-ray diffraction and scanning electron microscopy to determine particle and film orientation and morphology, respectively. Results show controlling particle morphology significantly influences crystal orientation in resulting films. Chapter 3 couples MOF formation with a deposition process. This study focuses on understanding the effects of solution shearing on films made from a copper-based MOF, HKUST-1. X-ray diffraction, profilometry and optical microscopy were used to characterize

particle and film orientation, thickness, and morphology, respectively. Results indicate solution shearing can control particle size, thickness and orientation during the thin film deposition process. The study is extended by using machine learning to create a virtual experimental space to understand solution shearing parameter relationship with film coverage and thickness. This model is used to identify parameters that minimize film thickness while maintaining a fully covered film.

Coupling other MOFs, such as the highly stable zirconium based UiO-66, to solution shearing proved to be a difficult task. This is because the crystallization process is not well understood. Thus, Chapter 4 and 5 study MOF crystallization. Chapter 4 uses x-ray diffraction and scanning electron microscopy to study the influence of reactant speciation on the rapid crystallization kinetics of MOFs. We show that tuning pH and forming the correct metal node topology prior to synthesis allows MOFs to crystallize on a seconds time scale at room temperature for several prototypical MOFs and conclude each system can be treated as a reactive-crystallization. Chapter 5 extends these concepts to study MOF formation using *in situ* wide angle x-ray scattering. The influence of synthesis parameters including reactant and modulator concentration, temperature, and addition of heterogeneous nucleation sites on crystallization kinetics is observed. Insight into a potential formation mechanism is discussed and used to motivate a new crystallization model developed by collaborators.

Chapter 6 highlights two applications using films developed from previous chapters. Rate of gas adsorption is measured using an adsorption analyzer. Kinetic selectivity between CO_2/CH_4 is shown to be orientation dependent for a zinc based anisotropic MOF developed in Chapter 2. Finally, the rapid synthesis developed in Chapter 4 is adapted to create MOF coated fabric. Pollution filtration is measured using a particle counter to show the addition of MOF enhances filtration efficiency for PM_{1-4} particles.

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The sun has come. The mist has gone. We see in the distance... our long way home. I was always yours to have. You were always mine. -Maya Angelou

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1 Introduction

1.1 Metal Organic Frameworks

Metal-organic frameworks (MOFs) are highly crystalline coordination polymers, composed of metal ions or oxo-metallic secondary building units (SBUs) that are coordinated with organic linkers to form a porous, open framework. Their high porosity and organic linker components allow for controlled pore geometry and functional chemistry. Thus far, tens of thousands of MOF structures have been created by combining over 130 SBUs with a wide range of organic linkers.^{1–3} By rationally selecting the appropriate node/linker topology and connectivity, pore size, shape and chemistry can be tuned for a variety of applications. The combination of rational pore design, high porosity and surface area and facile synthesis have made MOFs popular as versatile materials for an expanding portfolio of applications including gas storage, catalysis, separations, medicine, energy and pollution filtration.^{4–12}



Figure 1.1 Ball and stick model showing a zinc-based oxo-metallic secondary building unit (SBU) used to construct MOFs with varying pore sizes, where pore sizes are correlated with the length of the ditopic organic linkers benzene-1,4-dicarboxylic acid (BDC) and terphenyl-2,2'-dicarboxylic acid (TPDC). Used with permission from [5].

Omar Yaghi first reported MOFs in their current form in the late 1990's.¹³ Originally considered organic-based analogs to zeolites, the applications mimicked those of their inorganic counterpart in catalysis, gas storage and separations with more promise due to their remarkably high surface area and controlled pore size and chemistry.^{13,14} For example, Kaskel *et al.*

demonstrated an ultrahigh surface area MOF, DUT-60, that has a surface area of 7800 m²/g and adsorbed up to 3000 cm³/g of nitrogen.¹⁵ Additionally, controlled pore size and structural design has been shown to provide molecular size selectivity for catalysis in multiple occasions.^{16–19} In one interesting case, reported by De Vos *et al.*, a zirconium based MOF UiO-66-NH₂ acted as an acid-base catalyst for cross-aldol condensation.²⁰ In this case, they hypothesized the close proximity of the amino groups to the Zr sites in the MOF lead to superior selectivity in the synthesis of jasminaldehyde from benzaldehyde and heptanal. Such a mechanism highlights the utility of combining the chemical functionality and structural design of MOFs for catalysis.

Rapid research of new framework designs, post-synthesis modifications, and new morphologies and heterostructures have led to a wide variety of applications that leverage the chemical versatility of MOFs combined with the open framework structure.^{21–25} Advanced applications are focusing on incorporating highly functional groups into the material and incorporating MOFs into active heterostructures for high performance material properties.^{17,26,27} In one case, Phang *et al.* post synthetically sulfonated the linker in UiO-66 for enhanced proton conductivity.²⁸ This resulted in comparable proton conductivities to the commercially available Nafion proton exchange membrane at similar operating conditions.²⁸ For the same parent structure, Peterson *et al.* showed the addition of an amine group resulted in unprecedented removal capacity of the pollutant NO₂ (1.4g NO₂/g MOF).²⁹ These studies demonstrate that tuning functional chemistry allows for a parent structure to be modified for multiple applications. Further, incorporating MOFs and other active materials as MOF-based heterostructures has yielded highly efficacious results.^{18,23,24} In these cases, MOFs can act as selective coatings or encapsulate active nanoparticles to facilitate the selective transport of species to active surfaces.^{18,23,30}

Furthermore, advances in MOF crystal engineering allows the removal of organic linker or metal node sites known as defect control.^{31–35} Removing these components allows for the creation of open metal sites within the framework, as well as control of exposed crystal surfaces and morphologies.^{36,37} This type of structure allows for metals within MOF structures to behave as heterogeneous single-site catalysts, where active sites are well defined, spatially separated and periodic.^{6,38} Growing MOFs for specific faceting using a synthetic technique termed chemical modulation also allows for specific pore sizes to be exposed at interfaces, allowing for selectivity of a given MOF to vary based on orientation.³⁹

The field is ripe for innovation and exploration, where the combination of chemical functionality, crystallization control, and advanced heterostructures have established potentially high impact areas of research. Yet, many questions remain for the establishment of MOFs as truly useful materials. After all, the commercial and industrial adoption of these materials has been slow, with only a handful of real-world applications starting in 2016.⁴⁰ This is likely due to many syntheses and configurations not being commercially viable and scalable.^{12,41,42} As such, one of the themes of this dissertation is to continue demonstrating the high utility of MOFs while developing scalable synthetic techniques.

1.2 Thin Film Metal Organic Frameworks

Within the field of MOFs, thin films, coatings and mixed matrix membranes have emerged as highly sought-after configurations for applications ranging to separations, electronics and pollution capture.^{21,43,44} In these applications, thin film morphology is equally important as the porous structure of MOFs. Controlling the film properties allows for enhanced mass and charge transport in sensing and filtration applications. For example, the response time of a MOF sensor will depend on the mass transfer of analyte across the film thickness, but the sensitivity and selectivity will depend on the ability of the MOF material to enrich and selectively adsorb said analyte.⁴⁵ Similar requirements are necessary for separations applications. In this case the thin film must act as a separations barrier and minimize diffusion path length to enhance transport of ions or filtrates. Separately, the MOF structure and chemical makeup control size selective pore size and other interactions with the diffusing species (i.e. electrostatic).^{7,46}

Thus, depending on the final application, morphology becomes increasingly important to leverage the steric and chemical properties of MOFs. Film properties such as grain boundaries, pin holes (i.e. intercrystal voids), thickness, crystal alignment and defect density can have a significant influence on charge and mass transport behavior. Molecular dynamic (MD) simulations and experimental work have shown mass transport is highly influenced by crystal domain interfaces and defects for larger guest molecules in MOFs.⁴⁷ Thus, minimizing grain boundaries and defects in the transport direction may yield enhanced and more predictable results. Further, limiting diffusion path lengths, reducing, or eliminating pinholes and selecting the proper pore orientation should all contribute to enhanced mass transport and selectivity of separations and exchange membranes. Therefore, the ability to control MOF thin film characteristics, such as grain size, thickness, coverage, and crystal domain alignment will have major influence on the performance of MOF based devices, coatings and membranes. Achieving these qualities with methods that are scalable, controllable, and greener will only accelerate the adoption and broader impact of this relatively young class of materials.²¹ The next section will review current state of the art methods for achieving controlled thin films of MOFs under this context.

1.3 Current Technologies for Thin Film MOF Fabrication

Developing techniques that (a) are both scalable and controllable have typically been antagonistic. On one hand, scalable approaches focus on reducing production time and increasing the total area of material produced. On the other hand, fine tuning the control over MOF crystalline films requires long timescales to control the crystallization process or complex techniques thatare easily not translated into а continuous process. Figure 1.2 shows some of the different techniques ranging in film quality, which is typically determined by polycrystallinity, crystal orientation and film



Figure 1.2. (a) Schematic of thin film MOF fabrication using dip coating in a particle solution and precursor solution and (b) Thin film MOF fabrication using self-assembled monolayer functionalization to grow epitaxially. Used with permission from [50].

coverage. Many of these involve depositing pre-synthesized MOF particles, or confining and controlling MOF synthesis to a substrate.

In one approach to achieving rapid, oriented thin films, Bein *et al.* dipcoated a substrate functionalized with carboxylate self-assembled monolayers in a suspension of MOF particles.⁴⁸ This resulted in highly oriented particle films that could be used as oriented seed layers for secondary growth. However, the film was not fully covered (**Figure 1.2a**), and using a gold coated functionalized substrate significantly limits the number of useful applications. In another approach, Ji et al. developed a rapid and direct method to grow HKUST-1 and ZIF-8 thin films on metal substrates through electrodeposition in approximately 5 minutes. This method was able to confine growth on the substrate as the metal source was also the electrode during the deposition process. While it produced a thin film quickly, polycrystallinity and lack of alignment made it a low-quality thin film, indicating control of the crystallization process was not readily achievable.⁴⁹ Polycrystallinity provides varying film thickness with a large quantity of grain boundaries, which limits homogeneous diffusion through the film and may reduce selectivity due to grain boundaries allowing molecules through.⁵⁰

On the other hand, several groups have used liquid phase epitaxy to grow high-quality thin films of multiple MOFs with oriented and large crystal domains.^{50,51} Such a synthesis involves alternatively immersing a functionalized substrate into separate metal and ligand solutions and usually requires a washing step to remove unreacted material before the next step. By limiting the combination of reactants to the substrate surface, crystallization can only occur in a single layer. In this method, film nucleation is limited in favor of oriented growth, likely due to the stepwise addition of components. While beneficial for creating homogeneous, high quality thin films as research platforms, dip coating tens to hundreds of times requires an extensive amount of time and complexity when considering large area fabrication. After all, this technique is crystallizing layers by a half to one unit cell per dip. Attempts to speed up this process by spray coating have been

successful in reducing synthesis time from days to hours, however, crystalline quality was degraded, suggesting the timescale at which crystallization occurs may influence crystal quality.⁵²

Other techniques, such as interfacial growth on porous substrates presented by Brown *et al.* for ZIF-8, have shown sufficient quality, applications ready full films and provide a good balance between film quality and production time.⁵³ These techniques use a controlled diffusion interface to confine crystallization to a substrate placed at the interface. In this case a microfluidics device was used to create a single hollow tube membrane at a time, while offering great control over the deposition process, the slightly longer production time (hours) and small batch processing of these materials pose significant challenges to technology scale-up.

Considering these examples, it is clear a technique for rapidly producing high-quality thin film MOFs remains a challenge for the field. This is likely because confining and controlling the crystallization of MOFs to a substrate or thin layer are exceedingly difficult at seconds to minute time scales. Further adding to complexity, making these processes continuous and substrate independent are necessary for the scalability and access to the promising range of applications already shown for MOFs. While the challenge of developing these techniques is relatively new for MOFs, it is certainly not unique or specific to the field. Thus, the next section will focus on gaining inspiration from the field of organic molecule thin film crystallization to motivate our approach in producing high quality thin film MOFs at rapid time scales.

1.4 Continuous crystalline thin film deposition techniques

Solution processing of organic crystals is a rich field of research with parallels to controlling MOF crystallization at rapid timescales. A class of coating techniques termed convective deposition, doctor blading, or solution shearing have shown great success in rapidly

manufacturing and controlling the orientation and morphology of small organic molecule crystalline thin films.^{54,55} Of these, solution shearing is a meniscus guided coating technique that uses a shallow angled blade to coat a heated substrate. A solution containing the solute of interest is sandwiched between the blade and the substrate (Figure 1.3). As the blade is translated at a controlled speed, an evaporation front is created as liquid is drawn out into a film. The solvent evaporation causes an increase in the concentration of the solute in the film, causing supersaturation and then crystallization. Controlling the blade speed and the substrate temperature controls the rate of evaporation and the fluid thickness, thus controlling the crystallization kinetics. In this technique, the blade speed can vary from a range of microns per second to nearly 100 millimeters per second. While other related techniques such as drop casting⁵⁶, dip coating⁵⁷, ink jet printing⁵⁸, spin coating⁵⁹ and doctor blading⁶⁰ have all demonstrated crystallization control, solution shearing is a continuous process that offers a wide range of related parameters that can finely control concentration gradients and subsequent crystallization during deposition. These parameters include the substrate-blade gap and angle, blade speed, solution concentration and substrate temperature.



Figure 1.3. Schematic of crystallization from a precursor solution using solution shearing where solvent evaporates at the evaporation front and a concentration gradient develops between bulk solution and the deposited film. As the solvent evaporates the thin film solidifies on the substrate.

Solution shearing has been used to control the film thickness, orientation, morphology, or crystallinity of several materials, controlled by changing the blade speed, temperature and solution properties.^{54,55} Baigle *et al.* controlled the thickness of a multilayer phospholipid film by changing the blade speed of their flow coating device.⁶¹ They found film thickness was related to the blade speed in two distinct coating regimes. The first regime exists at lower blade speeds, where the evaporation time scale of the solution (controlled by temperature) is similar to the fluid deposition time scale (controlled by the blade speed). This is known as the evaporative regime, and the resultant film thickness can be related to shearing velocity by a mass balanced shown in Eq 1.1.

$$h = \frac{c}{\rho} \frac{Q_{evap}}{L} U^{-1} \qquad \qquad Eq. \ 1.1$$

Where C $[g/mm^3]$ is the concentration of solute in solvent, $\rho [g/mm^3]$ is the density of deposited solute material, $Q_{evap} [mm^3/s]$ is the evaporation rate of solvent, L [mm] is the width of the



Figure 1.4. Schematic of solution shearing for (a) evaporative regime with control volume for mass balance and (b) Landau-Levich regime with important geometric parameters

deposited film (perpendicular to velocity), and U [mm/s] is the velocity. Film thickness, h [mm] is inversely proportional to blade speed in the evaporation regime.

The second regime occurs at higher speeds, where viscous forces dominate, and solution is deposited at a much shorter time scale than evaporation. In this regime, a thin liquid film is first coated onto the substrate. After the blade has passed, evaporation of the solvent results in thin film crystallization. This is termed the Landau-Levich regime. In the Landau-Levich regime, a positive scaling relationship between final film thickness and velocity exists⁶¹, as opposed to the negative relationship derived for the evaporative regime. A transition regime exists in between the evaporative and the Landau Levich regime, where neither process dominates. Baigl *et al.* found that neither of the previously defined regimes could predict film thickness as shown in **Figure 1.6.** However, they did find a minimum film thickness was obtained in this region.



Controlling and predicting the minimum *Figure 1.5. Graph depicting the three regimes relating shearing speed to resulting film thickness showing a minimum in the transition regime.* thickness is extremely relevant in making thin films of MOFs, especially for applications involving transport process where thickness may affect performance.

In addition to film thickness, Giri et al. controlled the polymorphism, morphology and orientation of an organic semi-conductor (OSC) to tune the charge transport characteristics. By



Figure 1.6. (a) Schematic of solution shearing of a semi-conductor solution on a heated substrate (b-f) Optical microscope images demonstrating different morphologies and charge transport properties because of shear speed. Scale bar is 200 um Figure used with permission from [55].

altering shearing speed and changing solvents, able they were to preferentially orient crystal growth with large crystalline domains over large areas.^{55,62} They were also able to control the crystal packing and polymorphism of the organic semiconductors. They posited that spatial confinement in the thin film kinetically trapped the crystal as a metastable polymorph, which influenced charge transport.55 This study demonstrated that solution shearing can influence both polymorphism morphology and across nanometer to centimeter length scales.

We hypothesize that solution shearing could be applied to the MOF material class and may control thickness, morphology, and polymorphism of the resulting thin films. However, significant differences do exist between the two systems. In the case of OSC crystallization, the crystallization occurs from a well-known evaporative process that follows the principles of classical crystallization. In this case, the driving forces and biasing of nucleation and growth events are predictable and controllable via supersaturation of a single component. Further, the structure and crystallinity of the OSC used in the study by Giri et al. was dictated by π - π stacking, which is a weak non-covalent interaction. MOF coordination bonds tend to have higher energy than weaker interactions in single molecule crystallization (i.e. metal-oxygen coordination bonds).⁶³ Additionally, MOF crystallization requires a more complex coordination of multiple species and rapid crystallization is much less frequently reported. It should be noted that Park *et al.* were able to apply solution shearing to a copper based MOF, HKUST-1 concurrently to the work we report herein.⁶⁴ While they were able to describe their findings using the term supersaturation, the concept for MOFs is not well defined. This is because both metal and linker species possess their own solubilities and multiple reactions pathways are possible in these systems. Even more, the crystallization kinetics and mechanisms are not well understood. Thus, understanding the kinetics and mechanisms of MOF crystallization is required to leverage the advantages of solution processing techniques such as solution shearing.

1.5 Crystallization and MOFs

Depending

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In order to ground the discussion, this section will begin with a background on fundemental crystallization concepts. Crystallization from solution is the process of solvated matter self-Nucleation assembling into a crystalline state. The driving force for self-assembly is Growth termed supersaturation, which is a Rate measure of the chemical potential difference between the non-Supersaturation equilibirum and equilibrium states. Figure 1.7. Schematic demonstrating how nucleation and growth rates scale



supersaturation and presence of crystalline material, crystallization will proceed in three stages: induction (pre-nucleation), nucleation, and growth. Induction is when the solution is in a supersaturation state, but nucleation does not occur due to a free energy barrier associated with solid phase formation. This energy barrier can be overcome by increasing supersaturation to drive nucleation, providing crystalline material for growth, or using a surface that lowers the energy barrier for nucleation (otherwise known as heterogeneous nucleation). Nucleation occurs when a critical degree of supersaturation is met, resulting in spontaneous particle formation.⁶⁵ Growth can occur at low degrees of supersaturation as long as crystalline material is present. In solution based systems, nucleation rate scales much more strongly with supersaturation than does growth as shown in **Figure 1.7**. These concepts can be applied to multiple component systems such as MOFs, albeit cautiously, suggesting MOF crystallization can be controlled by controlling supersaturation when it is well defined.

Supersaturation can be controlled by evaporation of solvent to concentrate solute, cooling to change the solubility of solute, or via reactive-crystallization, where the crystallizing species is a product of a chemical reaction. Few studies actually classify MOF crystallization into these categories, where Ameloot *et al.* experimentally used evaporative crystallization to form HKUST-1⁶⁶, Singh *et al.* modeled the formation of the same MOF as a reactive-crystallization.⁶⁷ While these two findings do not necessarily refute eachother, determining how and if MOF crystallization relates to classical theories is an important consideration for understanding these systems.



Figure 1.8. Schematic showing two most popular hypothesized crystallization mechanisms for MOF formation. Used with permission from [69].

to understand zeolite formation have been applied to MOFs. In this case two dominant pathways have emerged. The first is the production of a monomeric species that features metal node and linkers and is referred to as a "building unit".⁶⁸ The forces determining said building unit have been hypothesized to range from stoichiometric representations of the bulk structure to point zero charge moelcules (pzc) building units that ultimately interact to make more

building units or self assemble into the final structure. ^{69,70} For these scenarious, it is possible that supersaturation relates to the concentration of the building unit, however direct experimental proof has yet to be published.

Other more non-classical pathways suggest a mechanism that more resembles observations from zeolites, where an amorphous coordination network forms as a gel, and ultimately forms a crystalline material.^{69,71} While a perfectly viable pathway, it should be noted gel phases are far less reported for MOF synthesis, and this pathway is often reported due to lack of precise experimental evidence rather than direct experimental evidence.^{72,73} Other non-zeolite models based on precipitation of ionic species from solution at first appear applicable to MOF systems due to their ionic constituents. However, applying these models has proved difficult due to high degree of

To understand the crystallization mechanism for a two component system, many ideas used

connectivity and more complex structures, where charge balancing occurs at multiple sites on each ionic species (i.e. polymer-like coordination networks).

Regardless of crystallization mechanism, MOFs kinetics have shown to follow classical physical models used to extract quantitative phase transformation information. One such is the often mis-used Avrami equation or Johnson-Mehl-Avrami-Kolmogorov (JMAK) equation, which was originally developed to model phase transformations in the solid state but is often applied to solution based systems.^{69,72,74} While originally used to emperically fit a formation rate constant and growth dimensionality constant, the applicability and interpretation of the latter is still debated in MOF literature.⁶⁹ Another model derived for zeolite growth, termed the Gualtieri model, is frequently used to gather quantitative kinetic insight into MOF growth and fits the kinetics of various MOFs quite well.^{69,72,75} Though limited in its own regard, this model was originally developed for crystallization from solution and is widely accepted by the field to model crystallization of MOFs from solution. ^{69,72,75} While we save the detailed discussion of these models for the chapters involving their use, it is important to note that MOF crystallization kinetics can be fit with physical models to extract quantitative kinetic values for deeper insight into their formation mechanisms.

1.6 Summary of Dissertation

Given the background presented above, this dissertation will focus on understanding and controlling MOF crystallization for thin film applications. Solution shearing is a promising, scalable technique for controlling MOF crystallization because it offers precise and tunable parameters to control crystallization kinetics during thin film fabrication processes. We hypothesize combining MOF crystallization and a thin film deposition process such as solution shearing will yield higher quality films at faster time scales than conventional methods presented above. Testing this hypothesis requires understanding and controlling MOF crystallization such that it can be solution processed. We first present several methods to combine MOF crystallization with solution shearing that demonstrates improved film characteristics at rapid deposition time scales. Then, this work is extended into more fundamental studies of MOF crystallization such that it can be coupled to solution shearing. The following is a brief synopsis of the work presented herein.

1.6.1 Pre-synthesizing MOFs for thin film fabrication

Chapter 2 will focus on growing and controlling MOF morphology before using thin film deposition techniques. Two studies within this chapter will highlight the ability to control final film properties by tailoring MOF synthesis prior to the thin film deposition process. By decoupling these processes, better control over the MOF particle and crystalline properties is available and the ability to apply them to various substrates as well as control their orientation and packing properties is discussed.

1.6.2 Synthesizing thin tilms of HKUST-1 during solution shearing

Chapter 3 explores the coupling of HKUST-1 crystallization from solution to solution shearing. Here we explore the ability to control crystal properties such as orientation, morphology, and film thickness. We further explore the extremely large parameter space with the assistance of machine learning. A machine learning model is developed by collaborators to create a virtual experimental space, where we explore the relationship between film properties (namely thickness

and coverage), with the processing parameters such as concentration, substrate temperature and coating speed.

1.6.3 Understanding the reactive-crystallization of MOFs and UiO-66

Motivated by the successes of Chapter 3, Chapter 4 and 5 take a deeper look at crystallization kinetics and mechanisms of MOF formation in order to better control them for thin film deposition processes. Chapter 4 focuses on understanding MOFs from a reactive-crystallization viewpoint to accelerate the formation kinetics. We demonstrate that understanding the reactant speciation is important for successfully synthesizing MOFs on seconds to minutes time scale. Chapter 5 takes a deeper look into the reaction crystallization kinetics of a zirconium-based MOF, UiO-66 to understand how the nucleation and growth may be biased during synthesis. Combined, these chapters try to detail the crystallization mechanisms such that UiO-66 crystallization can be controlled as precisely as HKUST-1 as presented in Chapter 3. It is important to note the understanding developed from these works is directly related to the rapid fabrication of UiO-66 thin films.

1.6.4 Select Applications of Thin Film MOFs

In Chapter 6 we present two potential applications using MOFs thin films fabricated from the previous chapters. This chapter highlights how rapidly fabricated thin films achieve the same efficacy at a given application compared to current state of the art fabrication techniques. Improvement to the fabrication techniques is discussed for future work.

1.6.5 Outlook & Future work

Finally, an outlook detailing preliminary data on *in situ* thin film formation studies is presented. We lay a roadmap for analyzing these rich data sets to understanding the thin film formation process from 2D wide angle x-ray scattering data. Further, we discuss the potential for

more in situ MOF study techniques such as small-angle scattering (SAXS) and x-ray absorption

spectroscopy (XAS) to gain a deeper insight into the bulk formation mechanisms of UiO-66.

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2 Thin Films with pre-synthesized MOFs

2.1 Abstract

The ability to control MOF thin film characteristics, such as grain size, thickness, coverage and crystal domain alignment is critical for the success and optimization of MOF based devices, coatings and membranes. This chapter will focus on developing films for two applications that require different film properties. In both instances, we focus on controlling MOF thin film properties by decoupling the MOF synthesis and thin film deposition process to control thin film properties based on the final application. The first method involves creating oriented thin films of an anisotropic zinc-based MOF, [Zn₂(NDC)₂(DABCO)]_n, where we show controlling the morphology of particles during synthesis has a significant effect on the orientation of resulting thin films as measured by x-ray diffractions (XRS). This result is particularly interesting due to the anisotropy of the crystal structure, as different pore apertures are oriented normal to the thin film. The second study focuses on using MOF thin films as catalysts supports. We found depositing a spray coated layer of UiO-66 particles on an electrode enhanced the water splitting efficiency. Further characterization using electron microscopy (SEM,TEM) and energy dispersive spectroscopy (EDS) was used to characterize the heterogeneous material to reveal UiO-66 acts as a porous templating agents. We posit the porosity and templating significantly enhance transport to the catalyst surface as well as maintain a high specific surface area of the self-healing catalyst.
2.2 Part I: Synthesizing and Orienting Anisotropic [Zn2(NDC)2(DABCO)]_n Thin Films Introduction

The efficient separation of CO₂ from CH₄ during natural and biogas refining and from emissions is critical for the technoeconomic success of these alternative energies and to reduce greenhouse gas emission, however current industrial separation techniques are energy intensive or require high capital and operational expenses.^{1,2} Metal organic frameworks (MOFs) are novel material that could potentially serve as a robust and inexpensive solution to this critical separation process. They consist of metal ion clusters bound together by coordinating organic linkers to form a porous, periodic structure. Their key features include high surface areas (>1000 m2/g), chemical customizability, and relatively easy and low temperature synthesis, which enable their application in a wide range of areas including catalysis, fuel cell development, drug delivery, data storage, and gas separations.^{3–8}

MOFs have shown promise as selective gas separators due to their ability to sterically and chemically restrict the species that pass through their pores. In previous works, MOFs have been combined with a polymer matrix to demonstrate a high selectivity in a CO_2/CH_4 gas mixture. It was hypothesized that the selective permeation was due to the well-defined sorption properties of the microporous, crystalline MOF.² Additionally, it has been shown that the unmodulated $[Cu_2(NDC)_2(DABCO)]_n$ MOF can separate gases in a CO_2/CH_4 system where CO_2 and CH_4 have differing kinetic diameters of 3.3 Å and 3.8 Å, respectively.^{9,10} This system is interesting for gas sorption kinetics due to its different lattice dimensions leading to anisotropic pore sizes (a = b = 10.819 Å, c = 9.635 Å).

Recent studies have shown that these gas adsorption capabilities can be further enhanced through the introduction of modulators during MOF synthesis, by altering the overall crystal growth process.¹¹ In anisotropic MOFs, such as those in the M₂(dicarboxylate)₂(N-ligand) series, the modulator-based growth control is dramatic and can significantly alter crystal aspect ratios.^{12–} ¹⁴ The introduction of modulators during synthesis can target either the carboxylate (h00, 0k0) or the amino (001) planes, inhibiting crystal growth along these planes and directing MOF crystal growth along unmodulated axes (**Figure 2.1**).^{12–14} Previous work has demonstrated the $[Cu_2(NDC)_2(DABCO)]_n$ (NDC = 1,4-naphthalene dicarboxylate; DABCO = 1,4diazabicyclo[2.2.2]-octane) member of the $[M_2(dicarboxylate)_2(N-ligand)]_n$ MOF series can be modulated to obtain rod or plate morphologies with the use of acetic acid (carboxylate) or pyridine (amino) modulators.¹⁵



Figure 2.1 Schematic of the modulation process for the [Zn2(NDC)2(DABCO)]n MOF. Acetic acid (red pyramids) competitively coordinates with 1,4-naphthalene dicarboxylate (red rods) to direct growth in the [001] direction, while pyridine (blue pyramids) competitively coordinates with DABCO (blue spheres) to direct growth in the [100] and [010] direction.

