Exploration of the Ability to use MOFs in Chromatography

A Major Qualifying Project Report

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Abstract

Porous metal-organic frameworks (MOFs) consisting of crystalline coordination polymers are of interest as host materials for molecular sorption and separation. MOFs display permanent porosity with channels that have high surface area and void volumes, high thermal stability, and can be modified through synthesis. We are currently exploring the utility of MOFs as stationary phases for chromatographic separation of organic compounds to determine how diffusion into the high-surface area channels of MOFs affects retention and separation of molecular guests compared to traditional solid supports such as silica gel and alumina. Toward this goal, the research on this project has focused in four areas: (1) preparation and characterization of a porous MOF solid, (2) development of a procedure to prepare thin films of MOF particles on glass plates as the solid support for thin layer chromatography (TLC), (3) assessment of solvent systems to identify a mobile phase suitable for separating compounds on MOF TLC plates, and (4) investigation of the chromatographic behavior of the MOF stationary phase toward separating a small library of aromatic dyes. Microcrystalline particles of MOF-5 were prepared by reacting benzene-1, 4-dicarboxylic acid with zinc nitrate and triethylamine at room temperature in dimethyl formamide. The structure, porosity and stability of MOF-5 was determined by powder X-ray diffraction and thermogravimetric analysis. TLC plates were prepared by depositing a slurry containing particles of MOF-5 or silica gel (control) in water with 20% plaster of Paris as the binding agent and allowing the solvent to evaporate to form solid films. Separation of organic dyes with a range of sizes and polarities was examined and the chromatographic behavior and relative retention compared to that on TLC plates of nonporous silica gel.

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1. Introduction

Metal-organic frameworks (MOFs) are a class of ordered crystalline solids consisting of crystalline coordination polymers that contain structured channels permeating the resulting solids creating permanent porosity. [1] The three dimensional framework of MOFs have rigid organic ligands along the edges and metal ion clusters at the joints linking the ligands that lead to high surface area and void volumes, and high thermal stability. Within the last twenty years interest in MOFs has led to a significant number of studies of MOFs pertaining to synthesis and characterization of different framework architectures and their properties and the development of MOFs as materials for molecular storage and separation as well as heterogeneous catalysis. MOFs share many properties such as permanent porosity and high internal surface areas and pore volumes with another class of porous material, zeolites. An important distinction between zeolites and MOFs is that due to the organic ligands present in MOFs, it is possible to modify the pore structure, surface properties and reactivity of MOFs via organic synthesis. Due to the high surface area and void volumes as well as the ability to modify the organic ligands within MOFs has made a focus of study their functions in molecular storage and separation.

Our group has investigated MOFs from different angles over the years. Some recent areas of study include designing and developing new families of MOFs with low-symmetry framework architectures, incorporation of porphyrins into the framework to allow for photolytic production of singlet oxygen to oxidize organic contaminants sorbed into MOFs, and the role of copper-containing MOFs in promoting and catalyzing Huisgen 3+2 "click" reactions between organic azides and alkynes.[2] Most recently the focus has turned to the use of MOFs in separation of organic molecules. We want to determine if MOF solids can be used as the solid phase in thin layer and liquid chromatography to effect molecular separation via differential interaction of compounds at the surface and within the channels of MOF particles. We hypothesized the porous nature and high internal surface areas of MOFs might lead to different chromatographic behavior than that of conventional solid phases, such as silica gel and alumina, due to the ability of organic compounds to interact at the surface of MOF particles, as well as with the channels. Previous work in our group has shown that MOFs exhibit a general selectivity for sorbing nonpolar compounds such as polyaromatic hydrocarbons (e.g., naphthalene, phenanthrene, pyrene, etc.) from solution due to the largely nonpolar aromatic surface area in the interior of channels. [13] In contrast, analysis of the crystal structures of MOFs reveals that polar functional groups such as carboxylic acids are exposed at the surface of MOF particles suggesting that dipolar intermolecular interactions (e.g., hydrogen bonding) should predominate at the surface of MOF particles. Accordingly, one reason for investigating molecular separation with MOFs was to assess the effective polarity of MOF solids relative to traditional polar solid supports such as silica gel. We also wanted to determine how diffusion of compounds into the interior of MOF particles might affect molecular separation compared to nonporous solid supports.

The project described here is the first step in an exploratory project to study utilizing MOFs as solid supports, or stationary phases, for separation of organic compounds via thin-layer chromatography (TLC). The chromatographic behavior of MOFs has not been examined previously, despite the unique properties of unusually high surface areas and void volumes of that class of porous materials being well known. We chose MOF-5 as a starting material of MOF systems because its structure, internal surface area (i.e, 3800 m^2/g) and void volume (52%), stability (>450 °C), and physical and chemical properties have been well characterized. [9]

Another considerations for selecting MOF-5 was that the cubic framework and associated channels have high symmetry allowing for optimal diffusion of guests into MOF-5 particles through 13 Å x 13 Å pore openings large enough to admit organic large compounds with a wide variety of structures. Lastly, MOF-5 is composed of molecules of benzene-1,4-dicarboxylic acid coordinated to tetrahedral clusters of four zinc(II) ions such that free carboxylic acid groups are exposed on the surface of MOF-5 particles and available to coordinate to a binding agent required to create stable thin films on glass substrates for TLC.