While many examples of the effect of modulators on individual MOF crystal growth have been studied, controlling the overall orientation of these crystals for membrane applications is also important. Previous work has shown that MOF crystals can be oriented on mixed matrix membrane post-synthesis, which then show an increased performance in separation applications.¹⁶ Ghorbanpour *et al.* have also shown that MOF crystals can be oriented post-synthesis through a solution shearing technique to form highly ordered thin films.¹⁷ These are highly desirable qualities for gas separation membranes, as oriented thin films, along with controlled crystal aspect ratios, allow for a higher flux than packed beds while retaining performance.¹⁸

In the first part of this work, we synthesized and characterized the $[Zn_2(NDC)_2(DABCO)]_n$ MOF and controlled its morphology using pyridine and acetic acid as modulators to form plates and rods, respectively. We then demonstrated the change in steric separation selectivity using these two crystal morphologies in a single component adsorption system for both CO₂ and CH₄ in Chapter 6. Finally, using solution shearing and drop casting, we show differing thin film orientation of the modulated crystals for future applications as thin film separation membranes.

2.3 Part I: Materials and Methods

Materials

The following chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA): dimethyl formamide (DMF, \geq 99.8%), acetone (\geq 99.9%), Zn(CH₃COO)₂·2H₂O (\geq 99.0%), and DABCO (\geq 99%). 1,4-napthalenedicarboxylic acid (98+%) was purchased from Alfa Chemistry (Ronkonkoma, NY, USA), while pyridine (ACS grade), acetic acid (ACS grade), toluene (99.9%), and isopropyl alcohol (laboratory grade) were purchased from Fisher Chemical (Hampton, NH, USA). Methanol (\geq 99.9%). Ethanol was purchased from Koptec (190 proof). Chemicals were used as received without further purification. Quartz tubes were purchased from Quartz Scientific, Inc (Fairport Harbor, OH, USA). CO₂ (99.99%), CH₄ (99.97%), and N₂ (99.999%) gases were purchased from Praxair Inc (Danbury, CT, USA).

Synthesis of [Zn₂(NDC)₂(DABCO)]_n MOFs

In a typical unmodulated MOF synthesis, a solution with 0.050 g of DABCO, 0.196 g of 1,4-NDC and 13.20 g of DMF was added to a solution of 0.277 g of Zn(CH₃COO)₂·2H2O and 19.82 g of DMF for a final molar ratio of Zn/DABCO/1,4-NDC/DMF of 2.8:2:1:400. The total mixture was stirred for 25 min, after which it was poured into a 50 mL Teflon lined acid digestion vessel (Parr Instruments, Moline, IL, USA) and heated at 100 °C for 24 h.

The same process was applied to synthesizing $[Zn_2(NDC)_2(DABCO)]_n$ rod and plate morphologies with the addition of a modulator. To synthesize rods, a solution with 0.045 g of DABCO, 0.171 g of 1,4-NDC and 11.80 g of DMF was added to a solution of 0.247 g of $Zn(CH_3COO)_2 \cdot 2H2O$, 3.37 g of acetic acid, and 17.70 g of DMF for a final molar ratio of Zn/DABCO/1,4-NDC/acetic acid/DMF of 2.8:1:2:125:400. To synthesize plates, a solution consisting of, 0.022 g of DABCO, 4.36 g of pyridine, and 0.086 g of 1,4-NDC, and 11.56 g of DMF was added to a solution of 0.120 g of Zn(CH₃COO)₂·2H2O and 17.34 g of DMF for a final molar ratio of Zn/DABCO/1,4-NDC/pyridine/DMF of 2.8:1:2:250:800.

After cooling for 1 h, the precipitate was centrifuged and washed once with fresh DMF and twice with EtOH. The resulting product was then heated to 80 °C under ~3 kPa vacuum overnight and stored as a powder under vacuum.

Characterization of [*Zn*₂(*NDC*)₂(*DABCO*)]_n *Films*

All X-ray diffraction (XRD) patterns were recorded on a PANalytical Empyrean X-ray diffractometer (Malvern Panalytical, Egham, UK) with a Cu K- α beam ($\lambda = 1.54$ Å). Scans were completed from 20 of 7° to 70° with a step size of 0.0035°. For Brunauer, Emmet, Teller isotherm (BET) analysis, MOF samples of 15–25 mg were degassed at 70 °C until a pressure of 1.3×10^{-3} kPa was obtained, after which the samples were heated at 80 °C for 8 h. BET surface areas were measured using nitrogen adsorption isotherms collected on a Micromeritics ASAP 2020 instrument (Micromeritics, Norcross, GA, USA) at a relative pressure range of 0.01–0.05 relative to the nitrogen saturation pressure at 77 K. SEM micrographs were collected with a FEI Quanta 650 at 3 kV with a spot size of 4 at various magnifications.

Solution Shearing of [Zn₂(NDC)₂(DABCO)]_n Particles

A solution shearing procedure previously outlined by Ghorbanpour et al. was used to make thin films from particle suspension.¹⁷ Solution shearing was conducted on 1 cm \times 1 cm silicon wafers washed thoroughly with toluene, acetone, and isopropyl alcohol prior to the deposition of 20 µL of 5 wt./wt. % MOF/EtOH solution on the silicon wafer substrate. The substrate was heated to 60 °C, and the shearing blade was translated at speeds of 0.1, 0.25, and 0.5 mm/s for each morphology. Drop-cast samples were created by depositing 20 µL of 5 wt. % MOF/EtOH solution on silicon wafers substrates heated to temperatures of 60 °C. The orientation of the solution sheared MOF thin film was quantified by dividing the intensity of the (110) peak by the (001) peak intensity in the XRD.

2.4 Part I: Results and Discussion

2.4.1 Characterization of Modulated [Zn₂(NDC)₂(DABCO)]_n

By extending the rationale developed by Pham *et al.*, rod and plate morphologies of the $[Zn_2(NDC)_2(DABCO)]_n$ MOF can be created with the use of acetic acid (carboxylate) or pyridine (amine) modulators, respectively.¹⁵ Figure 2.2 shows scanning electron microscope (SEM) images of particles synthesized with no modulator, 1.6 M acetic acid as modulator, and 1.6 M pyridine as modulator. Compared to the unmodulated synthesis, the modulated syntheses show larger crystals. The acetic acid modulator shows the formation of rod-like crystals, and the pyridine modulator shows the formation of plate-like crystals. This confirms that modulating for different coordination modes in a MOF composed of two distinct linkers can yield drastically different morphologies.



Figure 2.2 SEM image of [Zn2(NDC)2(DABCO)] (a) unmodulated resulting in bulk morphology (b) 1.6 M acetic acid as a modulator resulting in rod morphology and (c) 1.6 M pyridine as a modulator resulting in plate morphology. Scale bars are 5 μ m. It should be noted that at similar modulator concentrations, the $[Zn_2(NDC)_2(DABCO)]_n$ MOF was

found to produce single crystals which are a magnitude greater in size than the previously reported $[Cu_2(NDC)_2(DABCO)]_n$ MOF.¹⁵ Aspect ratios of these crystals are described in **Table 2.1** showing both modulators increase the aspect ratio of their respective morphologies.

Morphology	Minor Axis (µm)	Major Axis (µm)	Aspect Ratio	Major Surface Plane(s)
Bulk	0.3 ± 0.1	0.6 ± 0.3	2.1 ± 1.1	N/A
Rod	1.2 ± 0.5	10.5 ± 5.4	10.1 ± 5.3	(100), (010)
Plate	0.4 ± 0.1	2.7 ± 0.4	6.9 ± 2.5	(001)

The unmodulated MOF shows slight preferential growth to a rod-like morphology. While

Table 2.1 Minor axis, major axis, and aspect ratio measurements for different morphologies of [Zn2(NDC)2(DABCO)]n.

the major axis for the rod morphology is in the [001] direction, the major axes for the plate morphology are in the [100] and [010] directions (**Figure 2.1**). It should be noted the major planes on each particle (i.e., the surfaces parallel to the major axis or axes) are associated with the carboxylate-carboxylate or carboxylate-amine pore aperture as a result of the anisotropic crystal structure.

Figure 2.3 shows powder x-ray diffraction (PXRD) data collected for $[Zn_2(NDC)_2(DABCO)]_n$ MOF synthesis with and without the presence of the amine and carboxylate modulators compared to a simulated diffraction pattern. These patterns show that the modulators do not alter the crystal structure. It should be noted that texture in the bulk powder sample is observed. Differing relative intensities in the peaks, specifically in those matching the

(001) and (110) planes, are recorded for different morphologies. Since particle orientation affects the relative intensity of diffraction peaks, these patterns indicate а preferential crystal orientation for a bulk powder. This is likely due particle to



Figure 2.3 Powder XRD Data for synthesized [Zn2(NDC)2(DABCO)]n MOFs. Simulated XRD patterns were obtained from Furukawa et al. [24].

morphology influencing packing, orienting particles along their major axes and with respect to the substrate.¹⁹ This effect is highlighted in **Figure 2.2c**, where plates are observed to orient in stacks.

2.4.2 Orientation of [Zn₂(NDC)₂(DABCO)]_n Particle Films

Previous studies by our group have shown that well faceted MOF morphologies can be utilized in combination with flow coating techniques to control the crystal orientation of MOF thin films.¹⁷ Orienting MOFs to obtain selected pore apertures on substrates is desirable for high performance separations membranes.^{20,21} Solution shearing is a meniscus guided flow coating technique where a particle suspension or solution can be deposited on a substrate using a blade.^{17,22,23}As the blade is translated across the substrate at a prescribed speed, an evaporation front develops such that the crystalline material is deposited as a film in a controlled manner (**Figure 2.4**). The evaporation rate and fluid dynamics during deposition can be controlled by tuning the substrate temperature, blade speed, wetting properties of the substrate, or the solvent used for the suspension. Given our previous results with aligning faceted MOF particles and the well-faceted, high aspect ratio of the MOF used in this study, we identified the [Zn₂(NDC)₂(DABCO)]_n morphologies as good candidates for creating oriented thin films.



Figure 2.4. A conceptual diagram of the solution shearing process with a particle suspension, used to orient faceted particles on a substrate. Used with permission from [17].

The different $[Zn_2(NDC)_2(DABCO)]_n$ morphologies were drop cast and solution sheared with varied blade speeds, and the orientation of the solution sheared MOF thin films were measured by evaluating the orientation number, defined as the ratio of the intensities of the (110) and (001) peaks for each sample (**Figure A2.1**). As previously mentioned, the relative intensity of peaks can be used to determine the degree of orientation of a crystalline sample. It should be noted this method is not a precise measure of the orientation as peak intensity is a function of many factors in a polydisperse crystalline systems,²⁴ however it can show the deviation of crystal texture from an isotropically distributed powder. **Table 2.2** shows the orientation number for each morphology with varying film deposition techniques. The further an orientation number is from the ratio of intensities scattered by the (110) and the (001) planes for an isotropic powder (orientation number = 2.98), the more oriented the film. For lower orientation numbers, the (001) peak intensity increases and therefore the (001) crystal plane is preferentially oriented with respect to the substrate. For higher orientation numbers, the (110) peak increases, indicating that the (100) and (010) planes are preferentially oriented with respect to the substrate.

Table 2.2 Orientation number for different morphologies for different film deposition techniques, where orientation number is the ratio of (110)/(001) peak intensities for each XRD. An orientation number of 2.98 represents a uniformly isotropic powder. PXRD patterns of sheared samples can be found in the appendix.

Morphology	Isotropic Powder	Powder	Dropcast	Solution Sheared at 0.25 mm/s
Bulk	2.98	4.11	4.05	4.67
Rod	2.98	7.75	40.63	43.50
Plate	2.98	2.19	1.11	1.23

As previously mentioned, powder XRD scans show slight preferential orientation likely due to morphology influencing packing. Drop cast films have a measurable degree of orientation compared to an isotropic film. The rod and bulk morphologies show preferential orientation for the (100) and (010) to be parallel to the substrate, respectively, and is enhanced by solution shearing and drop casting the particle suspensions. The observed orientation is expected for the rod morphology, as the major surfaces are defined by the (100) and (010) plane and are expected to lay flat with the substrate due to shear alignment forces during convective deposition processes.²⁵ Furthermore, this result agrees with other convective deposition techniques used to orient rod-like particles.²⁵ It should be noted the (001) peak was not observed on the diffraction patterns for solution sheared rods. To quantify the orientation, we took the standard deviation of the signal noise as the maximum possible peak value for the (001) (**Table 2.2**). As previously mentioned, the bulk material gave a lower aspect ratio, rod-like morphology, which is likely why preferential orientation similar to the higher aspect ratio rods is observed.

The plate morphology shows a modest orientation number with preferential orientation of the (001) plane parallel to the substrate. This corresponds to the major surface of the plate morphology laying on the substrate. The lower degree of orientation for the plates may be explained by the stacking observed in SEM images taken of the plate morphology. In this case, shear alignment forces that orient particles during deposition would be reduced for a lower aspect ratio cluster or a mixture of clusters and plates.²⁵

It should be noted this result differs from our previous study in that solution shearing enhanced particle orientation compared to drop cast samples. This difference is likely due to the large particle size and high aspect ratios of $[Zn_2(NDC)_2(DABCO)]_n$ (3–10 µm and 7–10, respectively) compared to UiO-66 in our previous study (<1 µm and 1, respectively).¹⁷ In this case the larger size is not as greatly affected by the flow coating region during shearing or shear alignment forces exerted on large, high aspect ratio particles are comparable for the solution shearing and drop casting processes. However, more work is required to elucidate the importance of particle morphology and fluid forces on orientation.

2.5 Part I: Conclusion

This study highlighted the ability to use existing capabilities of MOF synthesis, mainly controlling particle size and shape, to influence the final film properties. In this case the morphology of the anisotropic MOF had a significant influence on how the crystal structure oriented to the substrate. Given the anisotropic pore apertures in this MOF, the orientation result extends to a specific pore aperture orienting with the surface. The ability to control pore aperture size and orientation is critical for the successful implementation of MOF coatings and membranes, as these are the features that enable the selective nature of the material. In Chapter 6 we will highlight pore aperture size effects on the transport of different gas species within the MOF used in this study. Further commentary on the utility of the films developed in this study will presented at the chapter conclusion.



Figure A2.1 PXRD patterns for solution sheared MOFs. XRDs were taken with the same XRD geometry reported in the main text, with no revolution during the scans. Additionally, these XRDs were taken parallel to the shearing direction of the material text.

2.7 Part I: References

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2.8 Part II: UiO-66 Thin Films as Porous Templating Agents for Electrocatalysis Introduction

Metal-organic frameworks (MOFs) have been used in numerous fields to enhance the surface area of heterogeneous materials.¹⁻⁶ They are highly porous, crystalline materials with readily controlled pore geometry and tunable chemical properties.⁷ These frameworks are composed of metal ions or oxo-metallic secondary building units (SBUs) coordinated with organic linkers to form a porous, open framework. MOFs have been increasingly applied in the field of heterogeneous catalysis as catalyst supports and sacrificial templating agents to create hierarchical structures that enhance transport of reactants and products to active sites.^{8–12} Typical approaches for creating MOF supports involve immobilizing nanoparticles or catalysts within the MOF framework.¹³⁻¹⁶ Dolbecq et al. immobilized a sandwich-type polyoxometalate (POM) in a porphyrinic MOF, MOF-545, to show a high photocatalytic activity and stability for water oxidation.¹⁴ Other approaches have used MOFs as sacrificial templates to create hierarchical catalyst structures. Hu et al. created a mesoporous nanostructure Co₃O₄-MOF hybrid with a porous structure consisting of cobalt oxide nanoparticles embedded in a porous matrix.¹⁷ The porous framework and versatile chemistry of MOFs has proven to be advantageous in enhancing the activity of heterogeneous catalysts in a variety of systems.

In this study, we aim to create a MOF-based microporous templating film to control the morphology of electrodeposited cobalt oxide films for the oxygen evolution reaction (OER) (**Figure 2.5**). We chose UiO-66 as our templating MOF due to its high thermal, chemical, and mechanical stability.^{18–21} UiO-66 is composed of $Zr_6O_4(OH)_4$ secondary building units (SBUs) in an octahedral geometry connected via benzene 1,4-dicarboxylate (bdc) linkers. This topology creates triangular pores around 6 Å in size with two pore cages exhibiting diameters of ~11 and

 \sim 8 Å.(42) We determine the UiO-66 acts as a templating agent on which Cobalt Oxide grows around the porous hierarchical structure formed by the MOF film. By controlling the deposition of the UiO-66 template and deposition of cobalt oxide films, we find a 2-fold enhancement in current density for select cases.



Figure 2.5 (A) Schematic showing spray coating of a solution of UiO-66 particles onto a FTO electrode. (B) Closed packed films of UiO-66 particles on the electrode. (C) CPE deposition of Co3O4 onto the UiO-66 films. (D) Conceptual diagram of Co3O4 electrocatalyst deposition onto the UiO-66/FTO layer. The catalyst grown on and around the MOF template increases the active site area present for catalysis.

2.9 Part II: Materials and Methods

Materials

The following chemicals were purchased from Sigma-Aldrich: dimethylformamide (DMF, \geq 99.8%), methanol (\geq 99.9%), zirconium(IV) chloride (ZrCl₄, \geq 99.9%), benzene-1,4- dicarboxylic acid (H₂bdc, 98%). Ethanol was purchased from Koptec (190 proof). Chemicals were used as received without further purification.

Synthesis of UiO-66 Crystals

UiO-66 was synthesized using the technique outlined by Cavka et al.(42) In a typical synthesis, 24.9 g of DMF was added 0.23 mmol of ZrCl4 in a beaker and sonicated for 2 min before adding 0.23 mmol of H2bdc. The mixture was stirred until fully dissolved. The solution

was placed in a Teflon-lined acid digestion vessel (Parr Instruments) and heated at 120 °C for 24 h. The vessel was cooled in air and the contents were centrifuged to isolate the solid product. The solid was centrifuged and washed once in DMF and twice in methanol before redispersion in methanol overnight to complete solvent exchange. A final centrifugation and resuspension in 12.6 g of methanol yielded a \sim 1 wt % solution of UiO-66 in methanol.

Spray Coating UiO-66 Films

FTO slides were cut to 1 cm \times 2 cm pieces, rinsed with ethanol, and dried with a stream of air. Slides were masked to expose a 1 cm \times 1 cm section and heated to 70 °C. An airbrush (Paasche H-CARD Single Action) was used to coat slides, where a \sim 1 s spray was equivalent to "1 pass". Between 1 to 20 passes of the spray coater was used to control UiO-66 thickness and coverage.

Catalyst Incorporation in UiO-66 Films

CoOxo modified electrodes were prepared based on prior literature.(57) Short (<20 min) deposition times were utilized to ensure catalyst and UiO-66 film thicknesses were similar. In a representative experiment, an FTO electrode was prepared (with and without UiO-66 present) by attaching a nichrome wire with Parafilm and electrical tape. The counter electrode was a glassy carbon rod in a gas diffusion tube separated by a glass frit and the reference electrode was an aqueous Ag/AgCl electrode (3 M KCl). Deposition was carried out in a phosphate buffer solution (pH = 7) with 1 mM cobalt(II) nitrate hexahydrate (Co(NO3)2·6H2O). CPE was carried out at ± 1.4 V (vs Ag/AgCl) for 10 min to deposit cobalt oxide onto the working electrode. Following deposition, electrodes were washed with deionized water and CV and CPE were conducted in a fresh phosphate buffer solution.

Characterization of UiO-66 Films

A Quanta 650 SEM (15 kV, spot size 4, Everhart-Thornley detector (ETD)) with EDS (Oxford Instruments, X-MaxN 80) was used to collect morphological and elemental analysis of cobalt oxide and UiO-66 films. Samples were prepared for SEM by coating with a protective layer (~20 nm thick) of gold–palladium using a precision etching and coating system. Selected films were submersed in DI water and sonicated using a Bransonic Ultrasonic Bath (40 kHz) to remove loose particles. All PXRD patterns were recorded on a PANalytical Empyrean X-ray diffractometer with a Cu K- α beam ($\lambda = 1.54$ Å). Scans were completed from 20 of 5° to 50°.

Cross sections of ~100 nm thickness were prepared from electrodes using a Helios Dual Beam FIB G4 UC. FIB milling and cleaning was performed with a Ga ion beam current ranging from 24 pA to 9.3 nA at 30 kV. To protect the surface, additional layers of protective material, consisting of carbon and platinum, were deposited. High resolution transmission electron micrographs (HRTEM), scanning transmission electron micrographs, and EDS (Ametek EDAX Titan 300ST) were taken of these 100 nm thick cross section samples using a FEI Titan (300 kV).

A Bruker Dektak XT Stylus Profiler was used to measure the film thicknesses. Using a blade, a line was cut along the center of the thin film to expose the substrate underneath. Using Vision64 software, an average height was calculated and compared against the bare substrate to determine the thin film thickness. Multiple thicknesses were determined along the line cut for each sample.

2.10 Part II: Results and Discussion

2.10.1 UiO-66 Films

Spray coating allows for uniform and controlled deposition of a UiO-66 suspension onto the fluorine doped tin-oxide (FTO) substrate. Film thickness and coverage was controlled by varying the number of times the substrate is sprayed with a 1 second burst of solution, termed "passes". **Figure 2.6** shows how the film morphology changes as a function of pass number. It was found that increasing the number of passes increased the surface coverage and average film thickness with a 20-pass spray-coated UiO-66 film resulting in complete coverage of the FTO electrode as seen by SEM (**Figure 2.6D**). Features resembling cracks were observed for UiO-66 films with complete coverage, likely due to capillary stresses developed in the film during the coating and drying processes.²² Cross sections of 20-pass samples as studied by SEM and profilimetry data typically yielded a UiO-66 layer thickness of several micrometers with high surface roughness and thickness variability between sample batches (**Table A2.1**).



Figure 2.6 Topographic SEM images comparing (A) blank FTO substrate, (B) an FTO substrate with 1 pass of spray-coated UiO-66, (C) an FTO substrate with 5 passes of spray-coated UiO-66, and (D) an FTO substrate with 20 passes of spray-coated UiO-66. Scale bar is 5 μ m.

2.10.2 Cobalt Oxide Electrodeposition

Cobalt Oxide electrodeposition and electrical characterization was performed by the Machan Group at the University of Virginia. This section briefly reviews effects of film properties on the deposition process. A more in-depth description of the hybrid material electrical properties can be found in the published work.²³ The effects of UiO-66 film coverage on the behavior of a co-deposited cobalt oxide catalyst were analyzed by cyclic voltammetry (CV). Surface coverage of the UiO-66 on FTO was found to be proportional to the thickness of the UiO-66 on the FTO (Figure 2.7 and Table A2.1). With increasing thickness of the UiO-66 film from 300 to 1500 nm, an internal comparison of changes in Co oxide behavior shows a consistent shift in potential from +0.52 to +0.72 V versus Ag/AgCl for the Co(IV)/(III) reduction. There is also a 2.7 times increase in catalytic current from 5.59×10^{-4} A/cm² for the cobalt oxide control to 1.51×10^{-3} A/cm² at +1.2 V versus Ag/AgCl (Figure 2.7). This suggests the number of active sites increases with greater coverage of UiO-66. Furthermore, the observation that the reduction peak potential of the Co(IV)/(III) feature in the return sweep from catalytic potentials moves to increasingly positive potentials with increased UiO-66 film thickness is suggestive of different Co oxide growth mechanisms (Figure 2.7). We propose that the thickness of the UiO-66 changes the distribution of available chemical environments for the electroactive Co sites. It was also observed that when the film thickness exceeded 1500 nm, a suppression of current which is attributed to the insulating effect of the UiO-66 film. 24-27



Figure 2.7 Topographic SEM images after 10 min deposition of cobalt oxide (1 mM) on FTO substrates spray coated with (A) 1 pass (290 nm average thickness) and (B) 5 pass (1200 nm average thickness). The scale bar is 5 μ m. (C) CV scan showing the effects of UiO-66 film thickness. Conditions: pH 7 phosphate buffer; glassy carbon rod counter electrode; Ag/AgCl reference electrode; referenced to Ag/AgCl; 100 mV/s scan rate.

2.10.3 Characterization of the Heterogeneous Material

For the catalyst characterization study, films with a 10 min deposition of cobalt oxide on FTO with a prepared 20-pass UiO-66 film were used unless otherwise noted. Films were probed using EDS during scanning electron microscopy (SEM) for areal sampling and transmission electron microscopy (TEM) for cross-sectional sampling. EDS mapping was used to show the relative elemental composition of the heterogeneous film (**Figure 2.8**). EDS maps for zirconium and cobalt suggests the spatial distribution of cobalt oxide is not significantly enhanced by the quantity of UiO-66 in a given region, as evidenced by the uniform distribution of cobalt coupled with a nonuniform distribution of zirconium (**Figure 2.8A**). Point measurements in cracked versus UiO-66 regions show the zirconium signature to cobalt signature ratio was lower in regions with cracks compared to those without (**Table 2.3**). The relative amount of cobalt, compared to the zirconium signature, was higher in the cracked regions.



Figure 2.8 (A) Topographic SEM image of the cobalt oxide/UiO-66/FTO substrate with 10-minute deposition of cobalt oxide (1 mM) on FTO substrates spray coated with 20 passes of UiO-66 with EDS elemental mapping of zirconium and cobalt and (B) Topographic SEM image with EDS elemental mapping for the same conditions and sonicated for 10 minutes to remove excess UiO-66. Scale bar is 5 μ m.

Table 2.3 Zirconium and cobalt signature ratios with varied deposition times of cobalt oxide on FTO substrates spray coated with 20 passes of UiO-66, FTO substrate with a 10-minute cobalt oxide deposition and a 10-minutes cobalt deposition that was sonicated for 10 minutes to remove loose UiO-66 particles.

	Zirconium (wt%)/Cobalt (wt%) Ratio		
Deposition Time (min)	UiO-66 Region	Cracked Region	
1	28.0 ± 5.8	20	
2	12.4 ± 4.0	4.5 ± 1.7	
5	9.9 ± 1.4	4.5 ± 1.2	
10	5.0 ± 0.7	1.5 ± 0.4	
10, sonicated UiO-66	0.16 ±	= 0.05	

To further study the cobalt distribution, the FTO electrode surface was characterized after sonication of the cobalt oxide/UiO-66 film in DI water. The sonication process mechanically removes both cobalt oxide and UiO-66 crystals that are weakly attached to the substrate. EDS point scans and mapping showed an increase in relative cobalt signature after sonication (**Figure 2.8B, Table 2.3**). The larger percentage of cobalt signature after sonication indicates that there is

more cobalt oxide present near the FTO substrate than UiO-66 film. Additionally, the presence of a zirconium signature on the substrate after sonication indicates the presence of UiO-66 on the FTO substrate even after sonication, interspersed with the cobalt oxide layer. With this data, we hypothesize that the deposition of cobalt oxide starts near the electrode and grows into packing defects around the crystallites of the UiO-66 film. The UiO-66 particles act to guide cobalt oxide growth, directing it to form a layer with a higher surface area compared to that formed on a control FTO substrate without UiO-66 (**Figure 2.5D**).

To confirm the preferential localization of cobalt oxide on the surface of the FTO substrate, a cross-section sample was characterized by TEM (Figure 2.9A). The TEM image cross-section was obtained with a focused ion beam (FIB) cutting procedure. A control TEM image of only cobalt oxide on an FTO substrate (Figure A2.2) revealed a ~50 nm cobalt oxide layer is deposited on the FTO surface. Similarly, a ~50 nm layer can be seen in the TEM image taken of the cobalt oxide/UiO-66 film. EDS line scans indicate a strong cobalt signature centered around this layer for the cobalt oxide/UiO-66 film, confirming cobalt oxide is deposited on the FTO electrode regardless of the presence of UiO-66. It should be noted that these length scales reach the limit of the EDS spatial resolution due to beam scattering and nearest atomic neighbor interactions, leading to the blending of cobalt, tin, and zirconium signatures.²⁸ The control sample in Figure A2.2A shows the same blending for the tin and cobalt signature without the presence of UiO-66. Figure A2.2B also shows a blending of the tin and zirconium signature for UiO-66 that is spray coated onto the FTO. However, the decay of both tin and cobalt signatures as the zirconium signature increases indicated cobalt oxide is not uniformly distributed through the height of the UiO-66 film and is instead preferentially located near the FTO substrate.



Figure 2.9 (A) HRTEM of a cross sectional cut through an oxide/UiO-66/FTO film of cobalt prepared in a Focused Ion Beam (FIB) system, HRTEM micrograph of cobalt oxide/UiO-66/FTO film. Scale bar is 200 nm. B) EDX line scan showing the relative composition of cobalt, zirconium, and tin representing cobalt oxide, UiO-66, and FTO, respectively.

2.11 Part II: Conclusion

We have demonstrated that UiO-66 can act as a template for the enhanced catalytic activity of cobalt oxide films through an increased surface area, using a facile UiO-66 spray coating and subsequent cobalt oxide electrodeposition method. Greater surface coverage and film thickness of UiO-66 on the working electrode was found to enhance the catalytic activity over control films of cobalt oxide; current enhancement is observed at +1.2 V versus Ag/AgCl for the MOF film with cobalt oxide deposited in comparison to cobalt oxide deposited on a blank FTO slide. This templating effect results in a larger active surface area of the electrodeposited cobalt oxide which has been shown to improve catalytic performance. While sacrificial templating agents must be removed for this surface area to be accessible to reactants.⁵⁶ By employing a highly stable, microporous MOF template, this work is able to constrain the active morphology of cobalt oxide to maintain high surface area while allowing transport of products and reactants through micropores in the template to the active surface of the cobalt catalyst. The presence of the MOF is also advantageous as the catalytic reforming of the cobalt oxide will be slowed due to spatial

restrictions. This study suggests MOF structures can successfully be integrated with electrodeposited catalyst films as heterofunctional materials. Future work will focus on leveraging the size- and chemoselectivity of different MOF structures and depositing cobalt oxide within the framework to enhance the molecular transport properties and catalytic activities.

2.12 Part II: Appendix

Table A2.1 Profilometry data showing average film thickness, standard deviation between sampled regions, and average surface roughness of 1, 5, 10, 15, and 20 passes of UiO-66 on FTO with 10 minutes of cobalt deposition and 5, 10, and 20 passes of just UiO-66 on FTO.

UiO-66 Pass Number	Co. Deposition Time (min)	Avg. Thickness (nm)	Std. Dev of Thickness (nm)	Avg. Roughness (nm)
1	10	290	150	140
2	10	650	60	180
5	10	1200	430	340
10	10	1520	180	540
15	10	4100	740	1460
20	10	2720	510	670
5	0	700	420	340
10	0	1100	1050	410
20	0	3190	570	1770



Figure A2.2 (A) FIB cross sectioned, HRTEM micrograph of 10-minute cobalt oxide deposition on FTO substrate. Scale bar is 200 nm B) EDX line scan showing relative composition of Cobalt and Tin representing cobalt oxide and FTO, respectively. (C) FIB cross sectioned, HRTEM micrograph of 20 pass spray coated UiO-66/FTO substrate. Scale bar is 200 nm D) EDX line scan showing relative composition of Cobalt, Zirconium, and Tin representing cobalt oxide, UiO-66, and FTO, respectively.

2.13 Part II: References

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2.14 Chapter Conclusion

Fabricating MOF thin films with pre-formed MOFs offer rapid production time scales and offer good control of the microstructural properties but are limited in the control of film characteristics. As previously mentioned, these studies highlight the need to understand final application requirements to ensure the desired film properties can be achieved. Controlling one film characteristic often sacrificed the control of another. For example, our first study highlighted the ability to align [Zn₂(NDC)₂(DABCO)]_n with a substrate for separations applications where the selectivity of the MOF depended on which pore aperture was normal to the film surface. While we were able to achieve alignment of these particles by controlling the morphology and using a convective deposition technique termed solution shearing, the films did not offer good coverage as they contained bare substrate and pin holes and would not force mass transport to occur purely through the MOF pores, rendering the film ineffective as a separation membrane without more development. Future work using this technique will focus on secondary nucleation and growth on aligned particle films to form a complete membrane.

Conversely, pin holes and orientation are less critical for heterogeneous catalysis compared to separations and proved to be beneficial in the heterogeneous material. With this application, we have demonstrated that UiO-66 can act as a template for the enhanced catalytic activity of cobalt oxide films through an increased surface area, using a facile UiO-66 spray coating and subsequent cobalt oxide electrodeposition method. Greater surface coverage and film thickness of UiO-66 on the working electrode was found to enhance the catalytic activity over control films of cobalt oxide. In this case the pin holes and mesopores acted as templating spaces for the catalyst to grow. In conclusion, thin films fabricated from pre-synthesized MOFs offer a key advantage in decoupling crystal growth and deposition. While these select studies offer insight into their benefits, there are drawbacks, largely in creating fully covered, uniform, and connected films. Future work in this dissertation will focus on controlling the crystallization of MOFs at rapid time scales and coupling the synthesis and deposition techniques to address issues in coverage and interconnectivity while maintaining desired features such as orientation observed in this chapter.

3 Synthesis of HKUST-1 Thin Films

3.1 Abstract

The previous work in chapter 2 focused on controlling MOF crystallization prior to the thin film deposition process to control particle and crystal characteristics. Here, we couple thin film deposition techniques with MOF synthesis to deposit thin films of HKUST-1. In an initial study, we explore how deposition parameters such as starting solution concentration, coating speed, and substrate temperature influence particle morphology and thin film morphology using optical microscopy and profilometry. Particle size is used to infer relative nucleation and growth rates, where smaller particles are considered to have higher nucleation than growth. Results relating particle size to supersaturation rate indicate HKUST-1 crystallization likely does not follow classical crystallization principles. Further, we observe a trend where crystal size is correlated with thickness. This suggests HKUST-1 crystallization may occur on a different timescale than solution shearing as the concentration gradient typically observed in solution shearing appears to have no influence on morphology asymmetry. Finally, we show these films are oriented using grazing incidence wide angle x-ray scattering (GIWAXS).

The second part of this study explores an expanded parameter space using a machine learning model where an additional parameter is included to allow multiple coating steps, or passes, on each film. The model is trained to predict both full coverage and resulting film thickness to understand the solution shearing parameter space that can be utilized to create HKUST-1 thin films with full coverage, and to minimize film thickness while maintaining full coverage. We discuss the utility of a synergistic parameter space exploration with machine learning and how this can be applied to understand and optimize the formation of other film features such as grain size or crystallinity.

3.2 Introduction

Within the field of MOFs, thin films and coatings have emerged as highly sought-after configurations for applications ranging from separations, electronics-including transistors and sensors and functional coatings.¹⁻⁷ This is because in many applications thin film morphology works in tandem with the porous structure of MOFs. In many cases, mass and charge transport through films rely on both the thin film properties and the microstructural and chemical properties of MOFs. One example of this is in sensors, where the response time depends on mass transfer of an analyte across its thickness and grain boundaries and the sensitivity and selectivity are dictated by the MOF material enriching and selectively adsorbing the analyte.⁶ In addition to thickness and grain boundaries, other properties such as pin holes, crystal alignment and defect density can have a significant influence on charge and mass transport. These considerations are required for separations or selective sensing when the film must act as a separations barrier and at the same time minimize diffusion path length to enhance transport of analytes or filtrates.^{6,8–11} Such features require closed-packed and intergrown films while maintaining minimal film thickness.^{12–14} Thus, the ability to control multiple film morphology features is critical for optimal performance of MOF-based devices and membranes. Scaling these processes to large areas while maintaining crystallization control is also a critical consideration when selecting a processing technique.³

Several large area techniques have been developed for MOF coatings and thin films. Wang *et al.* showed ZIF-8 could be grown on multiple substrates using a roll to roll process.¹⁵ While beneficial for pollution filtration, this technique could not create full film coverage and intergrown particles. In another study, Zhuang *et al.* employed a spin coating process and antisolvent precipitation to crystallize continuous and intergrown HKUST-1 on millimeter sized substrates.¹⁶ This method resulted in high quality films but scaling spin coating to larger areas is difficult.

Finally, Park *et al.* concurrently reported the creation of HKUST-1 thin films to our work using a convective deposition technique, termed meniscus guided coating (MGC) or solution shearing.¹⁴ They were able to control the monodispersity of particle size and packing by tuning coating parameters and equipment features (i.e. microstructured coating blade). Further, they showed the film thickness followed the coating regimes described by Baigl *et al.* as outlined in Chapter 1, demonstrating some of the film properties are predictable based on previous thin film deposition theory.¹⁷ While their study is seminal for rapid, large area thin film crystallization of MOFs, they only presented an exploration of a minor subset of the parameter space available for convective deposition of HKUST-1, with limited understanding of the crystallization system.

Optimizing thin film processing parameters is often a time-consuming process that relies heavily on the skills and experience of researchers navigating a complex parameter space.¹⁸ In the case of solution shearing HKUST-1, we estimate tens to hundreds of millions of possible parameter combinations across substrate selection, solvent type, copper concentration, metal to linker ratio, substrate temperature, coating speed, and the number of coating steps, or passes. Depending on the desired final film properties, navigating this parameter space becomes prohibitively time and resource expensive. Recently, the use of materials informatics, especially machine learning, has been used to navigate large parameter spaces for new synthesis and materials discovery in MOFs and other materials, and has been deemed the "fourth paradigm" of materials science.^{10,18–22} While these reports largely focus on discovery of novel structures or material properties based on existing data, only a few have highlighted the benefits of using machine learning techniques to supplement high-throughput processing experiments through iterative training, with no such studies existing in the field of MOFs.^{18,23–27}

This chapter focuses on two methods of understanding and controlling thin films of HKUST-1. First, to better understand how crystallization kinetics and coating parameters are related, we expand on work by Park et al. to better understand the crystallization of HKUST-1 thin films by changing concentration, blade speed and substrate temperature. Several concentrations of the precursors that form HKUST-1 were formulated to test the effects on crystal domain size. Blade speed and substrate temperature were also varied to reveal changes in HKUST-1 nucleation and growth. Films were characterized with microscopy, profilometry and grazing incidence wide angle x-ray scattering (GIWAXS) to determine film morphology, thickness, and crystal orientation, respectively. The next part of our study focuses on a collaborative parameter space search with the Balachandran group at the University of Virginia to achieve a fully covered, large area films of HKUST-1 with minimized thickness. We present a high-resolution view of the multidimensional processing parameter space to better understand coating parameter influence on the probability of films obtaining full coverage (i.e., no detectable pin holes) by training a machine learning model to predict coverage conditions. Further, experimental thickness data is used to predict processing parameter regions where thickness will be minimized while maintaining full coverage. The techniques presented here can be extended to any selection of measurable film properties to efficiently navigate processing parameter space to achieve application-based optimized thin films with a fraction of experiments compared to conventional process optimizations.

3.3 Materials and Methods

Materials

Acetone (99.9 %), toluene (99.9 %), trichloro(octadecyl)silane (OTS, \geq 90 %), methanol (\geq 99.9 %), copper (II) nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O, 98 %), trimesic acid (H₃BTC, 95 %), dimethyl sulfoxide (DMSO, 99.99 %), anhydrous dichloromethane (\geq 99.8 %), and dichloromethane (\geq 99.8 %) were bought from Sigma Aldrich. Glass substrates (1 mm thick), ITO coated glass substrates (1.1 mm thick and 100 Ω /sq), and isopropyl alcohol were purchased from Fisher Scientific. Silicon wafers, which have a 285 nm thick silicon dioxide layer, were obtained from University Wafer.

Substrate Preparation

Silicon wafers and ITO-coated slides were cut into approximately 0.5 " x 0.5 ". Silicon was rinsed with touluene, acetone then isopropyl alcohol with no further treatment. The glass slides were sonicated in methanol for 15 minutes. The ITO-coated slides were measured their electrical resistance to confirm the ITO coating on the substrate and were rinsed by isopropyl alcohol. Both substrates were dried via dry airflow. The glass slides were cleaned via UV-ozone for at least 10 minutes. Glass slides and ITO-coated slides were used as substrates.

Solution Shearing Blade Fabrication

Silicon wafer was decided to use as the coating blade. Initially, the wafer was cut to use the flat zone of the wafer as a coating region. The wafer was cleaned with toluene, acetone, and isopropyl alcohol, respectively, and dried with dry airflow. Then, the wafer was stored in the UVozone cleaner for at least 10 minutes. The wafer was then immediately put into a crystallization dish that was filled with the solution that was composed of 0.1 wt. % OTS in toluene. The crystallization dish was capped with the glass lid, and the solution was kept stirring at 45 °C overnight. Afterward, the wafer was taken out from the crystallization dish and was sonicated in acetone for 5 minutes. 95 $^{\circ}$ - 100 $^{\circ}$ of the contact angle of the wafer was targeted to determine the correct treatment by using deionized water.

HKUST-1 thin film fabrication

The HKUST-1 precursor solution was synthesized based on the work of Ameloot et al.²⁸ Briefly, copper (II) Nitrate hemi(pentahydrate) was fully dissolved in dimethyl sulfoxide. Trimesic acid was supplemented to the solution and was continuously stirred until it dissolved completely. The copper concentration in the precursor solution was varied from 0.05 M to 1.20 M. The metal to linker ratio was also varied within the range between 1.20 and 3.00. After the precursor solution of HKUST-1 was synthesized based upon the set of processing conditions, solution shearing was used to fabricate HKUST-1 thin film. The solution shearing blade was rinsed with toluene, acetone, and isopropyl alcohol and dried with the dry airflow. The blade was fastened under a top vacuum stage. Either silicon or ITO-coated substrates were tightly held to a bottom vacuum stage. The substrate stage was heated to the desired temperature. The range of the temperature of the substrate stage was from 100 °C to 180 °C. The blade angle and its height were controlled relative to the horizontal substrate, respectively. $1.75 - 35 \,\mu\text{L}$ of the well-mixed HKUST-1 precursor solution with different blade coating speeds was added into the gap between the blade and the substrate depending upon the processing conditions. The coating blade speed was set from 0.05 mm \cdot s⁻¹ to 5 mm·s⁻¹. The solvent of the precursor solution was evaporated as the coating blade was moved along with the substrate. HKUST-1 crystallites were grown on the substrate as the crystallization occurs due to the supersaturation.
Multiple passes of solution shearing

Multiple cycles of solution shearing was performed using the same procedure as the HKUST-1 thin film fabrication. After the initial solution shearing was completed, the substrate was left on the substrate holder for 60 s so that the solvent of the precursor solution could be fully evaporated. The coating blade was moved back to its original position, and the same volume of the precursor solution from the previous solution shearing cycle was injected into the gap between the blade and the substrate. The blade was then moved along the substrate again depending upon the processing parameters.

Characterization:

Microscope Images

Film coverage of the HKUST-1 thin films with the different processing conditions was observed by using a Zeiss Microscope Axio Scope.A1. The thin film was placed on the stage where condensed light focused on the thin film. Images were taken with 5x, 20x, and 50x objective lenses with the bright field mode. The taken images were quantified by using an image processing program (Fiji).

SEM

Scanning Electron Microscopy (SEM) micrographs were collected using a Helios Dual Beam FIB G4 UC with an accelerating voltage of 5 kV and 0.80 nA current.

Profilometry

The film thickness was measured using two methods. For areal topography, films were analyzed with a Zygo NewView 7300 white light interferometer in multiple regions for statistical significance. For thickness measurements used in the machine learning study, a Bruker Dektak XT Profilometer with a measurement range of 65.5 μ m, scan length of 800 μ m, duration of 90 s, and stylus force of 10 mg.

Machine Learning Model

More details on the machine learning model can be found in Huelsenbeck, L., Jung, S., Herrara del Valle, R. Balachandran, P., Giri, G. Accelerated Parameter Search of Solution Sheared HKUST-1 Films using Machine Learning. *In Preparation*, **2021.**

3.4 Results and Discussion



3.4.1 Characterizing HKUST-1 Thin Films Using Solution Shearing

Figure 3.1. (a) Schematic showing solution shearing of HKUST-1 with coating parameters and resulting film coverage. (b) Drop cast and solution sheared thin film morphologies for concentration of 144 mM Cu, 76 mM BTC 160°C on SiOx, where the solution sheared sample used a coating speed of 0.1 mm/s.

Solution shearing based crystallization is an evaporation-driven process. Figure 3.1a shows that during solution shearing, the shearing blade moves at a defined speed, and the meniscus that develops evaporates the solvent due to the energy supplied by the heated substrate. The solute becomes concentrated as solvent evaporates, and the phase change to the MOF crystalline phase becomes energetically favorable, after which nucleation occurs and crystal growth follows. The rate of concentration change is hypothesized to be a complex interaction of crystallization kinetics, evaporation rate, and other convective phenomena redistributing solute (i.e. Marangoni effect, capillary forces etc.). While these processes can occur during any evaporative driven crystallization, Figure 3.1b demonstrates how depositing the same HKUST-1 precursor solution at 160°C with drop casting and solution shearing at 0.1 mm/s has a significant influence on morphology, where solution shearing provides large, intergrown crystalline domains compared to drop casting. We hypothesize this is due to the precise control of concentration during the solution deposition process compared to drop casting, which ultimately influences the nucleation and growth of crystals. X-ray diffraction and nitrogen adsorption confirmed the deposited mass was indeed HKUST-1 (Figures A3.1-A3.2).

Drop cast and sheared samples were compared to determine the effects on crystallization of HKUST-1. Figure 3.1b shows typical morphologies observed in drop cast and solution sheared samples under similar crystallization conditions. Both exhibit hexagonal cross sections with triangular centers, which is a similar morphology observed by De Vos et al. and Park et al.^{14,28} However, crystal packing appears to be more planar and uniform in sheared cases, whereas drop casting results in clustered domains. A remarkable feature in both cases is the topographical difference observed between the crystal domain center and edge. Further analysis of these crystals using white light interferometry shows that the domain center is lower than the edge (Figure 3.2), resulting in faceted indentations in each domain. To the best of our knowledge, this morphology has not been reported in literature.^{14,16,28} Park et al, who used a carboxylic acid terminated substrate show particles with similar shapes, but more uniform thickness. Even in the case of a similar concentrations and longer timescales used by Zhuang et al. during spin coating, flat-faced hexagonal prisms were observed as the final morphology, similar to other reported equilibrium morphologies.¹⁶ The non-equilibrium morphology suggests that the rapid kinetics (i.e. less than 5minute crystallization) and substrate functionalization have a significant effect on the final morphology. We hypothesize there may be a localized region in the particle center that becomes isolated due to evaporation then undergoes de-supersaturation leading to little growth, however

this must be confirmed by *in situ* optical imaging to confirm.

Profilometry data taken from larger crystal domains showed the slope of the inner facets from center to edge ranged from ~11-25° relative to the substrate. This variability indicated no correlation between the facet angle and any lower order crystal plane of

This

further

HKUST-1.



Figure 3.2 Topographical image of an of a solution sheared HKUST-1 crystal domain showing particle center is shallower than the particle edge.

suggests the morphology is dictated by the kinetics of the system, as the inner facets do not represent crystal planes typically observed in equilibrium morphologies of HKUST-1. One possible explanation is that the initial stage of crystal growth occurs such that the 111 plane is oriented with respect to the substrate, which has typically been observed in other thin film HKUST-1 growth as a triangular/hexagonal shape observed in the particle center. ^{14,16,28} In the later stages, growth is controlled by the fluid dynamics and rapid evaporation of solvent, which kinetically traps the particles in the observed "non-equilibrium" morphology. However, *in situ* observations are required to definitively relate kinetic growth conditions such as evaporation rate and fluid flow to the resultant crystalline morphology.

To examine film morphology and orientation further, grazing incidence wide angle x-ray scattering (GIWAXS) was used to determine crystal plane alignment. As seen in **Figure 3.3**, several distinguishable peaks appear on the diffraction pattern for sheared samples. These peaks are indicative of an oriented thin film (**Figure A3.3**). Orientation was observed in samples sheared at 0.1 mm/s, 0.05 mm/s and drop cast samples, with concentrations ranging from 144 mM Cu^{2+} :

76 mM BTC to 576 mM Cu^{2+} : 304 mM BTC. The ratio of the copper to BTC was not varied to limit parameter space size and to only observe total precursor concentration effects on crystallization rather than metal to linker ratio.

For the oriented samples, a peak indexing program, indexGIXS²⁹, was



Figure 3.3. Typical 2D GIWAXS diffraction pattern for solution sheared HKUST-1. White diamonds represent projected peaks for HKUST-1 with the (111) plane parallel to the shearing substrate.

used to determine which plane was oriented with respect to the silicon substrate. Projected peaks associated with a specified orientation appear as white diamonds. It was found that a thin film with the (111) plane of the HKUST-1 thin films oriented with respect to the substrate matched the diffraction pattern closely. Many synthesis methods, including solvothermal and epitaxial growth, have found that the (111) plane is the preferred interfacial surface under near-equilibrium conditions when HKUST-1 is grown on a substrate.^{16,28,30-32} This is because this crystal plane has

the lowest free surface energy compared to other crystal planes, and is therefore favored as the surface interacting with the substrate.³²



Figure 3.4. Adjusted film thickness vs. coating speed for 144 mM Cu, 76 mM BTC 160°C on SiOx showing the development of two coating regimes and the resulting film micrographs at select speeds.

Figure 3.4 shows the two coating regimes exist when coating occurs at 160 °C, where adjusted thickness is the average film thickness multiplied by percent coverage of each sample and relative speed is given as a ratio between speed and theoretical transition speed (or the speed at which the evaporation regime transitions to Landau-Levich). Thickness was adjusted because the model proposed by Baigl et al. assumes a continuous film is deposited, which is not the case for the HKUST-1 system. For the evaporative regime, we observe thickness follows a -0.99 power law correlation to coating speed. This agrees with the theoretical model originally described by Baigl *et al.* and the results of Park *et al.* that predict and demonstrate powers of -1 and -1.14, respectively. ^{14,17} It should be noted v^* is defined as the transition speed between the evaporative regime and Landau-Levich regime determined by solution parameters, thus $v/v^*=1$ is where the regime change should be observed.¹⁷

For the Landau-Levich regime we observe an exponent dependence of 1.26. Our result shows a higher dependence than theory and previous reports of, 0.66 and 0.89, respectively. We hypothesize the difference in Landau-Levich occurs due to the wetting properties of our substrate, as theory suggests this regime is dominated by the competition of viscous forces and surface tension forces.^{17,33} It should be noted these films showed non-uniformities in coverage that may arise from film instabilities, which is also related to wetting properties. No significant difference in particle morphology or film thickness range was observed between the evaporation and Landau-Levich regimes, meaning the Landau-Levich regime offered no better control of film quality or particle morphology than that possible in the evaporation regime. Because of this, we chose to continue characterization in the evaporative regime.

3.4.2 Controlling Film Morphology through Coating Parameters

Given the predictable thickness control and our hypothesis that the film crystal morphology was kinetically controlled, we decided to explore how coating parameters influenced the final morphology of films as a function of coating speed, temperature and starting concentration. In contrast to the work by Park *et al.*, we chose to explore the deposition process based on a lower starting solution concentration. If treated as a classical crystallization, HKUST-1 precursor concentration should be proportional to supersaturation. As a base condition, we used 144 mM of Cu^{2+} and 76 mM BTC.^{14,28} We hypothesized that this concentration should maintain lower supersaturation and promote growth over nucleation. **Figure 3.5** shows conditions of temperatures between 100 and 160 ° C and concentrations ranging from 144 mM Cu^{2+} : 76 mM BTC to 576 mM Cu^{2+} : 304 mM BTC. Across the range of temperatures, the adjusted thickness is related to the solution shearing speed by the power law relationship of -1. Lower temperatures yield thinner films and higher temperatures yield thicker films. This trend is expected for lower temperatures because slower evaporation allows for less material to be deposited on the substrate per unit time. Higher concentrations are also expected to create thicker films as more material is being deposited per unit volume of deposited solution.



Figure 3.5. Plot of adjusted film thickness versus relative shearing speed with corresponding microscope images of select films where darker regions are HKUST-1 particles and white/pink is the silicon substrate.

Figure 3.5 also demonstrates that speed, temperature, and concentration can be tuned to yield comparable thicknesses and morphologies. For example, similar thicknesses, coverages and particle sizes can be achieved by depositing a 576 mM Cu^{2+} : 304 mM BTC solution at 160 °C and v/v* = 0.206 relative speed and a 144 mM Cu^{2+} : 76 mM BTC solution at 130 °C and v/v* = 0.013 relative speed as shown in **Figure 3.5(a)-(b)**. This is expected in terms of adjusted thickness, as both systems deposit a nearly equivalent amount of mass per unit area. However, a comparable particle size and morphology suggests nucleation and growth in each system evolves similarly

with respect to time to yield similar particle size and coverage. Such a relationship also suggests particle morphology and adjusted thickness are related.

To test this, we compared particle diameter to true average thickness (i.e. average particle height) and observe a linear correlation (dashed line) for all conditions measured (**Figure 3.6**).



Figure 3.6. Film thickness vs. particle diameter for all solution sheared samples observed in the study. Error bars for thickness are generated for N=3 samples, N=1 where error bars are missing. Error bars for particle diameter are from ~ N=30 from multiple film samples with the same shearing conditions.

These results indicate crystal growth is isotropic and is not influenced by the solution shearing process as observed in other single component crystallization systems. Further, the observed particles sizes (~0.5 μ m -20 μ m) matched the results of Park *et al.*, however decreasing the precursor solution concentration (starting

supersaturation) or decreasing evaporation rate (lower temperature) did not increase particle size as originally hypothesized (**Figure 3.5, Table A3.1**). Since particle morphology appears to not singularly depend on "supersaturation" rate, we hypothesize HKUST-1 growth may not follow a classical crystallization pathway.^{34,35}

Typically, highly asymmetric growth occurs in single component systems during solution shearing, where the growth of high aspect ratio crystallites occurs along the shearing direction driven by a concentration gradient at the meniscus.^{34,35} We hypothesize the results differ because HKUST-1 crystallization occurs at a slower timescale than the deposition process, such that concentration gradients from the convective deposition process are resolved before crystallization occurs. In this case the evaporation rate, solution concentration, and deposited solution thickness

are what drives the supersaturation rate of the deposited solution. The observation that smaller crystallites appear at slower evaporation rates (lower temperatures), or lower supersaturation rates, indicates crystallization may have a more complex relationship with temperature than only evaporation rate (**Table A3.1**). Typically, lower supersaturation rates are expected to yield larger crystallite sizes in classical crystallization.

In terms of film quality, some conditions did provide full coverage when sufficient material is deposited, however the boundary where full coverage existed was ill-defined. While it typically correlated with the amount of mass deposited, this was difficult to predict given the wide range of parameters for solution shearing and non-classical crystallization behavior. The next section will highlight how machine learning based approaches to searching a parameter space help quantitatively resolve the parameter space and give insight into processing fully covered films.

3.4.3 Machine Learning Assisted Film Property Exploration and Optimization

Multiple parameters can be independently controlled during solution shearing, including substrate type and functionalization, solvent, copper concentration, metal to linker ratio, substrate temperature, coating speed, and the number of passes, leading to a possibility of tens of millions of independent combinations of parameters. To simplify the parameter space associated with solution shearing of HKUST-1, we use a single solvent and substrate (dimethylsulfoxide and ITO glass) and focused our efforts on understanding the impact of copper concentration, metal to linker (M:L) ratio, substrate temperature, coating speed and number of passes. Upper and lower bounds of the parameters and their discretization were based on previous experiments and existing knowledge about the system (**Table A3.2**).^{14,16,28} Copper concentration was determined based on previous experiments showing ~1.1 M resulted in precipitation of a coordination complex from

the mother solution at room temperature. Metal to linker (M:L) ratio was centered around the ideal stoichiometric ratio found in HKUST-1 of 1.5, where we biased our range towards higher metal concentrations.^{14,16,28} A lower bound substrate temperature of 120 °C was set for DMSO, as this temperature was required to evaporate the solution during the coating process, instead of evaporation occurring after coating was complete. The upper bound was set according to the boiling point of DMSO (189 °C). Finally, the coating speed range was determined largely by maintaining coating in the evaporative regime, where we experimentally observed more uniform crystals and films, and the maximum pass number (8) was set to give a large space to explore the impact of multiple depositions on film coverage. With these ranges, each parameter was discretized using a resolution defined by instrument limitation (5 °C for Temperature, 0.05 mm/s for speed) or to sufficiently sample each parameter range without oversampling (0.05 M for Cu. Conc., 0.05 for M:L ratio, and 1 for passes).



Figure 3.7. a) Optical micrographs of a fully covered (green border) and not fully covered (red border) classified HKUST-1 thin films corresponding to the processing conditions shown in (b). Scale bar is $25 \ \mu m$. (b) Parallel plot showing processing conditions and coverage classification of the initial 18 experimental conditions (replicated 3x) determined by a generalized subset design (GSD), with a representative green trace showing a covered condition and representative red trace showing a not fully covered condition (c) Predicted coverage class of parameter space spanning $11 \ x \ 10^6$ conditions after 1 training iteration of machine learning.

The first experimental training (Experiment 1) set was composed of 18 samples determined by using a generalized subset design (GSD) to give a representative sample of the parameter space (Figure 3.7b).³⁶ Each sample was replicated three times and observed with optical microscopy to determine coverage classification (Figure 3.7a). Classification of each condition occurred in four tiers: Fully covered (3 samples show full coverage), likely fully covered (2 samples show full coverage), likely not fully covered (1 sample show full coverage), and not fully covered (0 samples show full coverage). Figure 3.7a shows examples of a covered film (green border) and not covered film (red border), where the substrate is visible between HKUST-1 particles. The first experiment showed 11% of the conditions were fully covered (solid green), 11% were likely fully covered (green with hash), 6% were likely not fully covered (red with hash), and 72% were not fully covered (solid red) (Figure 3.7b). Using the Experiment 1 data set, a support vector machine (SVM) model was trained to classify the parameter space into the four coverage tiers using 25 trials, where confidence level was defined by the number of trials that predicted fully covered or not fully covered in a similar fashion to the experimental results. The model resulted in over 11 million parameter combinations predicting 6% fully covered (75%+ trials voting fully covered), 4% likely fully covered (50-75% trials voting fully covered), 3% likely not fully covered (25-50% trials voting fully covered) 87% not fully covered (0-25% trials voting fully covered). To further refine the model and reduce uncertainty, a second experiment set (Experiment 2) selected 18 additional samples from the likely fully covered region and was used to train the model in a second iteration (ML Iteration 2) (Figure 3.8a). The additional sampling and training resulted in a final virtual parameter space predicting 13% fully covered, 3% likely fully covered, 3% likely not fully covered and 81% not fully covered. The second iteration showed a reduction 12.5% reduction in the regions of low certainty (i.e. likely fully covered and likely not fully covered) demonstrating a significant improvement in confidence for coverage classification.



Figure 3.8. (a) Schematic showing the classification distribution of ML Iteration 1, Experiment 2, and ML iteration 2 (b) Box plots of fully covered and not fully covered conditions for each parameter of the model (c) Graph showing the minimum number of passes required to achieve full coverage as a functions of substrate temperature and speed for processing conditions, with Cu. Conc. = 1 and metal to linker ratio = 1.8 (d) Graph showing the minimum number of passes required to achieve full coverage as a function of copper concentration and coating speed for processing conditions, at 165 °C and metal to linker ratio of 1.8.

One of the benefits of using machine learning in lieu of high-throughput experimentation and parameter space exploration is a high resolution and quantitative prediction of the outcomes in a multidimensional parameter space. Further, incrementally training the model with new experimental data increases the confidence in the quantification and classification.^{18,23,24,36} As such results from ML Iteration 2 were used to gauge the "intuition" developed by the machine learning model and compare this to intuition obtained from previous results and experimental knowledge as a means of qualitative validation. **Figure 3.8b** shows box and whisker plots for the confident fully covered and confident not covered classifications for Model 2. Here the box represents the interquartile range, with the centerline being the median parameter value of samples in each classification. The whiskers represent 2 standard deviations (i.e. 95% of the population) and any samples falling outside of this range are plotted as points. By comparing the box plots for covered and not covered conditions, it is possible to determine generally how single parameters influence coverage classification.

The box plots show higher copper concentrations ($\sim 0.8-1.0$ M) are more likely to result in full coverage, whereas lower concentrations tend to result in not covered films. The model intuition fits experimental observation and agrees with results from Baigl et al., who showed the amount of material deposited per unit area is proportional to solution concentration.¹⁷ With more material being deposited per unit area, there is a higher probability of achieving a fully covered film. This same relationship applies to the number of passes, where box plots show more fully covered conditions are achieved at a higher number of passes (6-8) compared to lower passes. This does not mean full coverage cannot be achieved at lower passes and concentrations, but that a larger portion of the fully covered parameter space is represented by these conditions. Interestingly, box plots for the metal to linker ratio indicate values slightly above the stoichiometric ratio found in the final structure (1.5) tends to give covered films. Further, the median M:L ratio (1.75) is similar to other reports of thin film HKUST-1 synthesis (~1.9), suggesting this ratio may be optimum for the evaporative crystallization of HKUST-1.^{14,16,28} However, given the overlap with the not fully covered condition distribution, we deduce this parameter is less influential in singularly determining the coverage classification.

Similar interpretations for speed and substrate temperature can be made, where high temperatures and lower speeds show a slight trend towards producing covered films but have less of an impact on determining the coverage outcome. These results again follow models proposed by Baigl *et al.*, where high temperatures and lower speeds deposit more material per unit area in

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the evaporative regime of film deposition.¹⁷ In a qualitative sense, the "intuition" of the model developed in this work matches experimental expectations and existing knowledge of the solution shearing system and demonstrates the ability to assign quantitative values to intuited trends for the complex system. While matching closely, it is important to note much of the experimental intuition has been developed for a single pass in the evaporative regime, whereas the model has developed a similar intuition for multiple passes.

Although the single parameter relationships observed in the preceding paragraph could be obtained through intuition, the machine learning model also offers the ability to quantitatively explore multi-parameter influence on coverage. **Figure 3.8c** shows the minimum number of passes required for full coverage as a function of coating speed and temperature at a fixed copper concentration of 1 M and metal to linker ratio of 1.8. The plot shows that 8 passes under these conditions typically gives full coverage across the temperature and speed ranges, except for high speeds (< 3 mm/s) and low temperatures (< 130 °C), where the amount of material deposited is expected to be lower. As the pass number is reduced, the space yielding covered films recedes to higher temperatures and slower speeds, demonstrating that full coverage is a balance between the number of passes and other coating parameters.

Similarly, this tradeoff is observed for pass number, coating speed and copper concentration. **Figure 3.8d** shows the minimum number of passes required for full coverage as a function of copper concentration and coating speed, when the temperature and metal to linker ratio is fixed at 165°C and 1.8, respectively. Here, we again observe that a higher number of passes allows for a wider range of parameters that result in fully covered films and observe a recession to high concentrations and low speeds as the number of passes is reduced. This again indicates

coverage is largely dictated by the quantity of material deposited, with more material deposited resulting in a greater probability of a fully covered film.

Quantified understanding of the processing parameters space allows for additional target property control (i.e. crystal grain size, thickness, etc.). For this work, we choose to minimize the thickness of fully covered HKUST-1 films, as this reduces mass transfer barriers for separations and sensing applications and is often a target property for thin films.^{4,5,12,13,37} We used thickness measurements from Experiments 1 and 2 to train a thickness prediction model. **Figure 3.9a** shows how the thickness prediction model trained from experimental data fits measurements from experimental data. The linear trend shows our model converged on a solution that predicts thickness as a function of the experimental solution shearing input parameters. While additional training rounds would enhance the prediction accuracy of this model, one training round was found to be sufficient in locating a predicted minimum region within the fully covered parameter space. It should be noted no other *a priori* relationships (i.e. those developed by Baigl *et al.* for thickness and speed) were used in training the thickness prediction model.



Figure 3.9. Graph of experimental film thickness vs. predicted thickness from the machine learning thickness prediction model (values are natural log) (b) Predicted thickness as a function of metal to linker ratio and substrate temperature at a copper concentration of 1 M, coating speed of 2 mm/s and 7 passes (c) Predicted thickness as a function of coating speed and passes for a copper concentration of 1 M, metal to linker ratio of 1.8 and substrate temperature of 165 °C with experimental conditions showing full coverage (filled circles), not covered (empty circles) and the experimentally observed minimum thickness (pink star). (d) Micrograph of the experimentally determined minimum thickness HKUST-1 film.

To understand the predicted minimum thickness region that would guide additional experiments, we observed the tabulated predicted thickness data as well as multi-parameter interactions. Predicted thickness data from the model revealed higher copper concentrations typically yielded the thinnest films within the fully covered parameter space (**Figure A3.4**). This is likely because high concentrations deposit more HKUST-1 per unit area while confinement from solution shearing maintains minimal thickness. Due to this trend we chose to continue the thickness minimization with a copper concentration of 1 M. Next, we observed the predicted thickness as a function of substrate temperature and M:L ratio. **Figure 3.9b** shows film thickness predicted by

our model as a function of metal to linker ratio and substrate temperature where the coating speed of 2 mm/s and 7 passes exemplifies the behavior observed for a majority of speeds and passes (**Figure A3.5**). A broad minimum is observed centered around a temperature of 165 °C and a metal to linker ratio of 2.1, predicting film thickness to be between 2-3 microns. In this case we fixed the metal to linker ratio at 1.8, as it showed comparable thickness prediction to the true minimum but was close to the stochiometric ratio found in HKUST-1. We hypothesize that keeping the metal to linker ratio close to the stochiometric ratio prevents defect formation within the MOF structure itself and the co-precipitation of excess metal salts during thin film formation.

After fixing copper concentration, metal to linker ratio, and substrate temperatures, the predicted thickness minimum was experimentally explored as a function of passes and speed. Figure 3.9c shows the predicted thickness as a function of passes and speed with a minimum predicted at 6 passes and 3.5 mm/s for a copper concentration of 1 M, metal to linker ratio of 1.8 and substrate temperature of 165 °C and the experimental points used to explore this space. Experimental thickness values can be found in the Appendix (Table A3.4). Coverage results of the experimental exploration are in good agreement with the model, showing experimental films are not covered in the regions predicted by the model. The green hash in Figure 3.9c represents likely fully covered films as predicted by the machine learning model. The experimental minimum was determined to occur at 4 passes and 3.5 mm/s resulting in a film thickness of $2.2 \pm 0.3 \,\mu\text{m}$. This result is 2.5x thinner than our previous experimentally reported results.⁷ Micrographs of the minimized thickness experiment show a uniform film with full coverage (Figure 3.9d). Interestingly, this minimum occurred in a parameter region where predicted coverage certainty was not confident, shown by the hashed light green area (Figure 3.9c). This follows from competing trends, where confident coverage is expected for more material being deposited per unit

area, but thinner films require less material per unit area. Thus, for the optimization put forth in this system, we expect the minimum to lie on the border of full coverage.

3.5 Conclusion

To conclude, we explored controlling HKUST-1 crystallization using the solution shearing thin film deposition technique. We found a non-equilibrium morphology in most films, which indicates particle morphology may be dominated by kinetics. Further we found the supersaturation and rate of supersaturation had an opposite effect on grain size and assymetry as expected for a single component, classical crystallization system. This indicates the crystallization of HKUST-1 may not behave as a classical crystallization system, however more work on understanding how crystallization kinetics couple to solution shearing is required. Finally, we demonstrate a correlation between film thickness and particle size, which indicates isotropic growth during the deposition process and suggests the crystallization time scale is likely different than the deposition time scale of solution shearing.

To decouple the particle size-thickness relationship and acquire fully covered films with minimum thickness, a machine learning model was used to quantitatively predict the coverage classification of thin film HKUST-1 fabricated by solution shearing across 5 processing parameters. We demonstrate the model develops an intuition found in previous thin film deposition studies for single and multi-parameter influence on coverage. Further, the model can quantify this intuition to give well-defined regions of the parameter space where full film coverage will exist. This was achieved by two 18 condition training sets and was able to generate an 11 million sample predictive parameter space. While the number of parameters used in this study and their ranges were limited to specified regions, we hypothesize this model can be further developed to include more parameters at larger ranges depending on research objectives and experimental and

computational allowances. Additional experimental training iterations are expected to improve the accuracy of the model. We further demonstrate how this model can incorporate other film characteristics, such as film thickness, to optimize the characteristic in the fully covered parameter space. This was shown provide a minimized thickness 2.5 times thinner than our previous experimentally optimized results and provided identical conductivities compared to the experimentally optimized films. Future work using this model will include optimizing additional characteristics of HKUST-1 thin films and their derivatives, such as crystal grain size, crystallinity, and conductivity while maintaining a fully covered film.

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3.6 Appendix



Figure A3.1. Nitrogen isotherm for drop cast HKUST-1 solution.



Figure A3.2. Integrated GIWAXS pattern for solution sheared HKUST-1 compared to simulated PXRD of HKUST-1. Tick marks along the x-axis demark peak locations of the PXRD pattern.



Figure A3.3. Illustration showing a 2D detector with typically observed diffraction patterns for different crystal arrangements in a thin film.

Table A3.1. Film morphology and HKUST-1 particle characteristics for samples sheared at varied conditions. Average particle diameter is taken from $\sim N=30$ particles across different samples from microscope images. Average thickness was measured for N=3 film samples with standard deviation shown as error. Samples without error were only measured once. Coverage was determined from microscope images and error was calculated using the same method as thickness.

Cu. Conc (mM)	BTC Conc. (mM)	Sub. Temp. (C)	Speed (mm/s)	v/v*	Avg. Particle Diameter (um)	Avg. Thickness (um)	Coverage (%)	Adj. Thick. (um)
144	76	160	0.05	0.006	11.8 ± 7.2	9.2 ± 3.6	99.7 ± 0.5	9.18
144	76	160	0.1	0.012	15 ± 6.9	5.3 ± 2.7	88.6±4.3	4.66
144	76	160	0.4	0.051	7.4 ± 3.3	1.8 ± 0.4	46.9 ± 7.7	0.83
144	76	160	1.6	0.20	3 ± 1.4	0.7 ± 0.1	32.4 ± 3.7	0.24
144	76	160	3.2	0.41	4.1 ± 1.5	1.1 ± 0.5	20.3 ± 2.1	0.22
144	76	160	6.4	0.82	2.3 ± 0.7	0.4 ± 0.2	14.3 ± 1.2	0.06
144	76	160	12.8	1.64	1.1 ± 0.4	0.1 ± 0.1	30.4 ± 2.7	0.04
144	76	130	0.06	0.012	7.6 ± 3.9	2.7	75.0	1.99
144	76	130	0.1	0.020	3.5 ± 2.2	1.6	74.4	1.21
144	76	130	0.4	0.083	3.1 ± 1.1	0.7 35.0		0.24
144	76	130	1.6	0.334	1.3 ± 0.6	0.1	43.5	0.06
144	76	100	0.1	0.038	1.2 ± 0.6	0.6	79.7	0.47
144	76	100	0.4	0.15	1.6 ± 0.4	0.1	28.7	0.03
144	76	100	1.6	0.61	0.8 ± 0.5	0	64.0	0.03
576	304	160	0.12	0.015	19.3 ± 5.4	13.7 100.0		13.68
576	304	160	0.4	0.051	11.9 ± 7.8	5	82.3	4.11
576	304	160	1.6	0.206	6.8 ± 4	2.4	64.2	1.53

Parameter	Minimum	Maximum	Resolution
Cu. Conc. (M)	0.05	1.05	0.05
M:L Ratio	1.25	2.5	0.05
Sub. Temp. (°C)	120	180	5
Speed (mm/s)	0.05	5	0.05
Passes	1	8	1

Table A3.2. Table showing the parameter limitations and resolution used for training the machine learning model and during experimentation



Figure A3.4 Plot of predicted thickness as a funciton of copper concentration for all other conditions as determined from the machine learning model.

Training Set	Sample ID	Cu Conc (M)	ML Ratio:	SubTemp (°C)	Speed (mm/s)	Passes
1	1	0.29	1.3	180	0.05	8
1	2	0.29	1.3	120	5	4
1	3	0.29	2.4	150	0.05	1
1	4	1.16	1.9	120	0.5	1
1	5	0.29	1.9	180	5	1
1	6	1.16	1.3	180	0.5	4
1	7	0.06	2.0	120	5	8
1	8	0.29	1.9	150	0.5	4
1	9	0.06	3.0	180	0.5	1
1	10	0.06	2.0	180	0.05	4
1	11	1.16	2.5	120	0.05	4
1	12	0.06	1.2	120	0.05	1
1	13	0.06	3.0	150	5	4
1	14	1.16	2.5	180	5	8
1	15	0.06	1.2	150	0.5	8
1	16	1.16	1.3	150	5	1
1	17	1.16	1.9	150	0.05	8
1	18	0.29	2.4	120	0.5	8
2	407855	1	1.3	145	0.85	8
2	237631	1.05	1.8	150	0.45	8
2	70372	1	2.1	155	0.97	8
2	452737	0.9	1.7	155	0.69	6
2	800672	1.05	1.9	160	4.42	8
2	239745	1	1.8	160	0.86	4
2	442531	1	1.6	160	3.45	7
2	662230	1	1.3	165	4.2	8
2	6231	0.95	1.3	165	4.86	8
2	80067	1.05	1.9	170	4.09	5
2	629118	0.4	1.6	170	0.84	6
2	1893	0.8	1.5	175	4.61	8
2	443847	0.75	1.4	175	4.53	6
2	262062	1.05	1.4	180	4.96	6
2	7037	1	2.1	180	2.79	4
2	616981	0.95	1.3	180	3.7	4
2	621100	0.7	1.5	180	4.68	5
2	448584	0.6	1.5	180	1.13	3
Thickness Opt	31	1	1.8	165	1.5	6
Thickness Opt.	32	1	1.8	165	2.5	6
Thickness Opt.	33	1	1.8	165	3.5	6
Thickness Opt.	34	1	1.8	165	3.5	4
Thickness Opt.	35	1	1.8	165	3.5	8
Thickness Opt.	36	1	1.3	165	3.5	6
Thickness Opt.	37	1	1.5	165	3.5	6
Thickness Opt.	38	1	2.1	165	3.5	6
Thickness Opt.	39	1	1.8	165	4.25	6
Thickness Opt.	40	1	1.8	165	5	6
Thickness Opt.	41	1.16	1.9	165	0.5	1
Thickness Opt.	43	1	1.8	165	3.5	3

Table A3.3. Table of the experimental parameters used for training the machine learning model and for exploring the minimized thickness and fully covered parameter space



Figure A3.5 Plots of thickness prediction as a function of substrate and temperature for 1 M Copper concentration and (a) speed = 2 mm/s, passes=3 (b) speed 1 mm/s, passes=7 (c) speed = 3 mm/s, passes=4 and (d) speed = 5 mm/s, passes = 8

Training Set	Sample ID	Triplicate Tag	Cu Conc (M)	ML Ratio	Sub Temp (°C)	Speed (mm/s)	Passes	Cov. Class	Avg. Thick. (um)
Thick. Opt.	31	А	1	1.8	165	1.5	6	1	9.4 ± 5
Thick. Opt.	31	В	1	1.8	165	1.5	6	1	6.7 ± 0.9
Thick. Opt.	31	С	1	1.8	165	1.5	6	1	11.2 ± 1.9
Thick. Opt.	32	А	1	1.8	165	2.5	6	1	5.2 ± 0.4
Thick. Opt.	32	В	1	1.8	165	2.5	6	1	5.2 ± 0.5
Thick. Opt.	32	С	1	1.8	165	2.5	6	1	7.3 ± 0.5
Thick. Opt.	33	А	1	1.8	165	3.5	6	1	5.2 ± 0.5
Thick. Opt.	33	В	1	1.8	165	3.5	6	1	3.6 ± 0.6
Thick. Opt.	33	С	1	1.8	165	3.5	6	1	4.6 ± 0.3
Thick. Opt.	34	А	1	1.8	165	3.5	4	1	1.8 ± 0.3
Thick. Opt.	34	В	1	1.8	165	3.5	4	1	2.2 ± 0.5
Thick. Opt.	34	С	1	1.8	165	3.5	4	1	2.4 ± 0.5
Thick. Opt.	35	А	1	1.8	165	3.5	8	1	5.7 ± 0.9
Thick. Opt.	35	В	1	1.8	165	3.5	8	1	4.4 ± 0.6
Thick. Opt.	35	С	1	1.8	165	3.5	8	1	4.1 ± 0.5
Thick. Opt.	36	А	1	1.3	165	3.5	6	1	4.6 ± 0.2
Thick. Opt.	36	В	1	1.3	165	3.5	6	1	3.9 ± 0.4
Thick. Opt.	36	С	1	1.3	165	3.5	6	1	4.2 ± 1.3
Thick. Opt.	37	А	1	1.5	165	3.5	6	1	4.2 ± 0.7
Thick. Opt.	37	В	1	1.5	165	3.5	6	1	4.1 ± 0.6
Thick. Opt.	37	С	1	1.5	165	3.5	6	1	3 ± 0.2
Thick. Opt.	38	А	1	2.1	165	3.5	6	1	6.6 ± 0.7
Thick. Opt.	38	В	1	2.1	165	3.5	6	1	5.4 ± 1.3
Thick. Opt.	38	С	1	2.1	165	3.5	6	1	4.9 ± 0.7
Thick. Opt.	39	А	1	1.8	165	4.25	6	1	3 ± 0.5
Thick. Opt.	39	В	1	1.8	165	4.25	6	1	4.9 ± 0.6
Thick. Opt.	39	С	1	1.8	165	4.25	6	1	3.2 ± 0.5
Thick. Opt.	40	А	1	1.8	165	5	6	1	2.5 ± 0.6
Thick. Opt.	40	В	1	1.8	165	5	6	1	4.5 ± 0.8
Thick. Opt.	40	С	1	1.8	165	5	6	1	2.6 ± 0.4
Thick. Opt.	41	А	1.16	1.9	165	0.5	1	1	2.7 ± 0.5
Thick. Opt.	41	В	1.16	1.9	165	0.5	1	1	3.2 ± 0.7
Thick. Opt.	41	С	1.16	1.9	165	0.5	1	1	2.3 ± 1.2
Thick. Opt.	43	А	1	1.8	165	3.5	3	0	-
Thick. Opt.	43	В	1	1.8	165	3.5	3	0	-
Thick. Opt.	43	C	1	1.8	165	3.5	3	0	-

Table A3.4 Table showing the coverage classification and average thickness for samples used to explore the machine learning optimized thickness parameter set

3.7 References

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4 Understanding MOF Crystallization through Reactive-Crystallization

4.1 Abstract

Metal-organic frameworks (MOFs) are a promising class of functional materials with applications in catalysis, separations, electronics, and drug delivery, among others. Despite a range of techniques utilized for MOF synthesis, a generalizable and scalable approach has yet to be developed for producing MOFs without using environmentally damaging organic solvents. Here, we look at MOF synthesis as a reaction in an aqueous medium and propose new methods of measuring conversion and selectivity. We show that controlling reactant speciation via pH is a generalizable approach to producing the prototypical MOFs UiO-66, UiO-66-NH2, ZIF-L, and HKUST-1 with space-time yields (STY) of over 2250 kg m⁻³ day⁻¹, which is a 1 order of magnitude improvement for zirconium-based MOFs. We show that UiO-66-NH₂ crystallization is complete in 5 min at room temperature, with 70% of the extent of reaction completed by 30 s. Finally, we apply the rapid synthesis approach to coating cotton fabric with up to 20 wt % UiO-66-NH₂ using a sequential dip-coating (SQD) technique and demonstrate particulate matter (PM1– 4) filtration up to 85%. This work shows a green-chemistry-based, generalizable pathway to rapid synthesis for multiple MOFs and demonstrates its utility for creating thin film coatings for filtration applications. Most importantly, this study demonstrates the kinetics of MOFs can be significantly enhanced and controlled by treating the system as a reactive-crystallization.

Metal organic frameworks (MOFs) are a class of highly porous, crystalline materials with an expanding portfolio of potentially high impact applications.^{1–4} Composed of metal nodes periodically linked by organic ligands, researchers have leveraged the versatile chemistry and porous structure for applications in catalysis, separations, electronics, and drug delivery.^{1–8} Conventionally, MOFs are created using batch synthesis, typically requiring harsh organic solvents such as dimethylformamide (DMF), high temperatures and pressures, and long synthesis times for relatively low space-time yields (STY), defined as the quantity of product per unit volume per time.^{9–11} However, to use MOFs in a given application, the technoeconomic viability (i.e. cost and scalability) and environmental impact of production must also be considered together with the chemical suitability.^{12,13} Thus, reduced use of organic solvents and improved STY have been identified as necessary processing conditions required for the successful scaling of MOF production.^{13,14}

A majority of approaches to enhancing MOF production focus on accelerating conventional solvothermal synthesis conditions. For example, Masel *et al.* were able to produce three MOFs in the IRMOF series in 25 seconds using microwave-assisted solvothermal synthesis.¹⁵ In another approach, Kim *et al.* utilized confined microdroplets in a fluidic device to produce several prototypical MOFs including HKUST-1, MOF-5, and the highly stable zirconium-based framework UiO-66, in 1 minute, 3 minutes, and 15 minutes, respectively.¹⁶ While these approaches achieved rapid time scales, they often require specialized equipment and harsh organic solvents at high temperatures that are not amenable to scaling. Other approaches have focused on water-based syntheses. Several groups have successfully synthesized UiO-66 and its derivatives using aqueous synthesis. For example, Szilagyi *et al.* were able to produce UiO-66-NH₂ in 1 hour in water at

room temperature.¹⁷ This was further enhanced to 1 minute by Maspoch *et al.* via heating and spray drying.¹³ Other work by Lai *et al.* showed that ZIF-8, could form in 5 minutes at room temperature, with precipitation occurring instantaneously.¹⁸ Thus far, rapid aqueous approaches have been heuristic in nature and specific to MOF families. Therefore, developing a generalizable framework for rapid aqueous synthesis of MOFs has significant implications for high volume applications.

In this work, we approach MOF synthesis from a reaction-based perspective, and control the concentration of reactants to tune the driving force for MOF crystallization.^{19,20} Typical MOF synthesis occurs in low pH conditions due to the acidic nature of the metal ion-clusters, organic linkers and additional modulators.^{17,21–26} However, at low pH, organic linkers that are fully protonated are unable to participate in the coordination reaction and thus act as a limiting reagent. Zhang *et al.* showed that by modulating linker deprotonation rate with acid-base adjustment, they could control nucleation rate and subsequent crystal size.²⁷

In another approach, Díaz *et al.* showed using the homologous organic salt of terephthalic acid accelerated the synthesis time of MIL-53(Al) from days to hours.²⁸ Achieving the required node geometry can also kinetically hinder MOF formation.²² The necessary geometric structure and lability of multinuclear metal-ion clusters is required to achieve open framework topologies. Férey *et al.* first demonstrated this by preforming hexanuclear zirconium oxoclusters using the controlled secondary building unit (SBU) approach to reduce the time and temperature requirements to form an UiO-66 analogue in 5 hours at room temperature.²⁹ Therefore, we hypothesize the rate limiting step in MOF formation kinetics to be the availability of both the deprotonated linkers and labile metal nodes during synthesis.^{27,30} Further, increasing the concentration of the deprotonated linkers while preserving the concentration and geometry of the



metal ion-cluster species will lead to a faster reaction, consequently leading to faster MOF synthesis (Figure 4.1).

Figure 4.1 Schematic showing the difference between conventional synthesis conditions and the rapid synthesis conditions used in this work. During conventional synthesis, linkers are primarily protonated and act as limiting reagents. In the rapid synthesis conditions used in this work, labile metal nodes and deprotonated linker species co-exist with high relative abundance and readily coordinate for rapid crystallization to make the prototypical MOFs UiO-66-NH2, UiO-66, HKUST-1, and ZIF-L.

An environmentally benign, aqueous system is ideal for testing this hypothesis, as the speciation of metals and organic acid linkers can be predicted through ion stability constants and dissociation constants, respectively. In addition, the concentration of both can be controlled through pH modulation. By pre-forming the metal ion-cluster nodes and tuning the pH to maximize the concentration of labile metal nodes and deprotonated organic acid linkers, we demonstrate a rapid coordination of nodes and linkers, leading to rapid MOF crystallization. We apply this hypothesis to several prototypical MOFs (UiO-66-NH₂, UiO-66, ZIF-L, and HKUST-1) to demonstrate a generalized approach, limited only by the linker solubility. We study the

crystallization kinetics of the UiO-66-NH₂ synthesis by kinetically arresting the reaction and show that 70% of the crystallization occurs within 30 seconds. We show that at the fast reaction conditions, we achieve STYs exceeding 2250 kg m⁻³ day⁻¹ for all MOFs tested with high product quality for UiO-66-NH₂, ZIF-L, and HKUST-1 as determined by specific surface area measurements, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). However, the product quality of UiO-66 suffered from a heavily defected structure, likely due to the low solubility of linkers in water.³¹ Finally, we apply our approach in Chapter 6 to allow for high throughput, scalable fabrication of MOFs is presented by rapidly manufacturing MOF coated fabric for particulate matter pollution filtration using a sequential dip coating (SQD) technique. SQD grows MOF films on the order of seconds and is faster than the conventional layer by layer techniques used to form MOF films. ^{5,33–39} The advantage of our high throughput manufacturing capable process is especially relevant with shortages in personal protective equipment (PPE) shortages experienced around the world during the COVID-19 pandemic.^{40,41}
4.3 Materials and Methods

Materials

All reagents were used as received with no further purification. Zirconyl chloride octahydrate (ZrOCl₂ ·8 H₂O, 98% Alfa Aesar), acetic acid (Glacial Sigma Aldrich), sodium hydroxide pellets (NaOH, 98% Sigma Aldrich), 2-aminoterephthalic acid (H₂ATA, 99% Sigma Aldrich), terephthalic acid (H₂BDC, 98% Sigma Aldrich) and deionized water were used for the rapid synthesis of UiO-66-NH₂ and UiO-66. Copper nitrate hemipentahydrate (Cu(NO₃)₂, 98% Sigma Aldrich), sodium hydroxide (NaOH, 98% Sigma Aldrich), trimesic acid (H₃BTC, 95% Sigma Aldrich), sodium hydroxide (NaOH, 98% Sigma Aldrich), trimesic acid (H₃BTC, 95% Sigma Aldrich) were used for the rapid synthesis of HKUST-1. Zinc nitrate hexahydrate (Zn(NO₃)₂, 98% Sigma Aldrich), sodium hydroxide, 2-methylimidazole (HmIm, 97% Alfa Aesar) were used for the rapid synthesis of ZIF-8. Hydrochloric acid (37 wt%, Alfa Aesar) was used to prepare an aqueous solution of 0.01 M HCl. Dimethyl sulfoxide (DMSO, 99% Sigma Aldrich), ethanol (EtOH, 95% Koptec), and methanol (MeOH, 99.8% Sigma Aldrich) were used for washing and activating MOFs. Napped Sateen Cotton fabric was purchased from Hanes (Hanes 0339061) and washed with an ethanol rinse before further processing.

Rapid Synthesis of MOFs

In a typical synthesis, a metal ion solution and a linker solution were prepared as described below. 10 mL of linker solution was placed in a 50 mL conical centrifuge tube and massed. The pH was adjusted to a predetermined value with 20 M NaOH and DI water to a total solution volume of 13.5 mL. Next, 7.5-10 mL metal solution (massed previously) was vigorously injected into the linker solution using a 10 mL pipette. The resulting mixture was immediately placed in a centrifuge at 12000 rpm for 5 minutes. Afterwards, supernatant was carefully decanted to a separate container and pH was taken (inLab Expert Pro). Except for HKUST-1, precipitate was placed in an oven at 70 °C for a minimum of 8 hours then washed with various solvents depending on the MOF and dried before characterization. All MOFs were stored under nitrogen shortly after synthesis and between characterization.

Rapid Synthesis of UiO-66-NH₂

A metal solution was prepared following synthesis outlined by Szilagyi *et al.*¹⁷ Briefly, 1.2880 g ZrOCl₂ ·8H₂O was dissolved in 5 mL Acetic acid and 12 mL of DI water, placed in a Teflon lined 20 mL scintillation vial, heated at 70 °C for two hours and allowed to cool to room temperature. The linker solution was prepared by mixing 0.7240 g of H₂ATA in a solution of 0.32 g NaOH in 20 mL DI water until dissolved. After centrifugation and drying, the solution was washed with a 0.01 M HCl solution, 0.001 M NaOH solution, DMSO and methanol to remove unreacted and soluble components of the precipitate. A solvent exchange with methanol was performed overnight before additional centrifugation and drying at 70 °C overnight.

Rapid Synthesis of UiO-66:

Solutions were prepared and washed similarly to UiO-66-NH₂ Briefly, 1.288 g ZrOCl₂ ·8H₂O was dissolved in 3 mL Acetic acid and 12 mL of DI water, placed in a Teflon lined 20 mL scintillation vial, heated at 70 °C for two hours and allowed to cool to room temperature. The linker solution was prepared by mixing 0.6640 g of H₂BDC in a solution of 0.32 g NaOH in 20 mL DI water until dissolved. After centrifugation and drying, the solution was washed and dried using the same procedure as UiO-66-NH₂.

Rapid Synthesis of HKUST-1

A metal solution was prepared with 0.4652 g Cu(NO₃)₂·2.5 H₂O was dissolved in 10 mL of DI water. The linker solution was prepared by mixing 0.2802 g of H₃BTC in a solution of 0.16 g NaOH in 10 mL DI water until dissolved. After centrifugation, the precipitate was immediately

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washed and solvent exchanged with ethanol to prevent HKUST-1 degradation from water. Samples were dried under vacuum (30 mmHg) at 90°C in a nitrogen atmosphere.

Rapid Synthesis of ZIF-L

A metal solution was prepared with $0.5950 \text{ g Zn}(NO_3)_2 \cdot 6 \text{ H}_2\text{O}$ was dissolved in 10 mL of DI water. The linker solution was prepared by mixing 0.3284 g of HmIm in 10 mL DI water until dissolved. After centrifugation and drying, the solution was stored in nitrogen atmosphere until characterization.

Flash Freezing Study of MOF reaction extent as a function of time

For short time points (1-10 seconds), a microfluidic device was used to combine metal and linker solutions at and mixed using a sonicator. Residence time in the microfluidic device (Fittings, Masterflex, FEP tubing, Altaflow) was taken as the reaction time and effluent from the reaction stream was immediately captured in liquid nitrogen to freeze the suspension. Samples were stored at -80 °C until lyophilization. No washing was performed before PXRD. After data collection, samples were washed with a 0.01 M HCl solution, DI water, DMSO and methanol to remove unreacted and soluble components of the precipitate and additional PXRD data was collected of washed samples.

Linker Solubility Study

Linker solutions of 0.2 M H₂ATA and H₂BDC were prepared by mixing equinormal sodium hydroxide and linker with DI water. Solution pH was adjusted using 10 M NaOH and 6 M HCl under vigorous stirring. Precipitation of the linker was observed with each addition of NaOH solution, indicating saturation. Solution pH was allowed to equilibrate before a 5 mL aliquot was vacuum filtered and vacuum dried at 80 °C for 4 hours. Dried precipitate was massed and converted to molarity using the molar mass of the respective organic acid.

Characterization:

Mass and Conversion

Individual linker solution mass and averaged metal solution mass were used to calculate the quantity of reactants in each synthesis. Since MOF stoichiometric values of reactants were used, the total mass of metal and linker were used in calculating percent conversion. Centrifuge tubes used for synthesis were massed before use and precipitate mass was determined as weight of empty tube plus the dried precipitate.

XRD

Powder x-ray diffraction (PXRD) patterns were collected using a PANalytical Empyrean X-ray Diffractometer (Malvern Panalytical, Egham, UK) with Cu K- α radiation. Scans were taken from $2\theta = 5^{\circ}$ - 20° for UiO-66-NH₂ and $2\theta = 5^{\circ}$ - 30° for UiO-66, HKUST-1, and ZIF-L. Diffraction patterns were analyzed using HighScore Plus X-ray Diffraction analysis software. *SEM*

Scanning Electron Microscopy (SEM) micrographs were collected using a Helios Dual Beam FIB G4 UC with an accelerating voltage of 5 kV and 0.80 nA current.

BET

Nitrogen uptake isotherms were measured at 77 K with a Micromeritics ASAP 2020 Surface Area and Porisimetry analyzer. Data was analyzed using the ASAP 2020 V4.04 software. All gases used were high purity. Typically, 50-100 mg of MOF sample were dried under vacuum at 80°C overnight before initiating previously reported degassing procedures for each MOF. *TGA*

The metal to linker ratio of MOFs was measured by Thermogravimetric Analyzer (TGA, Q50). In a typical experiment, a small amount of pre-dried powder or fabric (~10 mg) was loaded

into a Pt sample pan, and the sample pan was transferred into the heating chamber of the analyzer. The sample gas was air (flowrate = 60 mL/min), and the balance gas was nitrogen (flowrate = 40 mL/min). The sample was heated to 800 °C from room temperature at a rate of 10 °C/min. In the initial stage of the heating process, moisture adsorbed by the sample was evaporated, and the sample mass at 120 °C was taken as the dry mass. Further heating led to the decomposition of the sample (i.e., organic linkers and organic fabric were decomposed by oxidation and metal nodes were transformed into metal oxide), and the sample mass at 800 °C was taken as the mass of metal oxide.

4.4 **Results and Discussion**

As we hypothesize rapid MOF formation is limited by the availability of both the metal ion cluster nodes and the deprotonated organic linker at high concentrations in solution, we expect accelerated formation kinetics can be achieved in multiple MOFs by optimizing both concentrations. We selected four prototypical MOFs, ranging in metal-linker connectivity and metal node complexity, including UiO-66, UiO-66-NH₂, HKUST-1, and ZIF-L.^{21,32–34} These MOFs range in secondary building unit (SBU) complexity from hexanuclear zirconium oxoclusters (UiO-66, UiO-66-NH₂), dimeric copper (HKUST-1) to a singular zinc ion (ZIF-L). Further, the denticity of each linker varies between bidentate (UiO-66, UiO-66-NH₂, ZIF-L) and tridentate (HKUST-1). Generally, an acidic solution of labile metal nodes was vigorously mixed for 30 seconds with a basic solution of deprotonated linkers to form a precipitate, where the adjusted acidity and basicity of respective solutions determined the final pH of the mixture. The precipitate was allowed to react for an additional 4.5 minutes, centrifuged for 5 minutes, and decanted, for a total reaction time of 10 minutes. The pH of the supernatant was measured to obtain the relative abundance of the reactant species present during synthesis.



Figure 4.2 *a)-d)* Experimental pH conditions versus experimental yield during rapid aqueous synthesis of UiO-66-NH₂, UiO-66, ZIF-L and HKUST-1, at 10 min of reaction time (Error is standard deviation of N=3 trials). Lack of standard deviation in figures are due to the standard deviation being smaller than the marker size. The red lines show calculated relative concentration of labile metal ion clusters and the blue lines show calculated relative concentration of linkers with at least one deprotonated binding site as a function of theoretical pH. Inlays show corresponding linker structure, with pKa values used to calculate relative abundance of deprotonated linkers. e) – h) SEM micrographs of e) UiO-66-NH2 synthesized at pH 3.9 f) UiO-66 synthesized at pH 4.9 g) ZIF-L synthesized at pH 7.8 and h) HKUST-1 synthesized at pH 3.3.

Figure 4.2a-d shows MOF yield as a function of solution pH, with the reactions performed in aqueous conditions at room temperature. We determined yield as the product of total mass conversion and selectivity.³⁵ Here, conversion is defined as the total amount of isolated insoluble solid product after washing compared to the total mass of metal node and linker reactants used in the synthesis, and selectivity is defined as the relative crystallinity of MOF present in the sample

(Equation (A4.1), Figure A4.1). This method differs from conventional reports on MOF yield, which typically assumes a selectivity of 100% and does not consider quality or crystallinity of MOF product to have an impact on yield.^{12,17,33,36–39} We instead utilize a technique frequently used in semi-crystalline polymers to quantify relative crystallinity.^{40,41} The proportion of the desired crystalline MOF (i.e. selectivity) in each solid product sample was determined from PXRD by calculating percent relative crystallinity. Percent relative crystallinity was obtained by comparing amorphous and crystalline scattering using the analysis software HighScore Plus (Figure A4.1).⁴² The red lines in Figure 4.2a-d represent relative abundance of uncoordinated metal ions calculated from stability constants.^{43,44} The blue lines in Figure 4.2a-d represent the relative abundance of linkers with at least one deprotonated coordination site, calculated by using published pKa values for each organic acid.^{45–47} Combined, these relative abundances represent a guide of the relative concentrations of the metal and linker species present during the reaction at a given pH. It should be noted the speciation and stability constants of the hexanuclear zirconium oxocluster necessary to form UiO-66 and UiO-66-NH₂ have not been conclusively reported. However, reports on kinetic stability and potentiometric acid-base titration of the zirconium oxocluster containing UiO-66 suggest hexanuclear speciation and lability below pH 6.5.^{22,48,49}

For UiO-66-NH₂, there are three pKas for the linker (H₂ATA) that correspond to the deprotonation the first and second carboxylic acid groups (3.5, 4.4) and the amine group (estimated as 5) (**Figure 4.2a**).⁴⁵ Crystalline UiO-66-NH₂ was observed in the pH range between 2.5-5.1. A maximum MOF yield of $40 \pm 4\%$ was found to occur at pH 4.3 ± 0.1 where 77% of linkers are at least singly deprotonated based on speciation calculations. This corresponds to a STY of 3381 kg m⁻³ day⁻¹ of converted product, which exceeds other reported aqueous room temperature syntheses by an order of magnitude and exceeds the highest STY reported for any UiO-66-NH₂ synthesis by

25% (Microwave synthesis, 2679 kg m⁻³ day⁻¹) (**Figure 4.3a**, **Equation (A4.2)**, **Table A4.1**).^{12,17} UiO-66 has two pKas at 3.5 and 4.5 for the linker (H₂BDC) that correspond to the deprotonation of the first and second carboxylic acid groups (**Figure 4.2b**). Crystalline UiO-66 was observed in the pH range between 4.3-5.1 (lower pH values did not yield enough precipitate to perform PXRD). The maximum yield of $13 \pm 3\%$ occurred at pH 4.9 ± 0.1 , where nearly 97% of linker molecules are singly or doubly deprotonated. This corresponds to a STY of 2732 kg m⁻³ day⁻¹ of converted product, which is an order of magnitude higher than any previously reported technique (Figure **4.3a**, **Equation (A4.2)**, **Table A4.1**).^{33,36–39,50} We hypothesize the difference in maximum yield pH for UiO-66 and UiO-66-NH₂ is due to the solubility of their corresponding linkers, where the concentration of H₂ATA remains higher than H₂BDC at lower pH values (**Figure A4.3**). Thus, the presence of deprotonated linkers at sufficient concentrations is required to maximize the yield at short time scales.

The linker (HmIm) for ZIF-L has a pKa that corresponds to the amine group (7.9) (Figure 4.2c). Crystalline ZIF-L was observed in the pH range between 7.4-8.3. A maximum yield of $48 \pm 5\%$ was found at pH 7.8 \pm 0.3. It should be noted a slightly higher yield of $53 \pm 2\%$ was found at pH 8.3 \pm 0.3, but due to the comparable yields and variability in yields near pH 8.3 for ZIF-L, we decided to characterize the synthesis at pH 7.8. This region corresponds to where 47% of linkers are deprotonated and over 94% of zinc ions are available to coordinate based on calculated speciation curves. The STY for ZIF-L in this work (2879 kg m⁻³ day⁻¹) is two orders of magnitude higher than other reported ZIF-L syntheses and is of comparable magnitude when considering the more commonly researched polymorph, ZIF-8 (Figure 4.3a, Equation (A4.2), Table A4.1).^{14,18,34,38,51–53} The linker for HKUST-1 (H₃BTC) has three pKas associated with successive deprotonation of three carboxylic acid groups (3.1, 3.9, 4.7) (Figure 4.2d). Crystalline HKUST-1

was observed in the pH range between 2.0-5.7. A maximum yield of $50 \pm 3\%$ occurred at pH 3.3 ± 0.1 where 66% of the linker species are at least singly deprotonated and 100% of copper ions are available to coordinate based on speciation calculations. The STY for the highest yielding synthesis was calculated as 2288 kg m⁻³ day⁻¹ which is comparable to the highest reported STY values for aqueous, room temperature synthesis for HKUST-1 (**Figure 4.3a, Equation (A4.2)**, **Table A4.1**).⁵⁴ For all MOFs, the highest yields were obtained in the solution pH range where both labile metal nodes and partially deprotonated linkers were the most abundant species, confirming that a high concentration of both reactive species is required for the rapid formation of MOFs.

We further characterized the MOFs resulting from the maximum yield conditions from the pH study, which were pH 3.9 ± 0.1 for UiO-66-NH₂, pH 4.9 ± 0.1 for UiO-66, pH 7.8 ± 0.3 for ZIF-L, and pH 3.3 ± 0.1 for HKUST-1. Scanning electron microscopy (SEM) showed UiO-66-NH₂ and UiO-66 resulted in crystals with nanoparticle morphology (**Figure 4.2e,f**). Such a morphology indicates that a rapid coordination reaction between the metal ion cluster and the linker induces rapid nucleation.²⁷ The optimum yield of ZIF-L resulted in intergrown particles ranging from 1-2 µm, differing from the leaf-like morphology typically observed in conventional syntheses (**Figure 4.2g**).^{34,55} HKUST-1 yielded bimodal particle distribution including ill-defined nanoparticles and well faceted 5 µm particles with morphologies typically observed in HKUST-1 (**Figure 4.2h**).⁵⁶

To analyze the porosity and stoichiometry of each material, Brunauer-Emmett-Teller (BET) isotherm analysis and thermogravimetric analysis (TGA) were performed on the rapidly synthesized MOFs that gave the highest yield, and these numbers were compared to MOF controls synthesized using previously published solvothermal techniques (**Figure A4.4, A4.5**).^{34,57–59} TGA

is frequently used to study missing linker defects in MOFs.^{25,58,60} By considering the aerobic decomposition of the framework, the ratio between molecular weight of a MOF to its resulting metal oxide yields the metal-organic to metal-oxide ratio. Comparing this ratio to the ideal stoichiometry reveals deviations in organic to metal mass composition which can be used to estimate non-stoichiometric defects (i.e. missing metal-ion cluster or organic linker defects, where a lower ratio indicates lower organic content and higher ratio indicates lower metal ion cluster content).⁵⁸ The presence of both defect types has consequence on the porosity (and thus specific surface area) as well as potentially reactive open metal sites in the case of missing linker defects, which is desirable for reaction and adsorption-based applications.^{30,58,61,62} It should also be noted that stoichiometry as shown by TGA does not guarantee crystallinity, as the presence both defects at high concentrations may balance stoichiometrically, but yield a heavily defected structure. While there is some debate about the accuracy of TGA, this technique is widely accepted for determining missing linker defects in combination with PXRD.^{25,58,60} Nitrogen isotherms were measured to determine the porosity and surface area of each precipitate. Finally, PXRD was used to determine the amount of crystalline material.

	Approx. Linker per Node	BET Surface Area (m²/g)	% Conversion	% Selectivity	% Yield	STY (kg day ⁻¹ m ⁻³)
UiO-66-NH2						
Rapid	11.5 ± 0.2	717 ± 128	96 ± 1	38 ± 3	37 ± 3	3381 ± 54
Control	11.1 ± 0.2	87366	38 ± 4	47 ± 2	18 ± 3	6 ± 1
UiO-66						
Rapid	8.5 ± 0.1	339 ± 35	96 ± 1	17 ± 4	13 ± 3	2732 ± 90
Control	11.5 ± 0.3	112567	104 ± 5	44 ± 1	46 ± 3	58 ± 2
ZIF-L						
Rapid	1.7 ± 0.1	120 ± 20	103 ± 7	45 ± 3	48 ± 5	2879 ± 196
Control	2.0 ± 0.1	16143	71 ± 1	59 ± 1	42 ± 1	30 ± 2
HKUST-1						
Rapid	4.4 ± 0.2	1372 ± 279	86 ± 4	58 ± 1	50 ± 3	2288 ± 102
Control	4.0 ± 0.2	174068	83 ± 3	84 ± 1	69 ± 3	17 ± 1

Table 4.1 Table including approximation of linkers per node for each MOF, indicating missing linker defects, BET surface area, % conversion, % selectivity, % yield and space-time yield (STY) of converted rapidly synthesized MOF and solvothermal MOF products. Error is reported as the standard deviation of N=3 samples.

Table 4.1 shows the results of the analyzed TGA, BET specific surface area, and percent crystallinity of the highest yield samples and their respective solvothermal controls. The rapid synthesis of UiO-66-NH₂ was found to have similar missing linkers per node compared to the solvothermal control (11.5 ± 0.2 and 11.1 ± 0.2 , respectively) (**Table A4.2**). The specific surface area of the rapid synthesis was found be lower than the control at 717 vs. 873 m²/g, but falls within reported ranges for UiO-66-NH₂.^{33,57} The percent crystallinity, or selectivity, was also found to be lower at 38 vs. 47% for the rapid and solvothermal synthesis, respectively, which may indicate a more defected crystal structure for the rapid synthesis. UiO-66 was found to have significantly lower organic to metal mass ratio, specific surface area, and crystallinity. Upon further analysis, the TGA data reveals 8.5 ± 0.1 linkers per metal node compared to an ideal 12 (**Table A4.2**). Our result agrees with work performed by De Vos *et al.*, who concluded the UiO-66 lost significant structure and porosity at 7.7 linkers per node.⁶¹ The heavily defected structure aligns with our

hypothesis that the solubility limited concentration of deprotonated H₂BDC linkers resulted in lower linker composition of UiO-66 in the 10 minute synthesis. A similar trend with lower values for surface area and crystallinity was observed for ZIF-L. We estimate there are 1.7 linkers per node compared to the ideal 2 (**Table A4.2**). The missing linker defects likely contribute to the reduced specific surface area and crystallinity compared to the control. We found the linkers per node in rapid HKUST-1 to be comparable to the control ($4.4 \pm 0.2 \text{ vs } 4.0 \pm 0.2$) (**Table A4.2**). Further, the specific surface area of the rapid HKUST-1 remains lower compared to the control (1372 vs. 1740 m²/g), however this value remains within the range of reported surface areas.^{54,59} Given the full material characterization, we have demonstrated UiO-66, UiO-66-NH₂, ZIF-L, and HKUST-1 can all be formed in room temperature aqueous solutions in 10 minutes by tuning reactant concentrations via pH to favor the coordination reaction, however UiO-66 is hypothesized to be limited by reactant solubility and produced a heavily defected structure.

To better understand the timescale of formation for UiO-66-NH₂, we employed a flash freezing technique to arrest the optimal reaction that led to the highest MOF yield, at various time points. Frozen solutions were lyophilized to remove solvent, and PXRD was used to track the development of the strongest diffraction peak related to each MOF. **Figure 4.3b** shows the development of the integrated (111) peak intensity as a function of reaction time. The inset shows frames of the reaction mixture evolution in the first 15 seconds. No significant change in pH was observed during the reaction, indicating that relative abundance of deprotonated linker species remains constant during coordination and crystallization. Stills from the slow-motion video (**Figure 4.3b inset**) show precipitation occurring as linker solution is injected into metal solution, which is a combination of the linker and MOFs precipitating out of solution (**Figure 4.3c**). It can be seen that 70% of reaction yield as measured by crystallinity occurs within 30 seconds, with no

significant change in crystallinity from 5 to 30 minutes (**Figure 4.3b**). To the best of our knowledge, this is one of the fastest reported bulk formation of a zirconium-based MOF to date with the highest reported STY.^{12,15,17,39,50,63}



Figure 4.3 a) Space time yields of rapid synthesis performed in this work and highest reported values from literature for UiO-66-NH2, UiO-66, HKUST-1, and ZIF-L/ZIF-8. More information on techniques is available in Appendix Table A4.1. ^{12,14,16–18,33,34,36– ^{39,50,52–54,64} b) Time series of integrated (111) diffraction peak (black circles) and pH (white triangles) as a function of reaction time for UiO-66-NH2, with photographs of mixture at the early time points (inset). Scalebar is 20 mm. c) PXRD patterns of freeze-dried UiO-66-NH2 powders at different synthesis times with peak integration band for the (111) crystal plane.}

4.5 Conclusion

Here we demonstrate an approach to rapidly produce a range of MOFs using room temperature aqueous synthesis. By using a concentration limited reaction hypothesis and adjusting the appropriate reactant concentrations by using pH, we were able to enhance the coordination reaction kinetics to form MOFs at an accelerated time scale to achieve rapid synthesis for four prototypical MOFs, UiO-66-NH₂, UiO-66, ZIF-L and HKUST-1 with space-time yields greater than 2250 kg m⁻³ day⁻¹. In the case of zirconium-based MOFs, this is an order of magnitude higher than previously reported room temperature aqueous syntheses. We found tuning the relative abundance of deprotonated linkers, labile metal nodes, and the solubility of species via pH had significant impact on the yield of crystalline MOFs. Flash freezing measurements found that the precipitation of MOF crystals happened on the order of 30 seconds with complete crystallization occurring at 5 minutes. The time scale, yield, and aqueous synthesis all lend to developing scalable production techniques of several prototypical MOFs. We hypothesize the guidelines and techniques developed in this study can be extended to other MOFs, given the reactants meet speciation and solubility requirements outline in this work. Further, this work contributes two fundamental pieces of information for MOF thin film formation: 1) Formation is not inherently kinetically limited and can be adjusted by reactant speciation and 2) the time scale of MOF formation can be adjusted to reach typical thin film deposition time scales while maintaining crystallinity (e.g. seconds to minutes). Future work in this dissertation will focus on using the enhanced kinetics to form thin film coatings for select applications as well as exploring controlling nucleation and growth kinetics at second to minute timescales.

4.6 Appendix

MOF Crystallinity Calculations

% Crystallinity is determined by comparing the crystalline scattering intensities to all scattering from the sample using the HighScore Plus X-ray Diffraction analysis software.⁴² In this analysis we assume the background and incoherent scattering are negligible within the scattering angles used. It should be noted this assumption provides a lower bound of crystallinity by increasing the denominator. Additionally, we assume the chemical composition and density are approximately the same for precipitates showing a measurable degree of MOF crystallinity, as these are likely amorphous coordination polymers. This is evidenced by the absence of non-MOF diffraction peaks and similar solubility characteristics of the precipitate to MOF. Given crystalline MOF product is our desired species, we use crystallinity a proxy to obtain the reaction selectivity. The crystallinity is calculated by integrating over diffraction angles associated with several MOF planes and the total signal as follows:

% Crystallinity =
$$\frac{\int_{2\theta_1}^{2\theta_2} I_{cr} d(2\theta)}{\int_{2\theta_1}^{2\theta_2} (I_{cr} + I_{am}) d(2\theta)}$$
Eq. A4.2

The following demonstrates how I_{cr} and I_{am} were determined for a UiO-66 NH₂ sample using a background subtraction in HighScore Plus:



Figure A4.1. Schematic showing % crystallinity analysis comparing the area under diffraction curve due to crystalline diffraction (I_{cr^+}) vs. amorphous (I_{am}) scattering. Amorphous region is shown as black and crystalline region is shown as the hashed region.



Figure A4.2. Typical PXRD diffraction patterns used to determined % crystallinity as a function of pH for a) UiO-66-NH₂ b) UiO-66 c) ZIF-L and d) HKUST-1. Crystallinity is assumed to be 100% if conversion provided insufficient material for PXRD after washing, representing an upper bound for MOF obtained.

Tabulated Conversion, STY, and synthesis method of published rapid syntheses

Space time yield calculation for solvothermal synthesis:

$$STY = \frac{Washed and Dried Precipitate Mass (kg)}{Synthesis Time (days) * Synthesis Volume (m3)}$$
Eq. A4.3

 Table A4.1. Table of conversion, space time yield (STY), synthesis method and conditions for rapid production of prototypical MOFs

MOF	Conversion	STY (kg m ⁻³ dav ⁻¹)	Method	Conditions	Source
		in duy)			This
UiO-66-NH ₂	96%	3381	This work	10 min, RT, H ₂ O	work
UiO-66-NH ₂	ca. 70%	2679	Microwave	Continuous, 85 °C, H ₂ O	12
UiO-66-NH ₂	ca. 100%	716	Aqueous	1 hr, RT, H ₂ O	17
UiO-66-NH ₂	105%	43	Solvothermal	18 hr, 120 °C, DMF	36
UiO-66-NH ₂	122%	37	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66-NH ₂	97%	21	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66-NH ₂	68%	21	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66-NH ₂	105%	16	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66-NH ₂	39%	12	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66-NH ₂	70%	10	Spray Drying	Continuous, 90 ℃, H ₂ O	37
UiO-66	79%	2732	This Work	10 min, RT, H ₂ O	This work
UiO-66	67%	672	Flow Reactor	Continuous, 130 °C, DMF	50
UiO-66	90%	53	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66	90%	43	Microwave	2 hr, 100 °C, DMF	39
UiO-66	115%	33	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66	151%	30	Solvothermal	12 hr, 80 °C, DMF	33
UiO-66	90%	26	Solvothermal	24 hr, 120 °C, DMF	36
UiO-66	55%	21	Solvothermal	18 hr, 120 °C, DMF	36
UiO-66	70%	12	Spray Drying	Continuous, 115 °C, DMF+ H ₂ O	37
UiO-66	60%	4	Spray Drying	Continuous, 180ºC, DMF	38
HKUST-1	86%	2288	This Work	10 min, RT, H ₂ O	This work
HKUST-1	98%	36000	Hydroxy Double Salt	$1 \min, RT, DMF + H_2O$	64
HKUST-1	100%	4533	Plug Flow Reactor	Continuous, 140ºC, EtOH	50
HKUST-1	N/A	4399	Counter Current Reactor	Continuous, 300°C, DMF + H ₂ O + EtOH	52
HKUST-1	90%	2035	Aqueous	1 hr, RT, H ₂ O	54

				Continuous, 160°C, H ₂ O +	
HKUST-1	64%	494	Aerosol Synthesis	EtOH	53
HKUST-1	N/A	225	Electrochemical	2.5 hr, RT, MeOH	14
				Continuous, 120ºC, DMF	
HKUST-1	85%	30	Spray Drying	+ H ₂ O + EtOH	38
				Continuous, 90°C, DMF +	
HKUST-1	68%	5.8	Microfluidic Droplet	$H_2O + EtOH$	16
					This
ZIF-L	103%	2879	This Work	10 min, RT, H ₂ O	work
				Continuous, 300°C, DMF	
ZIF-8	N/A	3875	Counter Current Reactor	+ H ₂ O +EtOH	34
ZIF-8	80%	2337	Aqueous	5 min, RT, H ₂ O	18
ZIF-8	N/A	100	Electrochemical	2.5 hr, RT, MeOH	14
ZIF-8	17%	69.4	Aerosol Synthesis	Continuous, 50°C, MeOH	53
ZIF-8	50%	67	Solvothermal	1 hr, RT, Methanol	64
ZIF-L	90%	39	Aqueous	4 hr, RT, H ₂ O	34
ZIF-L	90%	31	Aqueous	1 hr, RT, H ₂ O	34
ZIF-8	10%	4	Spray Drying	Continuous, 180°C, H ₂ O	38

Solubility of Linkers as a function of pH



Figure A4.3. Solubility of H₂BDC (red) and H₂ATA (blue) as a function of pH up to 0.2 M. It can be seen H₂ATA remains more soluble at lower pH values indicating a higher concentration of linkers is available for the coordination reaction.



Figure A4.4. Thermogravimetric decomposition curves of rapidly synthesized (blue) and solvothermal control (dashed red) MOFs of a) UiO-66-NH₂ b) UiO-66 c) ZIF-L and d) HKUST-1. N=3. All solvothermal controls exhibited solvent loss up to 300 °C as shown by the gradual loss of mass. ZIF-L shows a sharp drop in mass around 250 °C which is the loss of organic HmIm in the structure. The horizontal dashed lines represent the wt% for ideal stoichiometry (i.e. no missing linker or metal defects). The vertical dashed lines represent the temperature at which the solvent free wt% is used to calculate metal to organic composition.

 Table A4.2. Table of equations used to calculate missing linker defects using thermogravimetric analysis results

 Missing linker defect calculation for UiO-66-NH₂:

$$226\% = \frac{Zr_6O_6(ATA)_x}{6ZrO_2} = \frac{(642 + 179x)\frac{g}{mol}}{739\frac{g}{mol}}$$
Eq. A4.4

Solving for 2x gives the number of linkers per oxocluster:

$$2x = 2 \cdot \frac{226\% \cdot 739 \frac{g}{mol} 6ZrO_2 - 642 \frac{g}{mol} Zr_6O_6}{179 \frac{g}{mol} ATA} = 11.5 \frac{ATA}{Zr_6O_6}$$
Eq. A4.5

Missing linker defect calculation for UiO-66:

$$181\% = \frac{Zr_6O_6(BDC)_x}{6ZrO_2} = \frac{(642 + 164x)\frac{g}{mol}}{739\frac{g}{mol}}$$
Eq. A4.6

Solving for 2x gives the number of linkers per oxocluster:

$$2x = 2 \cdot \frac{181\% \cdot 739 \frac{g}{mol} - 642 \frac{g}{mol}}{164 \frac{g}{mol}} = 8.5 \frac{BDC}{Zr_6O_6}$$
Eq. A4.7

Missing linker defect calculation for ZIF-L:

$$248\% = \frac{Zn(mIm)_x}{ZnO} = \frac{(65 + 81x) \frac{g}{mol}}{81\frac{g}{mol}}$$
Eq. A4.8

Solving for x gives the number of linkers per zinc node:

$$x = \frac{248\% \cdot 81 \frac{g}{mol} - 65 \frac{g}{mol}}{81 \frac{g}{mol}} = 1.7 \frac{mIm}{Zn}$$
Eq. A4.9

Added linker defect calculation for HKUST-1: $248\% = \frac{Cu_3(BTC)_x}{3CuO} = \frac{(192 + 207x) \frac{g}{mol}}{239 \frac{g}{mol}}$ Eq. A4.10

Solving for x gives the number of linkers per copper dimer node:

$$2x = \frac{272\% \cdot 239 \frac{g}{mol} - 192 \frac{g}{mol}}{207 \frac{g}{mol}} = 4.4 \frac{BTC}{2Cu}$$
Eq. A4.11

$Zr_6O_6(ATA)_6(s) + (45 + 3x)O_2(g)$	
$\rightarrow 6ZrO_2(s) + 48CO_2(g) + 6NO_x(g) + 12H_2O(g)$	Eq. A4.12
$Ideal Weight Percent = \frac{Zr_6O_6(ATA)_6}{6ZrO_2} = \frac{1718\frac{g}{mol}}{739\frac{g}{mol}} \times 100\% = 232\%$	Eq. A4.13
$Zr_6O_6(BDC)_6(s) + 45O_2(g) \to 6ZrO_2(s) + 48CO_2(g) + 12H_2O(g)$	Eq. A4.14
$Ideal Weight Percent = \frac{Zr_6O_6(BDC)_6}{6ZrO_2} = \frac{1628\frac{g}{mol}}{739\frac{g}{mol}} \times 100\% = 220\%$	Eq. A4.15
$ \frac{Zn(mIm)_{2} \cdot (HmIm)_{\frac{1}{2}} \cdot (H_{2}O)_{\frac{3}{2}}(s) + (17.75 + 3x)O_{2}(g)}{\overset{@250^{\circ}C}{\longrightarrow} Zn(mIm)_{2}(s) + 2CO_{2}(g) + 6NO_{x}(g) + 7.5H_{2}O(g)}{\overset{@400^{\circ}C}{\longrightarrow} ZnO(s) + 10CO_{2}(g) + 6NO_{x}(g) + 14.5H_{2}O(g)} $	Eq. A4.16
<i>Ideal Weight Percent</i> = $\frac{Zn(mIm)_2}{ZnO} = \frac{225 \frac{g}{mol}}{81 \frac{g}{mol}} \times 100\% = 277\%$	Eq. A4.17
$Cu_3(BTC)_2(s) + 16.50_2(g) \rightarrow 3CuO(s) + 18CO_2(g) + 6H_2O(g)$	Eq. A4.18
Ideal Weight Percent = $\frac{Cu_3(BTC)_2}{3Cu0} = \frac{\frac{605 \frac{g}{mol}}{239\frac{g}{mol}} \times 100\% = 254\%$	Eq. A4.19

Table A4.3. Table of thermal decomposition equations used to calculate the ideal weight percent (i.e. defect free) for each MOF and calculations for ideal stoichiometric starting weight percent for thermogravimetric decomposition.





Figure A4.5. Nitrogen uptake isotherms of rapidly synthesized MOFs a) UiO-66 NH₂ b) UiO-66 c) ZIF-L and d) HKUST-1. Isotherms were used to calculate surface area using BET theory. The isotherms for UiO-66-NH₂ and UiO-66 present some mesoporosity based on the additional uptake towards high relative pressures representing a Type II or IV isotherm. This is likely due to the presence of nanoparticle agglomerates, as observed in SEM.

MOF Conversion Calculations

All syntheses were performed using a metal to linker ratio matching stoichiometry in a pristine

MOF, where the pristine formula for each MOF is shown below:

MOF Name	Pristine Chemical Formula
UiO-66-NH ₂	$Zr_6O_4(OH)_4(ATA)_6$
UiO-66	$Zr_6O_4(OH)_4(BDC)_6$
ZIF-L	$Zn(mim)_2 \cdot (Hmim)_{1/2} \cdot 1.5 H_2O$
HKUST-1	$Cu_3(BTC)_2 \cdot 3 H_2O$

Table A4.4. Table showing the pristine formulas of prototypical MOFs used to calculate conversion

Assuming all deprotonated linker and metal node component can participate in a reaction, 100% conversion is calculated via mass balance of metal (or metal oxide) nodes and deprotonated linkers. An example calculation for UiO-66 NH₂ is shown below:

9.1242 g Metal Solution x 0.069
$$\frac{g ZrOCl_{2} \cdot 8H_{2}O}{g Metal Solution} x \frac{1 \ mol \ ZrOCl_{2} \cdot 8H_{2}O}{322.25 \ g \ ZrOCl_{2} \cdot 8H_{2}O}$$
 Eq. 20
x $\frac{1 \ mol \ Zr_{6}O_{4}(OH)_{4}}{6 \ mol \ ZrOCl_{2} \cdot 8H_{2}O} x \frac{679.34 \ g \ Zr_{6}O_{4}(OH)_{4}}{1 \ mol \ Zr_{6}O_{4}(OH)_{4}} = 0.2212 \ g \ Zr_{6}O_{4}(OH)_{4}$

10.3171 g Linker Solution x 0.034
$$\frac{g H_2 ATA}{g Linker Solution} x \frac{179.15 g ATA^{2-}}{181.15 g H_2 ATA}$$
 Eq. 21

$$= 0.3510 \ g \ ATA^{2-}$$

Therefore, 100% conversion of all reactants:

$$0.2212 g Zr_6 O_4 (OH)_4 + 0.3510 g ATA^{2-} = 0.5722 g Zr_6 O_6 (ATA)_x$$
 Eq. 22

Where x depends on the number of linker defects present in the precipitate. It should be noted the HmIm was the limiting reagent for the ZIF-L reaction, therefore conversion was calculated with respect to HmIm.

Tabulated Yield Results

MOF	pH @ 10 Minutes	% Conversion	% Crystallinity	% Yield
UiO-66-NH ₂	2.5 ± 0.1	4 ± 1	N/A (1)	4 ± 1
	2.7 ± 0.1	18 ± 10	N/A (1)	18 ± 10
	3.4 ± 0.1	96 ± 1	42 ± 4	40 ± 4
	3.9 ± 0.1	96 ± 1	38 ± 3	37 ± 3
	4.0 ± 0.1	96 ± 1	40 ± 1	39 ± 1
	4.4 ± 0.1	92 ± 2	37 ± 2	34 ± 3
	4.7 ± 0.1	84 ± 1	30 ± 4	26 ± 3
	5.1 ± 0.1	81 ± 7	18 ± 1	14 ± 2
	6.2 ± 0.4	62 ± 3	0	0
	13.2 ± 0.4	47 ± 1	0	0
	Control	38 ± 4	47 ± 2	18 ± 3
UiO-66	2.9 ± 0.1	4 ± 1	N/A (1)	4 ± 1
	3.7 ± 0.1	9 ± 1	N/A (1)	9 ± 1
	4.3 ± 0.1	34 ± 4	22 ± 2	8 ± 2
	4.9 ± 0.1	79 ± 2	17 ± 4	13 ± 3
	5.1 ± 0.1	74 ± 2	13 ± 2	10 ± 2
	5.2 ± 0.1	71 ± 3	14 ± 5	10 ± 4
	6.8 ± 0.3	60 ± 2	0	0
	12.5 ± 0.3	40 ± 1	0	0
	Control	104 ± 5	44 ± 1	46 ± 3
ZIF-L	7.0 ± 0.1	13 ± 1	N/A (1)	13 ± 1
	7.4 ± 0.1	89 ± 8	49 ± 2	44 ± 5
	7.6 ± 0.1	102 ± 3	48 ± 1	49 ± 3
	7.8 ± 0.3	103 ± 7	46 ± 2	48 ± 5
	8.3 ± 0.3	107 ± 1	49 ± 1	53 ± 2
	8.2 ± 0.2	108 ± 2	43 ± 8	47 ± 9
	9.1 ± 1.0	107 ± 1	21 ± 18	22 ± 19
	Control	71 ± 1	59 ± 1	42 ± 1
HKUST-1	2.0 ± 0.1	49 ± 11	45 ± 4	22 ± 7
	3.3 ± 0.1	86 ± 4	58 ± 1	50 ± 3
	3.8 ± 0.1	99 ± 2	42 ± 1	41 ± 1
	4.1 ± 0.1	100 ± 2	34 ± 2	34 ± 2
	4.9 ± 0.1	100 ± 1	22 ± 1	23 ± 2
	5.2 ± 0.1	97 ± 1	19 ± 1	18 ± 1
	5.7 ± 0.1	95 ± 2	12 ± 4	12 ± 4
	6.5 ± 0.2	89 ± 1	0	0
	7.0 ± 0.1	75 ± 5	0	0
	Control	83 ± 3	84 ±1	69 ± 3

Table A4.5. Table of pH value after 10-minute reaction time, % conversion, % crystallinity, and % yield for rapidly synthesized MOFs and controls. N=3 syntheses. Crystallinity is assumed to be 100% if conversion provided insufficient material for PXRD, representing an upper bound for MOF obtained.

4.7 References

Sections of this chapter are published following works:

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5 In situ Studies of UiO-66 Formation

5.1 Abstract

Understanding MOF crystallization is required to control morphology, crystal quality, and to improve thin film deposition processes. This is especially true for MOFs that have more complex metal oxocluster nodes that tend to show greater chemical and thermal stability as well as a wider range of applications. Here we utilize *in situ* wide angle X-ray scattering (WAXS) to gain insight into the crystallization mechanisms that govern the nucleation and growth of a zirconium oxocluster based MOF, UiO-66. In this study, we build on previous work that details understanding MOF crystallization from a reaction-crystallization framework and separate formation steps for a more detailed view of the process. A frequently used model, termed the Gualtieri model, is used to extract quantitative kinetic rate constants for nucleation and growth. By observing the crystallization kinetic response to varying reaction parameters, we gain insight into the crystallization mechanism and find the activation energies associated with nucleation and growth rate constants are nearly identical 78 ± 9 kJ/mol for nucleation and 83 ± 3 kJ/mol for growth, indicating energetically similar mechanisms. Further, we explore the kinetics as a function of initial reactant concentrations by varying metal, linker, and modulator concentrations. Observations of these effects allow us to propose a formation mechanism for UiO-66 that has led to the development of a simulation model for UiO-66 crystallization.

With the exponential growth and proven utility of MOFs, understanding and controlling the crystallization at enhanced timescales has become increasingly important for controlling morphology and quality for thin film deposition processes and beyond. The crystallization of MOFs is often compared to their inorganic analog, zeolites. Classical crystallization concepts involving nucleation and growth from a monomeric building unit have frequently been applied to both systems. In the case of MOFs, the governing principles for this building unit composition have ranged from requiring the units to be a 'point zero charge molecule' (pzc) or primary or secondary building units (PBU, SBU) defined as the smallest stoichiometric and structural unit of the framework, respectively.^{1,2} Under this mechanism, nucleation and growth are proceeded by the monomeric addition of building units to form MOF bulk material. Other non-classical mechanisms have been proposed and observed experimentally for nucleation and growth of MOFs. Two-step nucleation, where a densified amorphous gel or polymer forms prior to self-assembly, is often experimentally observed in zeolites. Additionally, growth mechanisms involving aggregation and population balance models have also been proposed, where nano-crystalline particles aggregate to form larger particles. This has been observed experimentally, where oriented attachment and growth of $[{Cu_2(ndc)_2(dabco)}_n]$ nanoparticles has been directly observed using transmission electron microscopy (TEM).³ With a variety of viable formation mechanisms, it is important to understand the early stage formation of MOFs to better control subsequent crystallization.

MOFs with metal oxocluster nodes are of particular interest due to their high thermal and chemical stability, as well as their catalytic activity.^{4–6} These are typically formed from less complex metal salts that reassemble to a metal oxocluster topology found in the final MOF structure. Several *in situ* studies have focused on understanding the crystallization kinetics of

zirconium-based MOFs.^{1,7} Reported studies tend to focus on observing the effect of a chemical modulator on the resulting formation kinetics from a zirconium salt. For example, Gascon *et al.* demonstrated hydrochloric acid played an autocatalytic role in the crystallization of UiO-66 from an amorphous framework using *in situ* x-ray scattering combined with density functional theory. In another study, Behrens *et al.* explored the effect of solvent and modulator on the formation mechanism of a Zr-fumarate MOF. In this case they showed the addition of modulator had an accelerating effect on the formation kinetics. In both cases, the formation mechanism of the zirconium oxocluster node and nucleation and growth are lumped as an apparent rate, even though it is known the formation of zirconium oxocluster species tend to be kinetically hindered.⁸ Such an approach obfuscates crystallization mechanism insight by lumping early-stage crystallization with a kinetically hindered precursor formation step. Thus, we posit that studying the reaction-crystallization of UiO-66 by separating the oxocluster formation from the reaction will give further insight into a nucleation and growth mechanism at an accelerated timescale.

In Chapter 4, we reported a rapid synthesis for multiple MOFs, including UiO-66 that employed the controlled SBU approach. We demonstrated the kinetics were significantly enhanced by treating the system as a reactive-crystallization, where pre-forming the oxo-cluster and controlling the deprotonated linker species precipitated MOF in seconds. Here, we choose to study a modified synthesis originally developed by Farha *et al.* which also uses a preformed zirconium oxocluster in a DMF solution modulated by acetic acid.⁹ This synthesis was chosen because all species remain solubilized, permitting unhindered *in situ* studies using wide-angle X-ray scattering (WAXS). In this study, we employ a formation mechanism posed by Whittingham *et al.* to explain our findings.¹ They hypothesize a soluble metal complex is formed upon dissolution that likely complexes with the organic linkers to form a basic building unit (**Figure 5.1a**). We combine this

with our understanding of the kinetically hindered hexanuclear oxocluster formation to complete the framework. An more simple physical model is used to fit kinetic parameters for MOF and zeolite growth, termed the Gualtieri model (**Figure 5.1b**). We relate model kinetic parameters to reaction conditions of temperature, metal and linker concentration ratio and acetic acid concentration to gain insight into the nucleation and growth mechanisms as they relate to reaction conditions. To the best of our knowledge, this is first *in situ* study deconvoluting the oxocluster formation step from UiO-66 crystallization to give a clearer picture of the formation mechanisms.



Figure 5.1. (a) Schematic showing the proposed reaction-crystallization mechanism of UiO-66 where metal and linkers first coordinate to form a building unit, then building units coordinate to form the crystalline structure (b) the resulting diffraction pattern as a function of time with the (111) peak area normalized over time(black circles) for fitting the Gualtieri model (red line) and nucleation probability derived from the model (blue dash).
5.3 Materials and Methods

Materials

All reagents were used as received with no further purification. Zirconium (IV) propoxide solution (70 wt% in 1-propanol, Sigma Aldrich), acetic acid (Glacial, Sigma Aldrich), and N,N dimethylformamide (DMF, 99.8%, Sigma Aldrich) were used to synthesize a node solution. Terephthalic acid (H₂BDC, 98%, Sigma Aldrich) and N,N dimethylformamide (DMF, 99.8%, Sigma Aldrich) were used to prepare linker solution. Graphite (powder, $< 20 \mu m$, synthetic, Sigma Aldrich) was used in the nucleation type study.

UiO-66 Synthesis

The synthetic procedure was adapted from work by Farha *et al.*⁹ A zirconium oxocluster node solution was prepared by mixing 142 μ L of Zirconium (IV) propoxide in a mixture of 4 mL of acetic acid and 7 mL of DMF in a 20 mL scintillation vial. The solution was wrapped in foil and heated on a hotplate at 155 °C for 2.25 hours and resulted in a pale yellow solution. Linker solution was prepared by mixing X g of H₂BDC in 5 mL of DMF until fully dissolved. For a typical synthesis, 5 mL of zirconium node solution was placed in a custom glass reactor along with 4.5 mL of fresh DMF and a stir rod. 0.5 mL of linker solution was loaded into a computer controlled syringe pump. Temperature was controlled via thermocouple places in the reactor and heating tape wrapped around the reactor. The reaction was initiated by rapidly injecting linker solution into the stirred metal solution. Concentration was varied by adjusting the initial amount of metal solution in the reactor or the quantity of linker solution injected with volumes held constant by the addition of solvent (DMF or a DMF/acetic acid mixture).

In Situ Wide Angle X-ray Scattering (WAXS) Experiments

In situ WAXS experiments were performed at beamline 10-2 in the Stanford Synchrotron Radiation Lightsource (SSRL) at SLAC National Laboratory (Menlo Park, California) with a beam energy of 17 keV. Two dimensional patterns were recorded at 1 second exposure times with an Eiger 1M Hybrid Photon Counting (HPC) detector (Eiger) with a sample to detector distance of 1 m. A custom blown glass reactor with a 1 mm solution X-ray pathlength was used to run each synthesis. Linker solution injection and data collection were synchronized via computer control. Temperature was controlled using a thermocouple submerged in the reaction solution and a heating tape surrounding the reactor. The reactor was scrubbed with soap and water, then sonicated and rinsed with DI water and acetone after each reaction.

WAXS Data Analysis

WAXS data was reduced and analyzed with a Python script with the pyFAI module. After background subtraction, peaks were fit with Gaussian curves to determine curve area and FWHM for each frame for the (111) and (222) peak. Resulting values were exported as raw data to calculate extent of crystallization and coherence length, respectively.

Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) micrographs were collected using a Helios Dual Beam FIB G4 UC with an accelerating voltage of 5 kV and 0.80 nA current.

Thermogravimetric analysis

The metal to linker ratio of MOFs was measured by the Thermogravimetric Analyzer (TGA, Q50). In a typical experiment, a small amount of pre-dried powder (\sim 10 mg) was loaded into a Pt sample pan, and the sample pan was transferred into the heating chamber of the analyzer. The sample gas was air (flowrate = 60 mL/min), and the balance gas was nitrogen (flowrate = 40

mL/min). The sample was heated to 800 °C from room temperature at a rate of 10 °C/min. In the initial stage of the heating process, moisture adsorbed by the sample was evaporated, and the sample weight at 400°C was taken as the dry weight. Further heating led to the decomposition of the sample (i.e., organic linkers and organic fabric were decomposed by oxidation and metal nodes were transformed into metal oxide), and the sample weight at 800 °C was taken as the weight of metal oxide.

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The controlled SBU approach allows for UiO-66 synthesis to be studied 1) at a rapid time scale and 2) as a step-wise process, where crystallization from the coordination between the cationic metal cluster node and anionic linker can be studied separately from the node-complex formation. Briefly, an oxocluster node solution is prepared by heating zirconium proposide in the presence of acetic acid at 155 °C for two hours and allowed to cool before mixing with a linker solution. The base condition was considered with a metal to linker ratio equivalent to that found in the final MOF at 25 °C (~1:1, 14.4 mM Zr, 16.3 mM H₂BDC). To understand this reaction crystallization in more detail, the system was varied by changing metal cluster concentration relative to linker concentration, temperature, and acetic acid modulator concentration. The kinetics were evaluated by observing the growth of the (111) Bragg reflection to give the extent of crystallization, α (Figure 5.1b,c). The Gualtieri model was then fit to determine kinetic rates including the nucleation rate constant, k_n (defined as l/a in the model), growth rate constant, k_{α} , and growth dimensionality, n and nucleation probability distribution, b, and these values were compared across conditions.¹⁰ A full description of the model derivation is offered in the Appendix.

$$\alpha = \frac{1}{1 + e^{-(t-a)/b}} \left[1 - e^{-(k_g t)^n} \right]$$
 (Eq. 5.1)

5.4.1 Temperature Effects



Figure 5.2. (a) Extent of crystallization of the 111 Bragg reflection for UiO-66 at 25 °C, 35 °C and 45 °C and (b) Arrhenius plot of nucleation rate constant and growth rate constant used to calculate the activation energy associated with each rate

Table 5.1. Gualtieri fitting parameters and synthesis conditions for UiO-66 at different temperatures. It should be noted the base condition was run 4 times to understand variability in the experiment. All conditions were run at the following concentrations: 14.4 Zr, 16.3 H₂BDC, 3.18 HAc.

	Gualtieri Rate Constants					
Temp (°C)	kg (1/s)	kn(1/s)				
25	$2.6E-03 \pm 3.6E-04$	$7.0E-03 \pm 9.3E-04$				
35	7.28E-03	1.60E-02				
45	2.14E-02	5.11E-02				

UiO-66 was synthesized between 25 °C and 45°C with constant metal, linker and acetic acid concentrations of 14.4 mM, 16.3 mM and 3.2 M, respectively, in DMF. Figure 5.2a shows the extent of crystallization occurs faster as temperature increases with the 25 °C synthesis requiring about 3600 seconds and the 45 °C synthesis reaching a plateau around 2000 seconds. Each curve was fit with the Gualtieri model to better quantify the kinetics with values reported in Table 5.1. As expected for a reaction, the growth rate constant is observed to increase as a function of temperature, as does the nucleation rate constant. The rate constants associated with MOF growth have widely been reported as following the Arrhenius relationship for both the nucleation

Activation energy results match reports for other MOFs in the range of ~50-100 kJ/mol.⁷ Among these reports, nucleation and growth rate constant activation energies remain similar in magnitude if not nearly identical.^{7,12,13} In the case of zirconium based MOFs, a zirconium fumarate MOF synthesized from a salt metal source in DMF was reported as 71 ± 3 kJ/mol for nucleation and 66 ± 6 kJ/mol for growth.¹³ Other approaches using zirconium salt, DMF and hydrochloric acid report 46 kJ/mol for nucleation and 39 kJ/mol for growth.¹² In cases of using zirconium salts, we hypothesize the formation of the metal node is the rate limiting step as the formation of hexanuclear zirconium is known to be kinetically hindered.^{8,14} To test this with our synthesis, we tried synthesizing UiO-66 at 25 °C without preforming the metal node first and no detectable crystals form. Additionally, the SBU approach requires much lower temperatures to proceed, indicating it is not kinetically hindered. Because of this, we hypothesize the previous reports of nucleation and growth rate activation energies are equivalent because they may be largely represented by the activation energy of the zirconium oxocluster formation, as it may have been the rate limiting step during formation.

When the rate limiting step is removed using the SBU approach the induction time decreases (minutes compared to hours) and overall reaction rate increases compared to the salt synthesis. Direct comparison of the activation energies of salt-based syntheses and SBU proves difficult due to varied chemical modulating species and complex reaction mechanisms. However, the same activation energy relationship is observed as the salt based synthesis, where nucleation and growth activation energies are equivalent, indicating the hexanuclear oxocluster formation

may not be rate limiting at higher temperatures.^{7,12,13} The closeness of these values leaves differentiating the nucleation and growth mechanisms as a function of temperature for UiO-66 a difficult task. Given the preformed SBU, it is reasonable to think both nucleation and growth most simply occur by the replacement of the acetate modulator with a bridging terephthalate ligand, which has been hypothesized to be independent of cluster or bulk crystal size for other zirconium based MOFs.¹³ While more work on differentiating nucleation and growth is required, the current observations suggest the aggregation and addition of building units during nucleation and growth

of UiO-66 appear to be kinetically similar.¹





Figure 5.3. (a) Extent of crystallization of the 111 Bragg reflection for UiO-66 at varied metal to linker ratios and (b) Extent of crystallization of the 111 Bragg reflection for UiO-66 at varied acetic acid concentrations

			Gualtieri Rate Constants					
Zr Conc (mM)	H ₂ BDC Conc (mM)	Acetic Acid Conc (M)	kg (1/s)	kn(1/s)	kn/kg			
14.4	16.3	3.2	$2.6E-03 \pm 3.6E-04$	$7.0E-03 \pm 9.3E-04$	2.7 ± 0.1			
7.2	16.3	3.2	1.5E-03	2.5E-03	1.7			
14.4	8.15	3.2	2.4E-04	6.2E-04	2.6			
14.4	16.3	6.0	4.7E-05	1.3E-04	2.9			

Table 5.2. Gualtieri fitting parameters and synthesis conditions for UiO-66 at different reactant concentrations. It should be noted the base condition was run 4 times to understand variability in the experiment. All experiments were run at 25 °C.

To test the effect of metal, linker and modulator concentration on the crystallization kinetics, each was varied independently at a constant temperature. **Figure 5.3a** shows the extent of crystallization over time for a base condition, 14.4 mM Zr, 16.3 mM H₂BDC and 3.2 M Acetic Acid at 25 °C, compared to when the metal concentration is halved (7.2 mM Zr, blue squares) and when the linker concentration is halved (8.2 mM H₂BDC, green triangles). The plots show there is a differing kinetic dependence between the metal and linker concentrations. The half-linker solution sees almost a 10-fold decrease in nucleation and growth rate constants (e.g. 7.0E-3 s⁻¹ to

6.2 E-4 s⁻¹ for k_n) with the nucleation to growth rate ratio staying the same as the base condition $(k_n/k_g=2.6)$ (**Table 5.2**). Interestingly, the metal concentration shows an overall weaker influence on rate constants, but a stronger influence on the nucleation rate constant, showing almost a ~2.8-fold reduction versus a ~1.7-fold reduction for the growth rate constant. Such trends are indicative of a reaction-crystallization, where the crystallization is driven by a concentration dependent reaction.

The above trends indicate two important characteristics: 1) rates of UiO-66 formation are more strongly dependent on linker concentration and 2) metal node concentration biases the crystal formation mechanisms towards growth. To explore these effects, we looked towards syntheses with non-stoichiometric metal to linker ratios.^{4,15–17} Lillerud *et al.* were able to synthesize a defect free UiO-66 using a 1:2 Zr:BDC ratio as in this work. They hypothesized the higher linker concentration shifted solution equilibrium in favor of the BDC-Zr bond to create a defect free structure. In a similar fashion, we hypothesize the linker-modulator (BDC:Ac) ratio changes the equilibrium of how many dangling organic linkers attach to the building unit. In the case of reduced metal concentration, the BDC:Ac ratio remains the same. Thus, building units will be at a lower concentration with the same number of dangling linkers. For this condition we draw an analogy to supersaturation from classical crystallization, where lower supersaturations (i.e. concentrations of building units or solute) tend to bias growth over nucleation.

A different case arises when the linker concentration is lowered by half. Here the BDC:Ac concentration is reduced and the number of dangling linkers on each building unit is reduced. De Vos *et al.* showed the UiO-66 requires a minimum of ~8 linkers per node to form a crystalline structure.¹⁶ We hypothesize this requirement translates to the building unit, where a viable building unit must at minimum have ~4 dangling linkers per metal node to participate in crystallization,

where 4 dangling linkers corresponds to 8 linkers per node in the final structure. As such, lowering the BDC:Ac ratio significantly limits the number of viable building units and the production of building units becomes rate limiting. "Supersaturation" becomes so low that the nucleation and growth rates are equivalent as viable building units are consumed as fast as can be produced. A similar effect is observed when we add acetic acid and keep the metal to linker ratio constant, however the overall rate of production of viable building units appears to significantly reduce with higher acetic acid concentration resulting in significantly lower nucleation and growth rate constants (**Table 5.2**).

To further understand how reaction conditions influenced the final UiO-66 structure, thermogravimetric analysis (TGA) was used to determine the metal to linker ratios in each condition. TGA found only slight differences in the metal to linker defects across the concentration (**Table A5.2**). The half metal and half linker conditions showed identical linkers per node at ~8.8 and ~8.7, respectively. These values are close to the viable linker per node proposed earlier and support the viable building unit hypothesis. A slightly higher linker to node count was found for the higher acetic acid condition at ~9.4 linkers per node. We hypothesize this is likely due to the higher reaction time, where defect healing occurs on the same time scale as the crystallization.

5.4.3 Nucleation Type

The Gualtieri model also suggests type of nucleation based on nucleation the probability distribution, b. Where b > 1200 is autocatalytic nucleation, b < 900 s is heterogeneous b=1200 and is homogeneous. These classifications are based on empirical observations hypotheses developed from and



Figure 5.4. Extent of crystallization of the (111) peak for UiO-66 with and without the addition of 0.5 wt% graphite with an inset showing the early time scale curves

zeolite formation from gels, hence we are hesitant to directly apply them to our system.^{10,18} In all cases presented in this work we observe heterogeneous nucleation as defined by the Gualtieri model except for the high acetic acid concentration case, which is autocatalytic (**Table A5.3**). For additional insight into the nucleation mechanism, we introduced 0.5 wt% of 20 μ m graphite particles to act as heterogeneous nucleation sites. With the addition, we estimate the total available surface area to be 3 times that of the synthesis vessel, we hypothesized an increase in nucleation rate should occur.

Figure 5.4 shows the extent of crystallization curves generated for the base reaction condition and the base condition with the addition of 0.5 wt % graphite. The initial increase of the curve and induction time appear to not be significantly influenced by the additional nucleation sites. **Table 5.3** shows the addition of graphite only slightly decreases the induction time from 146

	Gualtieri Fitting Parameters						
Graphite	a (s)	b (s)	kg (1/s)	kn(1/s)	kn/kg		
0	146 ± 20	53 ± 3	$2.6E-03 \pm 3.6E-04$	$7.0E-03 \pm 9.3E-04$	2.7 ± 0.1		
0.5 wt %	110	42	2.88E-03	9.1E-03	3.2		

Table 5.3. Gualtieri fitting parameters for UiO-66 synthesized with 14.4 mM Zr, 16,3 mM H_2BDC and 3.2 M Acetic Acid at 25°C with and without the addition of graphite. It should be noted the base condition without graphite was run 4 times to understand variability in the experiment.

 \pm 20 s to 110 s corresponding to a moderate increase in nucleation rate constant (7.0 \pm 0.9 E-03 s⁻¹ vs. 9.1 E-03 s⁻¹). First order approximation would estimate the heterogeneous nucleation rate would scale proportionally as a function of area of available nucleation surfaces.¹⁹ While direct measurement of a nucleation rate is difficult, we do not observe such a drastic change using both the induction time and Gualtieri rate constant as proxy values. Even evaluating initial slopes seen in the inset of **Figure 5.4** yields no appreciable difference with respect to early-stage crystallization rate.

We interpret these results with two potential descriptions. The first is the driving force for crystallization is so high in the system that we are observing burst nucleation, where crystallization occurs rapidly and a monodisperse particle size is observed. Our system demonstrates both features in the kinetic curves and the monodisperse particle sizes observed under scanning electron microscopy (SEM) (**Figure A5.2**). In this case the addition of nucleation sites shows a minimal effect because the high driving force already makes crystallization favorable. The second is the nucleation mechanism is entirely independent of non-specific (i.e. non-UiO-66) heterogeneous nucleation surfaces. We hypothesize an autocatalytic mechanism may occur, where either the building unit formation or nuclei are templated by existing UiO-66 structures. In this case the increase in nuclei increases the rate of crystalline phase formation or building units and an "explosive" phase is observed.^{18,20} More work is required on unfolding this mechanism, however

instrumentation limitations and the vague definition of nuclei from an experimental viewpoint may limit more direct answers.²⁰

5.4.4 Towards a mechanistic model

Definitive insight into the nucleation and growth mechanisms of UiO-66 becomes increasingly difficult with pure experimental techniques as it is refined. Thus far, a combination of computational and experimental approaches has proven to be the most successful in detailing and understanding crystallization mechanisms of MOFs at a range of length scales. Experimental techniques, such as Fourier transfer infrared spectroscopy (FTIR), Raman spectroscopy, photoluminescence spectroscopy (PL), and extended x-ray absorption fine structure (EXAFS) have all been used for the *in-situ* tracking of synthesis components and building units at a length scale of angstroms to nanometers but fail to capture the long-range ordering and larger scale crystallization kinetics.^{11,21} Modeling and simulations at similar length scales have proven to show similar limitations.^{22,23} Density functional theory (DFT) and molecular dynamics (MD), while powerful in predicting structures, material properties, and early stage self-assembly, are limited to several hundred atoms and fail to capture long range ordering mechanisms. Conversely, experimental techniques such as small angle X-ray scattering (SAXS), wide angle X-ray scattering, transmission electron microscopy (TEM) and atomic force microscopy (AFM) have captured crystallization kinetics of MOFs on the lengths of nanometers to millimeters.^{7,11,24,25}

To compliment these techniques, rudimentary physical models such as the Johnson–Mehl– Avrami–Kolmogorov (JMAK) and Gualtieri Model have been successfully applied to a range of MOF kinetic studies, including this one.^{7,10} While these models offer insight into crystallization rate constants, growth dimensionality, and probability of nucleation (Gualtieri), they offer little to no insight into the crystallization mechanism and lack the ability to predict crystallization kinetics due to a limiting understanding of the system. Thus, the development of a kinetic model capable of detailing formation mechanisms at each scale remains a challenge in understanding MOF crystallization.



Figure 5.5. (a) Schematic of the initiation mechanism for the building unit P1 in the reaction model (blue) chain and step additions of clusters for the growth polymerization (green) and the surface-stabilized termination mechanism where Pmacs is the maximum aggregating cluster size.

To this end, we have used insight from the kinetic studies presented in previous sections to develop a mechanistic kinetic model of UiO-66 crystallization with our collaborators, the Singh group at the University of Illinois, Chicago. **Figure 5.5** shows a schematic of the mechanisms used as the foundation of the model. The first step involves formation of a primary building unit, P_i , which is composed of a zirconium oxocluster node with dangling linkers originally hypothesized in our kinetic studies. In this model, the building unit P₁ is formed by an autocatalytic reaction mechanism by metal nodes and linkers. The crystallization is then modeled by borrowing monomer addition and aggregation concepts from polymerization. The addition of P₁ to larger clusters occurs as chain growth, whereas aggregation of larger clusters occurs as step growth. Finally, this model introduces a surface- stabilized growth termination condition where a maximum aggregating cluster size, P_{MACS} , does not participate in step growth due to surface stabilization.

By combining this model with the *in situ* data from the WAXS study, we hope to develop greater insight into the mechanisms posed. Currently, the model appears to predict extent of crystallization behavior accurately. Additionally, data from WAXS coherence length detailing crystal domain size was also used to compare cluster size as a function of time, giving the model a more granular and spatial detail not found in Gualtieri or Avrami. A draft of this manuscript is currently being written for publication.

5.5 Conclusion

To conclude, we used in situ WAXS data to gain more insight into the crystallization mechanisms of UiO-66. By using the controlled SBU approach, in which metal oxocluster nodes are preformed, we were able to probe the crystallization mechanisms of UiO-66 more purely. Doing so eliminated the hypthosized rate limiting step, which we showed was indeed the metal oxocluster formation. The activation energies associated with the Gualtieri nucleation and growth rate constants were found to be approximately the same value at 78 ± 9 kJ/mol and 83 ± 3 kJ/mol, respectively. We interpret this as the nucleation and growth mechanism being kinetically similar. Further, we tested the effects of reactant concentration and modulator concentration. Our results could be explained by a building unit with dangling linkers hypothesis originally posed by Whittingham *et al.*¹ We showed how tuning the BDC:Ac concentration affected the viability of building units, whereas tuning the metal concentration tuned the overall concentration of building units. Such understanding fit with the concept of supersaturation from classical crystallization and this framework may be used to further control the crystallization of UiO-66. Finally, we explored the type of nucleation by introducing heterogeneous nucleation sites via graphite powder. No significant increase in nucleation was observed, which indicated either a burst nucleation scenario

or an autocatalytic nucleation mechanism. These results were all interpreted and developed into a mechanistic model that we are currently working on publishing with collaborators.



5.6 Appendix

Figure A5.1 Thermogravimetric decomposition curves for UiO-66 synthesized at varying conditions. Curves see solvent and free linker loss up to 400 C, after which the UiO-66 structure remains

Table A5.1. Table showing calcualtion of linkers per node from TGA data from UiO-66

Missing linker defect calculation for UiO-66:	
$181\% = \frac{Zr_6O_6(BDC)_x}{6ZrO_2} = \frac{(642 + 164x)}{739}\frac{g}{mol}$	Eq. A5.23
Solving for 2x gives the number of linkers per oxocluster: $2x = 2 \cdot \frac{181\% \cdot 739 \frac{g}{mol} - 642 \frac{g}{mol}}{164 \frac{g}{mol}} = 8.5 \frac{BDC}{Zr_6O_6}$	Eq. A5.24

	Linkers per	
Condition	node	
14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 25 °C		8.5
14.4 mM Zr, 8.2 mM H2BDC, 3.2 M Ac, 25 °C		8.7
7.2 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 25 °C		8.8
14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 35 °C		9.3
14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 45 °C		9.9
14.4 mM Zr, 16.3 mM H2BDC, 6.0 M Ac, 25 °C		9.4

Table A5.2. Linkers per node calcualted from TGA for select UiO-66 synthesis conditions

		Acetic					
Zr	H ₂ BDC	Acid					
Conc	Conc	Conc	Temn				

Table A5.3. Gualtieri Fitting Parameters for all conditions run in the study. All syntheses were performed in DMF.

	112000	1 I CIU							
Conc	Conc	Conc	Temp						
(mM)	(mM)	(M)	(°C)	a (s)	b (s)	kg (1/s)	n	kn(1/s)	Comment
14.4	16.3	3.18	25	172	57	2.10E-03	0.6	5.83E-03	Trial 1
14.4	16.3	3.18	25	130	50	2.74E-03	0.6	7.68E-03	Trial 2
14.4	16.3	3.18	25	152	53	2.62E-03	0.7	6.58E-03	Trial 3
14.4	16.3	3.18	25	129	51	2.94E-03	0.5	7.76E-03	Trial 4
14.4	16.3	3.18	25	110	42	2.88E-03	0.7	9.07E-03	0.5 wt% Graphite Added
14.4	16.3	3.18	35	62	29	7.28E-03	0.4	1.60E-02	
14.4	16.3	3.18	45	20	15	2.14E-02	0.4	5.11E-02	
14.4	8.15	3.18	25	1622	574	2.40E-04	1.4	6.17E-04	
7.2	16.3	3.18	25	395	112	1.50E-03	0.7	2.53E-03	



Figure A5.2. SEM micrographs of (a) 14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 25 °C (b) 14.4 mM Zr, 8.2 mM H2BDC, 3.2 M Ac, 25 °C (c) 14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 35 °C, (d) 7.2 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 25 °C (e) 14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 45 °C (f) 14.4 mM Zr, 16.3 mM H2BDC, 6.0 M Ac, 25 °C. It should be noted (f) has a different scale bar than other panels

The Gualtieri model assumes nucleation probability occurs as a Gaussian distribution centered around an induction time, a, with distribution, b and is equivalent to the nucleation rate, dN/dt:

$$P(n) = \frac{dN}{dt} = e^{-(t-a)^2/2b^2}$$

Where the number of nuclei at an time, *t*, is given be the integral with respect to time:

$$N(t) = \frac{1}{1 + e^{-(t-a)/b}}$$

Each nuclei then supports the growth process, where the expression for growth is derived from the JMAK equation, where k_g is the growth rate constant, and *n*, relates to dimension of growth:

$$G(t) = \left[1 - e^{-(k_g t)^n}\right]$$

Multiplying the number of invisible nuclei by the growth they support yields the extent of crystallization as α :

$$\alpha = \frac{1}{1 + e^{-(t-a)/b}} \left[1 - e^{-(k_g t)^n} \right]$$



Figure 5.3. Gualtieri fitting of the (111) development over time with the nucleation probability calculated from Gualtieri fitting parameters for 14.4 mM Zr, 16.3 mM H2BDC, 3.2 M Ac, 25 °C

Sections of this chapter are adapted from the following works:

Huelsenbeck, L.*, Dighe, A.*, Verma, P., Singh, M., Giri, G. Fundamental Insights into UiO-66 Synthesis Mechanism from Operando Wide Angle X-Ray Scattering and Kinetic Modeling Studies. *In Preparation*, **2021.** *Authors contributed equally to this work.

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6 Select Applications of Thin Film MOFs

6.1 Abstract

This chapter is used to highlight select applications resulting from MOF materials and coatings developed in previous chapters. In Part I, we investigate the [Zn₂(NDC)₂(DABCO)]_n MOF from Chapter 2 Part I as a potential gas separation material by controlling its morphology for either rods or plates, thereby altering the size of the MOF's major pore aperture. Single-component equilibrium and kinetic adsorption data for CO₂ and CH₄ were collected using a physisorption analyzer. Equilibrium analysis indicates a slight selectivity towards CO₂ with all conditions showing similar equilibrium selectivity. Kinetic data shows lower diffusion time constants for the smaller, yet heavier (3.3 Å, 44 g/mol) CO₂ compared to the larger, but lighter (3.8 Å, 16 g/mol) CH₄, which agrees with the mass dependent Knudsen type diffusion. Further, only CH₄ shows an anisotropic intracrystalline diffusivity which we relate to anisotropic pore sizes. This contrasts a nearly constant intracrystalline diffusivity for CO₂. Mass transfer resistances on each species is discussed.

In Part II, we demonstrate the utility of a rapid MOF synthesis developed in Chapter 3 to coat a common cotton textile with a highly stable zirconium-based MOF, UiO-66-NH₂. A technique termed sequential dip coating (SQD) is developed to vary the mass loading of MOF as function of coating cycles. Scanning electron microscopy (SEM) and powder x-ray diffraction (PXRD) indicate crystalline MOF develops rapidly to coat individual fabric fibers, and thermogravimetric analysis (TGA) is used to determine the mass loading of MOF up 20 wt% for 12 SQD cycles. Finally, the pollution capture efficacy of multi-layer fabric is measured using a pollution generation device, demonstrating up to 84% of PM1-4 captured for treated fabrics compared to 53% for the untreated substrate.

6.2 Part I: Anisotropic CO₂/CH₄ kinetic selectivity of [Zn₂(NDC)₂(DABCO)]_n Introduction

The efficient separation of CO₂ from CH₄ is critical for the technoeconomic success of the natural and biogas industries, but current industrial separation techniques are neither energy efficient nor economical. Common separation processes such as cryogenic distillation require a significant amount of energy and capital to complete and do not align with "green" chemistry practices, highlighting the need to find alternative approaches.^{1,2} Recent attempts at making these tasks more efficient involve the use of polymer membranes. While these membranes require a lower energy input, a lower concentration of feed CO₂ must be sent in to prevent membrane plasticizing.³ Other approaches utilize zeolites, but these materials are often synthesized with non-ideal particle morphologies, offer a limited range of pore sizes and chemistry, and have energy and capital-intensive syntheses. ⁴ An ideal approach is one which uses materials which are easily created, easily tuned, and are effective regardless of intake quantities and concentrations.

MOFs have previously been used in combination with a polymer matrix to demonstrate a high selectivity in a CO_2/CH_4 gas mixture.^{2,5} Vankelecom *et al.* showed a zinc based MOF, ZIF-7, impregnated in a polyimide matrix a high CO_2 to CH_4 selectivity.⁵ It was hypothesized that selective permeation was due to the molecular sieving properties of the MOF, where the pore size selects for a smaller kinetic diameter CO_2 (3.3 Å) compared to the larger diameter CH_4 (3.8 Å).⁵ Additionally, it has been shown that the unmodulated $[Cu_2(NDC)_2(DABCO)]_n$ MOF can separate gases in a CO_2/CH_4 system.^{6,7} In this case, Betard *et al.* found the sorption properties between gas and MOF as well as the diffusion properties influenced the membrane selectivity of a $[Cu_2(NDC)_2(DABCO)]_n$ film, where the quadrupolar CO_2 tends to have stronger electrostatic interactions with polar groups within the MOF.⁶ Given these competing factors, MOFs can be

tuned with either electrostatic properties (i.e. defects, or polar functional groups) or pore size to enhance the selectivity of membranes. However, determining the isolated effects of pores size, defect control and the addition of a functional group have been difficult as the chemical and topological features of MOFs are largely interdependent (e.g. introducing a defect leads to a change in pore size). Thus, a method to isolate the effect of each MOF property is important for designing the next generation of MOF membranes beyond current experimental methods.

In Chapter 2 Part I, we synthesized and characterized the $[Zn_2(NDC)_2(DABCO)]_n$ MOF and controlled its morphology using pyridine and acetic acid as modulators to form plates and rods, respectively. We then controlled the orientation of these particles using solution shearing and drop casting and showed thin film orientation could be controlled by choosing the appropriate modulated crystal. We posited future applications as thin film separation membranes. Here, we demonstrate the change in separation selectivity using these two crystal morphologies in a single component adsorption system for both CO₂ and CH₄.

The intrinsic anisotropy of the unit cell, combined with modifying the crystal aspect ratio, exposes pore apertures of different dimensions on the crystal surface while maintaining identical bulk composition and properties. The choice of modulator determines which pore aperture is exposed as the major pore aperture on the crystal surface, allowing for selection of the surface pore dimension, as well as the total internal channel length of each pore type. For example, the use of an amino modulator creates a plate morphology where a carboxylate-carboxylate aperture predominates on the crystal surface, while the use of a carboxylate modulator creates a rod morphology where more of the carboxylate-amino aperture is present on the surface of the crystal. These morphologies can be used to create and tune molecular sieves for specific separation applications within the same topology. We hypothesized the mass transfer properties and kinetic selectivity of differently modulated particles would change due to different exposed pore sizes. Thus, the objective of this study was to 1) demonstrate MOF membrane selectivity can be enhanced by controlling the orientation of an anisotropic MOF thin film and 2) determine the isolated influence of pore size on CO_2/CH_4 selectivity.

6.3 Part I: Methods and Materials

Materials

The following chemicals were purchased from Sigma Aldrich (St. Louis, MO, USA): dimethyl formamide (DMF, \geq 99.8%), acetone (\geq 99.9%), Zn(CH₃COO)₂·2H₂O (\geq 99.0%), and DABCO (\geq 99%). 1,4-napthalenedicarboxylic acid (98+%) was purchased from Alfa Chemistry (Ronkonkoma, NY, USA), while pyridine (ACS grade), acetic acid (ACS grade), toluene (99.9%), and isopropyl alcohol (laboratory grade) were purchased from Fisher Chemical (Hampton, NH, USA). Quartz tubes were purchased from Quartz Scientific, Inc (Fairport Harbor, OH, USA). CO₂ (99.99%), CH₄ (99.97%), and N₂ (99.999%) gases were purchased from Praxair Inc (Danbury, CT, USA).

Synthesis of [Zn₂(NDC)₂(DABCO)]_n MOFs

Modulated and unmodulated MOFs were synthesized according to procedures outline in Chapter 3 Part I.

CO₂ and CH₄ Kinetic and Equilibrium Experiments

Single-component adsorption equilibrium and kinetics of CO₂ and CH₄ were measured volumetrically using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer using the Rate of Adsorption Software (ROA v1.02, Micromeritics, Norcross, GA, USA) at 273.15 K with pressures up to 105 kPa. Initially, 100–400 mg of MOF sample was degassed using the same process outlined for BET isotherms. Samples were degassed between subsequent runs by holding

a pressure of 1.3×10^{-3} kPa for minimum of 5 h at room temperature and stored under nitrogen atmosphere. Kinetic data was taken at pressures of ~53 kPa and ~93 kPa. At these pressures, adsorbate was dosed into the sample chamber nominally at 5 cm³/g and the resulting change in pressure was recorded and converted to an uptake volume as a function of time. The first 1 s of data was discarded to account for valve switching time and gas expansion into the sample chamber. The final adsorption amount at 1.05 atm was used as the equilibrium quantity.

6.4 Part I: Results and Discussion

6.4.1 Equilibrium Sorption Properties of [Zn₂(NDC)₂(DABCO)]_n for Nitrogen, Methane, and Carbon Dioxide

A formal description of the synthesis, characterization, and fabrication of oriented thin films of $[Zn_2(NDC)_2(DABCO)]_n$ is described in Chapter 3 Part I. Here we focus on the morphology-based gas sorption performance and characterization, where the morphology of each particle determines the dominant surface pore aperture. Nitrogen isotherms of the synthesized $[Zn_2(NDC)_2(DABCO)]_n$ MOF were used to verify the microporosity of the synthesized material for the bulk and modulated samples (**Figure A6.1**). The BET surface area (**Table 6.1**) and isotherms are comparable to that of reported values for the Zn and Cu analog of $[M_2(NDC)_2(DABCO)]_n$ (M = Zn,Cu)^{8,9}. Experiments show that the $[Zn_2(NDC)_2(DABCO)]_n$ surface area measurements are highly sensitive to the drying procedure (**Table A6.1**). The sensitivity is likely due to solvent stabilization effects observed in the $[Zn_2(dicarboxylate)_2(N$ $ligand)]_n$ MOF family.⁸ Previous results have shown that a MOF with a similar zinc-based topology had reduced crystallinity after activation, indicating a partial collapse of the framework.⁸ Given this information, it is difficult to ascertain surface area contributions from defects due to modulation (i.e., defect engineering) or degradation from activation for the different modulated syntheses. However, a similarity in measured surface area between morphologies shows that any effect is similar in all three cases.

morphology and fou	r (4) samples of the plate-like and rod-like morpho	logies of [Zn2(NDC)2(DABCO)]n and c	a reference value.
	Morphology	BET Surface Area (m ² /g)	
	Zn ₂ (NDC) ₂ (DABCO) Bulk ¹⁰	1000	

Table 6.1 BET surface areas and standard error calculated from nitrogen isotherms at 77 K for three (3) samples of the bulk

101 photogy	
Zn ₂ (NDC) ₂ (DABCO) Bulk ¹⁰	1000
Bulk	1226 ± 16
Rod	1100 ± 68
Plate	946 ± 127

Figure 6.1 shows the single-component isotherms for CO_2 and CH_4 of $[Zn_2(NDC)_2(DABCO)]$ at 273 K for different morphologies. The total uptake of rod and plate tends to be lower than that of the bulk morphology, which correlates to the BET surface areas. This behavior is expected for physisorption as the quantity adsorbed is a function of the accessible surface area. The Langmuir isotherm model (**Equation (6.1**)) provides an accurate approximation of the adsorption with fitting parameters listed in **Table 6.2**.

$$q = a_m \frac{bP}{1+bP} \tag{6.1}$$

where q (mmol/g) is the quantity adsorbed per mass of adsorbate, a_m (mmol/g) is the maximum adsorbed quantity per adsorbate mass to form a complete monolayer, b (kPa⁻¹) is the affinity or Langmuir constant and P (kPa) is the dosing pressure.

The product of a_m and b yield another constant termed Henry's constant (*K*), which provides a linear approximation of the adsorption isotherm. The ratio of Henry's constants for CO₂ and CH₄ provides an equilibrium selectivity, α .



Figure 6.1 Adsorption isotherms for bulk, plate and rod morphologies of $[Zn_2(NDC)_2(DABCO)]_n$ at 273 K for (a) CO₂ and (b) CH₄.

Table 6.2 Langmuir isotherm fitting parameters (a_m and b), Henry's constant (K) and CO₂/CH₄ selectivity for different morphologies of [$Zn_2(NDC)_2(DABCO)$]_n.

Mornhology	Adsorbato	a_m	b	K (mmol/g	CO ₂ /CH ₄ Selectivity,
Morphology	Ausorbate	(mmol/g)	(kPa ⁻¹)	kPa)	α
Bulk	CO_2	12.78	0.0066	0.0842	3.85
	CH ₄	9.38	0.0023	0.0219	
Rod	CO ₂	10.35	0.0069	0.0716	4.46
	CH ₄	5.26	0.0031	0.0161	
Plate	CO ₂	10.21	0.0070	0.0719	4.26
	CH ₄	6.16	0.0027	0.0169	

 $[Zn_2(NDC)_2(DABCO)]$ demonstrates moderate selectivity towards CO₂ compared to CH₄. This value is comparable to selectivity for other MOFs under similar conditions such as the ZIF family (3.9–10.1)¹¹, MIL-101 (3–5)¹² and MOF-177 (4.43).¹³ The higher affinity of CO₂ to adsorb on the surface is likely due to a higher quadrupole moment.^{12,14} Both modulated morphologies (amine and carboxylate) show a moderate increase in selectivity compared to the bulk. This may be because more defect sites are preferentially interacting with CO₂ ¹⁵, however more work is required to confirm this interaction.

6.4.2 Surface Pore Aperture and CO₂/CH₄ Kinetic Selectivity

As previously mentioned, the major surface for each crystal morphology, defined as the surfaces parallel to the crystal major axes, is associated with a crystallographic plane. More specifically, the plate morphology will have a major surface with a pore entrance aperture defined by the carboxylate-carboxylate frame, whereas the rod morphology will have a major surface with a pore entrance aperture defined by the carboxylate-amine frame (**Figure 3.1**). Each pore aperture is expected to present different mass transfer resistances.¹⁶ Therefore, diffusional differences between carboxylate-carboxylate and carboxylate-amine pore apertures will exist and variation in kinetic selectivity between morphologies can be expected for the differently sized adsorbates CO₂ and CH₄. Given the high aspect ratio of each morphology, a significant portion of diffusion is expected to occur through the major surface pore. Further, since the bulk sorption properties of each morphology are nearly identical, the diffusional difference will mainly be a function of pore aperture.



Figure 6.2 Fractional uptake versus time for the bulk morphology of [Zn2(NDC)2(DABCO)]n at 273 K for CO2 and CH4.

Figure 6.2 shows representative data taken for the uptake of CO₂ and CH₄ for the bulk morphology. CH₄ is adsorbed more quickly, reaching 90% of the total uptake at around 50 s compared to about 125 s for the CO₂. This contradicts other work in microporous MOFs, which determined the diffusion of CO₂ is much quicker than CH₄ due to the difference in kinetic diameter.¹⁷ However, such a trend agrees with the Knudsen diffusion model, which states molecules with larger mass will diffuse more slowly in pores with a diameter below that of the mean free path, as is the case for gas in microporous materials. To better understand the diffusion of each species with respect to morphologies, we apply a single-component adsorption micropore diffusion control model developed by Ruthven et al. ¹⁸ to adsorption rate data collected for CO₂ and CH₄ that has successfully been applied to several MOF particle systems.^{12,19}

$$\frac{m}{m_{\infty}} \approx \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_c t}{r_c^2} - 3\frac{D_c t}{r_c^2}}$$
(6.2)

Where m/m_{∞} is the mass uptake relative to the equilibrium uptake mass, D_c is the intracrystalline diffusivity, r_c is the crystal radius, and t is time. It should be noted **Equation (6.2)** is valid for $\frac{m}{m_{\infty}} < 0.85$.¹⁸ This model assumes the intracrystalline diffusion resistances are much greater than macroporous resistances in particle aggregates, diffusion is constant within the crystalline material, and the concentration of adsorbate is constant outside of the particle. All of these assumptions are valid given that the free diffusivity of gases in macropores are much greater than those in the micropores ¹⁸, the gases do not condense in the micropores under the sampling conditions, and the sample tube volume can be approximated as an infinite reservoir compared to the volume adsorbed.

Table 6.3 Diffusion time constants from fitting Equation (6.2) to kinetic adsorption data of CO₂ and CH₄ and kinetic selectivity for varied morphologies. Individual trial data can be found in supplemental materials (Table S3).

Morphology	$CO_2 D_c/r_c(s^{-1}) \times 10^{-3}$	$CH_4 D_c/r_c(s^{-1}) \times 10^{-3}$	CO ₂ /CH ₄ Kinetic Selectivity
Bulk	1.57 ± 0.07	5.24 ± 0.44	0.300 ± 0.028
Rod	1.73 ± 0.13	8.75 ± 0.74	0.197 ± 0.022
Plate	1.88 ± 0.15	4.72 ± 0.27	0.399 ± 0.039

Table 6.3 shows the diffusion time constants, D_c/r_c^2 , found by fitting **Equation (6.2)** to multiple uptake curves for each gas species and morphology at 94 kPa (700 mmHg). Kinetic selectivity was found by dividing the diffusion time constant for CO₂ by the diffusion time constant for CH₄. It can be seen that kinetic selectivity exists for CO₂/CH₄ as a function of morphology. Interestingly, the CO₂ diffusion time constant remains relatively constant across the different morphologies. This implies that the diffusional resistances on CO₂ within the framework are not highly dependent on diffusion direction (i.e., the pore aperture size or frame chemistry) and may be dominated by more complex electrostatic interactions with the framework.^{20,21} A two-fold

increase in diffusion time constant is observed for CH₄ between the plate and rod, suggesting the different pore apertures have a significant effect on diffusion through the framework. These data show the diffusion through the carboxylate-amine frame (rod) is nearly twice as fast as the carboxylate-carboxylate frame (plate). Since CH₄ is thought to have little chemical or intermolecular interactions with the framework, the diffusion is likely determined by pore aperture size.²² Given the linker geometry and bond rotation of 1,4-naphthalenedicarboxylate, the pore aperture in the carboxylate-carboxylate frame may be significantly smaller than the carboxylate-amine frame. Such a geometry could explain why the diffusion is faster through the carboxylate-amine frame, however more work is required to understand the chemistry and structure around each pore aperture.

6.5 Part I: Conclusion

BET characterization showed modulation had little effect on the microporosity of the resulting materials. Furthermore, $[Zn_2(NDC)_2(DABCO)]_n$ has a moderate equilibrium selectivity of around 4 for all morphologies, which is comparable to other MOFs. Interestingly, we found the CO₂ diffusion time constant did not depend on pore aperture, indicating the diffusion of CO₂ within $[Zn_2(NDC)_2(DABCO)]_n$ is likely dominated by electrostatic interactions. Kinetic selectivity experiments showed the diffusion of CH₄ into the framework as measured by a diffusion time constant was much faster than CO₂ and nearly doubled for the rod morphology compared to the plate morphology (8.75 ± 0.74 and 4.72 ± 0.27 s⁻¹ × 10⁻³, respectively). These results yielded a CO₂/CH₄ kinetic selectivity of ~0.2 and ~0.4 for the rod and plate morphologies, respectively, suggesting a membrane with the carboxylate-amine pore aperture oriented normal to the surface would offer the highest selectivity for future work.

6.6 Part I Appendix



Figure A6.1 Representative nitrogen isotherms for varied morphologies of [Zn2(NDC)2(DABCO)]n.

Drying Procedure	BET Surface Area (m ² /g)
Degassed at 90°C, heated at 100°C for 12 hours	451 ± 122
Degassed at 80°C, heated at 85°C for 8 hours	780
Degassed at 70°C, heated at 80°C for 8 hours	1100 ± 68

 Table A6.1 BET Surface Areas and standard error of [Zn2(NDC)2(DABCO)]n with differing drying procedures.

Morphology	CO2 Uptake	CH₄ Uptake	CO ₂ /CH ₄
	(mmol/g)	(mmol/g)	Selectivity
Bulk	0.184 ± 0.022	0.042 ± 0.006	4.38 ± 1.16
Rod	0.650 ± 0.300	0.152 ± 0.008	4.27 ± 0.42
Plate	0.232 ± 0.021	0.056 ± 0.006	4.15 ± 0.85



Figure A6.2 PXRD patterns for MOF material pre and post- competitive gas adsorption procedure showing peak broadening for all samples, indicating sample degradation.

Rod	$D/r^2 CO_2 (1/s)$	D/r ² CH ₄ (1/s)	CO2/CH4
			Selectivity
700mmHg			
Trial 1	2.11E-03	6.31E-03	
Trial 2		1.22E-02	
Trial 3		1.09E-02	
Trial 4		9.01E-03	
Trial 5	1.80E-03	7.30E-03	
Trial 6	1.50E-03	7.56E-03	
Trial 7	1.50E-03	7.93E-03	
AVG	1.73E-03	8.75E-03	1.97E-01
STDERR	1.26E-04	7.43E-04	2.21E-02
Bulk	$D/r^2 CO_2 (1/s)$	$D/r^2 CH_4 (1/s)$	CO2/CH4
			Selectivity
700mmHg			
Trial 1	1.46E-03	6.40E-03	
Trial 2	1.53E-03	4.84E-03	
Trial 3	1.73E-03	4.06E-03	
Trial 4		5.65E-03	
AVG	1.57E-03	5.24E-03	3.00E-01
STDERR	6.74E-05	4.38E-04	2.82E-02
Plate	$D/r^2 CO_2 (1/s)$	D/r ² CH ₄ (1/s)	CO2/CH4
			Selectivity
700mmHg			
Trial 1	2.21E-03	6.25E-03	
Trial 2	2.50E-03	4.03E-03	
Trial 3	2.03E-03	4.21E-03	
Trial 4	1.53E-03	4.61E-03	
Trial 5	1.55E-03	4.61E-03	
Trial 6	1.47E-03	4.61E-03	
AVG	1.88E-03	4.72E-03	3.99E-01
STDERR	1.48E-04	2.73E-04	3.90E-02

*Table A6.3 Diffusion time constant data for CO*₂ *and CH*₄ *at 700 mmHg and 273 K for multiple trials*

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6.8 Part II: Rapid formation of Cotton@UiO-66-NH2 for Pollution Capture Introduction

The rapid time scale of MOF formation developed in Chapter 3 allows for technologies to be developed and fabricated at a significantly faster timescale for applications. As an example, we developed a sequential dip coating (SQD) technique to grow MOFs on common substrates within seconds, including on cotton fabric. Several studies have leveraged MOF coated fabrics to enhance capture of particulate matter pollution and volatile organic compounds (VOCs), degrade chemical warfare agents, and offer biocidal activity.¹⁻⁴ However, most of these techniques employ lengthy batch processes (hours to days). In addition, these techniques may also require high temperature solvothermal growth of MOF on functionalized substrates using organic solvents, which may not be ideal for textiles. The ability to produce filters for use in PPE at scale has become even more pressing in light of the COVID-19 pandemic, where supply shortages of protective materials have been observed worldwide.^{5,6} Existing techniques of producing MOF fabrics are not scalable due to lack of large area processing (i.e. continuous methods) and the use of expensive and harsh organic solvents. ^{7,8} To overcome such limitations, Wang et al. developed coating process by developing a roll-to-roll hot press technique to grow ZIF-type MOFs directly on polymer based substrates with similar loading and filtration efficiency, but were limited to MOFs in the ZIF family. ⁹ The synthesis method studied in this work solves the problem of developing a rapid, environmentally friendly MOF-textile production technique capable of immediate deployment as fabric filters.

6.9 Part II: Materials and Methods

Materials

All reagents were used as received with no further purification. Zirconyl chloride octahydrate (ZrOCl₂ ·8 H₂O, 98% Alfa Aesar), acetic acid (Glacial Sigma Aldrich), sodium hydroxide pellets (NaOH, 98% Sigma Aldrich), 2-aminoterephthalic acid (H₂ATA, 99% Sigma Aldrich), terephthalic acid (H₂BDC, 98% Sigma Aldrich) and deionized water were used for the rapid synthesis of UiO-66-NH₂ and UiO-66. Hydrochloric acid (37 wt%, Alfa Aesar) was used to prepare an aqueous solution of 0.01 M HCl. Dimethyl sulfoxide (DMSO, 99% Sigma Aldrich), ethanol (EtOH, 95% Koptec), and methanol (MeOH, 99.8% Sigma Aldrich) were used for washing and activating MOFs. Napped Sateen Cotton fabric was purchased from Hanes (Hanes 0339061) and washed with an ethanol rinse before further processing.

*UiO-66-NH*₂ *Precursor Solutions Preparation*

A metal solution was prepared following synthesis outlined by Szilagyi et al.¹ Briefly, 1.2880 g ZrOCl₂ ·8H₂O was dissolved in 5 mL Acetic acid and 12 mL of DI water, placed in a Teflon lined 20 mL scintillation vial, heated at 70 °C for two hours and allowed to cool to room temperature. The linker solution was prepared by mixing 0.7240 g of H₂ATA in a solution of 0.9808 g NaOH in 27 mL DI water until dissolved.

Synthesis of UiO-66-NH₂@Cotton Fabric

Fabric was cut into 5 cm diameter circles and soaked in ethanol and dried at 80 °C to clean. MOF was applied by using an alternating dipping process. Dried cloth was dipped in a UiO-66-NH₂ metal solution for ~5 seconds, gently dried with a paper towel to remove excess solution, then dipped in a linker solution 5 seconds. The linker solution used corresponded to optimum conditions found in the pH study (0.3620 H₂ATA, 13.5 mL DI water and 0.4904 g NaOH). After a metal and linker dip, fabric was submerged in DI water and sonicated to remove any unattached particles. The dipping process was repeated up to 12 times to vary the amount of MOF loaded onto fabric. Fabrics were dried at 120 °C overnight in a convection oven and stored for characterization. *Characterization:*

XRD

Powder x-ray diffraction (PXRD) patterns were collected using a PANalytical Empyrean X-ray Diffractometer (Malvern Panalytical, Egham, UK) with Cu K- α radiation. Scans were taken from $2\theta = 5^{\circ}$ - 20° for UiO-66-NH₂ and $2\theta = 5^{\circ}$ - 30° for UiO-66, HKUST-1, and ZIF-L. Diffraction patterns were analyzed using HighScore Plus X-ray Diffraction analysis software.

SEM

Scanning Electron Microscopy (SEM) micrographs were collected using a Helios Dual Beam FIB G4 UC with an accelerating voltage of 5 kV and 0.80 nA current.

TGA

The metal to linker ratio of MOFs was measured by Thermogravimetric Analyzer (TGA, Q50). In a typical experiment, a small amount of pre-dried powder or fabric (~10 mg) was loaded into a Pt sample pan, and the sample pan was transferred into the heating chamber of the analyzer. The sample gas was air (flowrate = 60 mL/min), and the balance gas was nitrogen (flowrate = 40 mL/min). The sample was heated to 800 °C from room temperature at a rate of 10 °C/min. In the initial stage of the heating process, moisture adsorbed by the sample was evaporated, and the sample mass at 120 °C was taken as the dry mass. Further heating led to the decomposition of the sample (i.e., organic linkers and organic fabric were decomposed by oxidation and metal nodes were transformed into metal oxide), and the sample mass at 800 °C was taken as the mass of metal oxide.

We chose optimal synthetic conditions determined from our previous study in Chapter 4 on UiO-66-NH₂ at a final pH of 4.3 and apply it to the SQD sequence. Using this synthesis requires only 10 seconds to apply metal and linker solutions, with more time required for drying and washing between cycles. Each cycle can be hastened with rapid drying and washing processes currently available in roll to roll processing for large scale applications. ¹⁰ The time scale achieved in coating is approximately an order of magnitude faster than previously reported MOF fabrics, which normally take hours to days in batch conditions. 9,11-13 With the rapid time scale, continuous nature of fabrication, and room temperature, aqueous based chemistry, this process can be scaled to create large areas of MOF coated cloth with minimal post processing steps. Cotton was chosen as it is a widely available, low cost substrate, and it absorbs the working solvent and solute readily. The cotton was briefly soaked in a zirconium oxocluster solution for 5 seconds, padded with an absorbent towel to remove excess solution, then dipped into a H₂ATA linker solution for another 5 seconds. We hypothesize the MOF reaction occurs at or near the surface of cotton fibers, as we observe little precipitation in the linker solution after several dipping steps, indicating that a significant portion of MOF preferentially grows on the surface of the fabric. This is unlike previous layer by layer-based techniques, where we hypothesize our method grows more than one unit cell of the MOF is grown during each SQD cycle.¹⁴ SEM and XRD observations confirm MOF forms on the fabric and is uniformly distributed along the surface (Figure 6.3f-g, Figure A6.3). Additionally, we demonstrate that repeating the metal-linker dipping process with an intermediate washing step increases the weight loading of MOF on cotton as measured by XRD and quantified by ZrO₂ remaining after TGA experiments (Figure 6.3c,h, Figure A6.4).



Figure 6.3 a) Schematic of the sequential dip coating (SQD) procedure used to fabricate rapid UiO-66-NH2 on cotton fabric (cotton@UiO-66-NH2). Optimized synthetic conditions for UiO-66-NH2 at pH 4.3 were used to fabricate all samples in the following: b) optical image of fabric before and after 8 dip SQD c) PXRD of cotton substrate, UiO-66-NH2 control powder and cotton with increasing sequential dips d,e) SEM image of bare cotton substrate f,g) SEM image of 8 dip SQD cotton h) Mass loading on fabric and pollution filtration performance for particulate matter between 1-4 μ m of three MOF-fabric layers as a function of dipping cycles for UiO-66-NH2. Error is reported as the standard deviation from N=3 trials.

Figure 6.3h shows the weight percent loading of MOF on cotton fabric and pollution

filtration efficiency for PM₁₋₄ as a function of SQD cycles. Increasing the number of dip cycles increases MOF loading on the fabric, increasing up to 21 ± 3 wt% MOF for 12 SQD cycles. The loading achieved is comparable to other solvothermal techniques used for attaching MOFs to natural and organic fibers around 20 wt%.^{9,11,15} However, the attachment process is on the order of minutes at room temperature aqueous conditions compared to day long, high temperature, and organic solvent based processes.^{9,11,15} Additionally, we tested the pollution filtration efficiency of the SQD manufactured MOF fabric for particles ranging in size from 1-4 µm. We found that filtration efficiency increased with MOF loading up to 18 ± 2 wt% MOF and $84 \pm 9\%$ filtration efficiency, after which point the addition of MOF did not have an effect. SEM micrographs indicate a majority of cotton fibers are fully coated at this loading (**Figure A6.3**), suggesting a

plateau in active MOF surface area (i.e. MOF exposed to polluted air flow) that is added with subsequent SQD cycles.

6.11 Part II: Conclusion

This study demonstrated the utility of approaching MOF crystallization from a reactioncrystallization perspective. Using this approach, we were able to tune the MOF metal and linker species to rapidly react at a substrate surface to create a uniform UiO-66-NH₂ particle coating on cotton. We demonstrated the loading of UiO-66-NH₂ on fabric can be controlled by changing the number of sequential dip coat (SQD) cycles achieving a loading of up to 21 ± 4 wt% of UiO-66-NH₂ on cotton with 12 SQD cycles. Further, the functionalized fabric showed significant improvement over the control substrate, enhancing the pollution capture efficiency from 53% for the bare substrate up to 84% for cotton treated with 12 SQD cycles. It is also notable the coating process occurred on the order of seconds to minutes, at room temperature. We believe this route is readily scalable to a continuous process and is economically and environmentally advantageous when compared to standard techniques that require hour to day time scales, high temperatures, and harsh organic solvents.

6.12 Part II: Appendix



Figure A6.3. SEM micrographs of UiO-66-NH₂ on fabric including: a) untreated cotton fabric b) 1 dip SQD UiO-66-NH₂ on cotton c) 2 dip SQD UiO-66-NH₂ on cotton d) 4 dip SQD UiO-66-NH₂ on cotton e) 8 dip SQD UiO-66-NH₂ on cotton f) 12 dip SQD UiO-66-NH₂ on cotton. Micrographs show the presence of nanoparticles on the surface of fibers, with increasing coverage as a funciton of SQD cycles.



Figure A6.4. Thermogravimetric decomposition curves of UiO-66 NH2 (red dash), Cotton Fabric (red solid), and UiO-66-NH2 loaded onto cotton fabric with different number of sequential dips. UiO-66-NH2 shows solvent loss up to 300 °C, whereas cotton fabric and SQD show little solvent mass loss up to 300 °C. The dip at 340 °C shows the decomposition of the organic cotton material, whereas the dip at 360 °C represents the decomposition of UiO-66-NH2. It can be seen as more MOF is loaded onto fabric, the decomposition curve representing UiO-66-NH2 becomes more pronounced and the remaining wt% (ZrO2) increases, indicating more metal is loaded on the fabric due to MOF loading.

A weighted average method was used to calculate the mass weight percent of UiO-66

 NH_2 on cotton:

$$Wt\% Ui066NH_2 = \frac{Z\% - Y\%}{X\% - Y\%} \qquad Eq. \ A6.25$$

Where Z% = the ash percent of UiO-66-NH₂ (*a*) Cotton, Y% = Cotton fabric ash mass

percent, and $X\% = UiO-66 NH_2$ ash percent.

Table A6.4. Table of wt% ash and MOF loading as calculated from weighted average technique for different number of SQD cycles. N=3. Results were calculated using data shown in Figure A6.4 and Supplementary Equation (A6.1).

SQD Dips	Wt% ash	MOF Loading
UiO-66 NH ₂ Control	$37.3 \pm 1.7\%$	100%
Cotton Control	0.6 %	0%
1 dip	$3.0 \pm 0.4\%$	$6.2 \pm 1.3\%$
2 dip	$3.9\pm0.2\%$	$8.9\pm1.0\%$
4 dip	$5.0\pm0.9\%$	$12.1 \pm 3.1\%$
8 dip	$7.3 \pm 0.3\%$	$18.2\pm1.8\%$
12 dip	$8.2 \pm 0.8\%$	$20.7\pm3.2\%$

Table A6.5. Table of downstream pollution concentration data used to calculate capture efficiency and capture efficiency of control cotton filter and varied SQD cycles. N=3*.*

Sample	Average Downstream Concentration (µg/m ³)	% Capture
No Filter	506 ± 35	0
Cotton Control	240 ± 14	53 ± 7
1 dip	178 ± 17	65 ± 11
2 dip	159 ± 1	69 ± 5
4 dip	111 ± 7	78 ± 10
8 dip	81 ± 4	84 ± 10
12 dip	78 ± 5	85 ± 11

6.13 Part II References

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7 Conclusion and Future Work

Understanding how solution processing and MOF crystallization can be coupled is necessary to fabricate high quality thin films that meet design requirements for the range of applications promised by the field of MOFs. Ensuring the scalability, controllability and minimal environmental impact of processing thin films MOFs is critical for the adoption and broader impact of this young class of materials. This dissertation has approached meeting processing and morphological requirements by exploring the processing of MOF thin films using a rapid, large area thin film deposition technique, termed solution shearing, among others. We presented several techniques that combine solution shearing with MOF crystallization to achieve controlled film characteristics such as orientation, coverage, and thickness on a seconds to minutes time scale. Further, we present several studies on MOF crystallization kinetics and mechanisms to better understand how crystallization can be controlled during solution shearing deposition.

7.1 Pre-synthesizing MOFs for thin film fabrication

Chapter 2 demonstrated that growing and controlling MOF morphology before solution processing had a significant effect on the film orientation, morphology and thickness. De-coupling the MOF crystallization from solution processing allows for concise control of particle and MOF chemical properties and influences how particles orient and pack as films during solution deposition. Future work could explore using these techniques to orient pre-synthesized particles in thin films to create seeded substrates. In this case the oriented particle would act as a secondary growth site to support oriented growth from solution onto a substrate. Such a method would allow for complete film coverage and has shown to be successful for other non-oriented MOF thin films.^{1,2}

7.2 Synthesizing Thin Films of HKUST-1 during solution shearing

Chapter 3 showed the coupling HKUST-1 crystallization with solution shearing. We showed how this process was able to control thickness, orientation, and particle morphology. Further, we accelerated the exploration of the vast parameter space by using machine learning models to predict processing parameters that yielded fully covered films and predictable film thickness. While the degree of control in the explored parameter space was enough to create fully

covered films with minimized thickness, we still observed particles that maintained isotropic growth (i.e. low aspect ratio crystal domains, where thickness was similar to lateral crystal size).

Future work on this system should focus on understanding the complex coupling of solution shearing fluid dynamics and the crystallization kinetics of HKUST-1. Preliminary in situ grazing incidence x-ray diffraction (GIXD) was run on multiple conditions understand how processing to parameters influence the crystallization kinetics of HKUST-1 (Figure 7.1). While presenting this data is out of the scope of the dissertation, there are several instrumentation limitations that must be overcome to achieve high quality and repeatable in situ data. Often, signal artefacts from moving components and variations in signal strength due to subtle movements during the coating process yielded results that were difficult to analyze with confidence beyond a general time scale. Interestingly, preliminary results indicate growth occurs in an oriented manner (Figure 7.1) as evidence by the first diffraction orientation peak matching the final peak orientation, but more work is required to validate this claim. Coupling in situ work to another technique such as high-speed



Figure 7.1. Schematic and data demonstrating the in situ GIWD collection technique using a focused x-ray microbeam at the Cornell High Energy Synchrotron Source (CHESS)

microscopy, ellipsometry, or other complementary metrology would greatly assist in accurate interpretation of the data. We hypothesize using this data to match the growth time scale to the deposition time scale may yield non-symmetrical, high aspect ratio morphologies by controlling the concentration gradient of HKUST-1 precursor.

7.3 Understanding the reactive-crystallization of MOFs and UiO-66

Chapter 4 and 5 approached solution processing of MOFs with a more fundamental approach, where we hypothesized the system behaved as a reactive-crystallization and could be controlled as such. Chapter 4 shows how controlling the reactive crystallization by identifying the appropriate reacting species could significantly enhance the synthesis time scale of four proto-typical MOFs. While not guaranteed, we hypothesize the insight from this study can be applied to a range of MOFs fitting solubility and reactant species conditions. It also gave brief insight into the rate limiting formation steps of the multi-step formation of the UiO-66 family. Chapter 5 continued this work using *in situ* studies to gain insight into the reactive-crystallization mechanism that governed UiO-66 crystallization. By varying concentration of metal and linker precursors, modulator, and temperature we were able to detail a reaction mechanism that will be modeled by collaborators to give more insight into UiO-66 crystallization.

The potential extension of this work has two directions, the first involving a deeper exploration of the fundamental formation mechanisms and the second leveraging knowledge gained in this system to develop a precursor solution for solution processing. For the first direction, additional *in situ* data, including small angle scattering and *in situ* spectroscopic techniques can be used to further validate and confirm the formation mechanisms posed in the initial study and resulting model. X-ray absorption spectroscopy (XAS) for example can be used to study nearest neighbor and second nearest neighbor atoms to the metal node in MOFs.³ Tracking these local structures around the metal nodes would be invaluable to elucidating the formation mechanism when coupled with other techniques. Further, small angle x-ray scattering (SAXS) is often used to identify how matter condenses and can yield information about the surface properties and particle morphology during crystallization. Coupling SAXS and WAXS has been explored for understanding MOF growth for ZIF-8 and but it resulted in an uncertain conclusion due to instrumentation limitations.⁴ This is because the limit of detection for WAXS compared to SAXS is not well known, which makes understanding the long range order of particles first detected by SAXS difficult to interpret. Thus, finding methods to aid in the interpretation of these results, either

experimentally or with more rigorous scattering models, would be beneficial to answering questions about the crystallization pathway.

The second direction involves using knowledge gained about controlling UiO-66 synthesis from these studies and applying it to solution processing. Preliminary results show that using a controlled SBU synthetic approach with a high modulator concentration produces oriented thin films of UiO-66 during solution shearing. Working with this system to grow oriented thin films that are fully covered is a natural extension of the work presented in Chapter 3 and Chapter 5.

7.4 Towards thin film applications

Many applications, such as separations, have additional mechanical requirements that cannot be achieved by a free-standing MOF thin film due to brittleness and grain boundaries. The synthetic techniques presented in this work can be coupled with any number of existing solutions to enhance the fabrication timescale. For example, combining MOFs with polymers in mixed-matrix membranes (MMM) has shown success in leveraging the microstructural benefits of MOFs and the mechanical benefits of polymers.^{5,6} The synthetic and processing techniques developed in this dissertation can readily incorporate polymers during thin film deposition to create a continuous and mechanically robust thin film of polymer and MOF.

7.5 Final Remarks

The work presented here is intended to continue the ushering of MOFs into the field of chemical engineering, where controlling the synthesis and processing of these materials is considered at multiple length scales with applications driven design requirements. While the field of MOFs has provided a lot of excitement and promise for the future of many high-impact applications, delivering on these promises and maintaining the excitement depends strongly on transferring this technology to an impactful scale. It is the hopes of the author that with the work developed in this dissertation and its continuation, a clear pathway in the scaling and processing of thin film MOFs can be achieved.

7.6 References

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