The specific aims of this project were the following: (1) to synthesize and characterize the stability and porosity of microcrystalline particles of MOF-5; (2) to determine if it is possible to prepare TLC plates consisting of mechanically stable thin films of MOF-5 particles on glass using a binding agent, and develop a protocol for doing so reproducibly; (3) to examine the chromatographic behavior of a small library of organic dyes of varying size and polarity on TLC plates of MOF-5 to identify and optimize suitable solvent systems (mobile phases); and (4) to compare the chromatographic behavior of those dyes on MOF-5 TLC plates against TLC plates of silica gel as controls.

2. Background

2.1. Thin Layer Chromatography

Chromatography is when mixtures are separated by passing it through a solid material, referred to as the stationary phase, using a liquid or a mixture of liquids, referred to as the mobile phase, which will move the components of the original mixture at different rates.[3] As shown in Figure 1, thin layer chromatography (TLC) uses a thin stationary phase with a nonreactive backing, often times glass, with a mixture applied to the surface in small amounts. The mobile phase, also referred to as the solvent, is a liquid or mixture of liquids that wicks up the submerged bottom of the plate and moves the mixture to be separated along the stationary phase. Differential intermolecular interaction with the mobile and stationary phases leads to separation of compounds in a mixture as they are moved up the plate by the mobile phase. The distance that the different components of the mixture move up the plate is determined based off of their interactions with both the mobile phase and the stationary phase. On TLC plates utilizing polar silica gel as the stationary phase, component of the mixture that are less polar interact weakly with the silica gel and are carried the further up the TLC plate by the mobile phase. Compounds with greater polarity that interact strongly with a polar stationary phase such as silica gel move more slowly up the TLC plate relative to less polar compounds. In order to determine if a good solvent system is being used then the retention factor (R_f) should be calculated. The R_f is the distance that the sample traveled (in Figure 1, distance between initial final spot and initial spot) divided by the distance traveled by the solvent (in figure 1, distance between solvent line and initial spot). If a mixture is being tested via TLC it is likely that the different components of the mixture will have different R_f values. Individual substances can also be tested on a TLC plate. An ideal R_f for an individual substance if being tested individually would be between 0.20 and 0.4. To get such a value the mobile phase may have to be adjusted to be more or less polar.

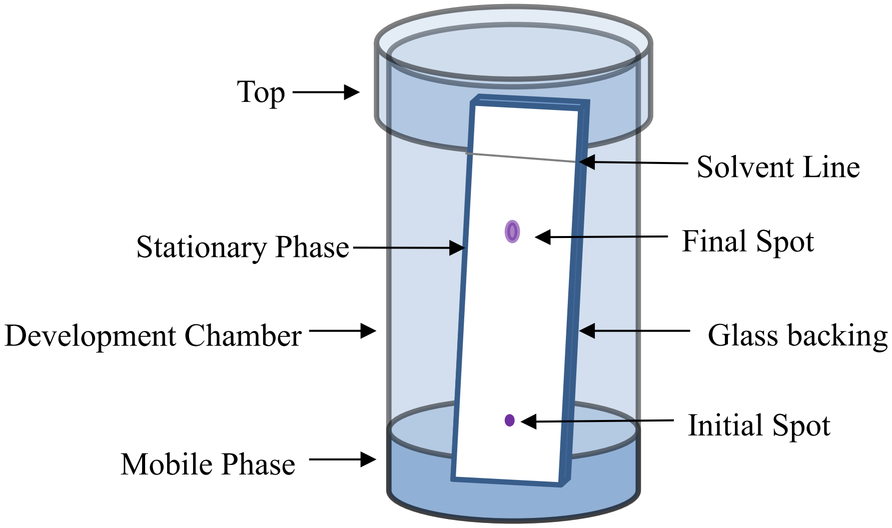

Figure 1. Diagram of a thin layer chromatography system.

2.2. Porous Solids

Substances that are classified as porous solids by definition have channels or pores permeating their structure that allow the diffusion of guests into the structure. In addition, the porous structure of these solids should remain even when the guests are completely removed. The porosity, the fraction of void volume to total volume of the substance, of these substances range from 0.2-0.95. [4] Pores make these materials good candidates to be used for molecular adsorption. The variation in pore sizes allows for different sized guest to make their way into the materials. Porous materials can be classified into groups based on their size according to regulations put in place by The International Union of Pure and Applied Chemistry (IUPAC).[5] Materials such as sponges would be macroporous (>50 nm), silica gel would be considered mesoporous (2-50 nm) and finally zeolites and MOFs would be microporous (0.2-2 nm). As the pore size gets smaller fewer guests are able to enter the pores within the guest allowing for a separation of guests that may not be able to be achieved in another way. Porous materials can also be classified as ordered and disordered. Disordered porous solids contain pores that are randomly arranged and that cannot be reproduced in a repeating pattern. Ordered solids such as MOFs and zeolites have ordered channels that are both predictable and reproducible. [6]

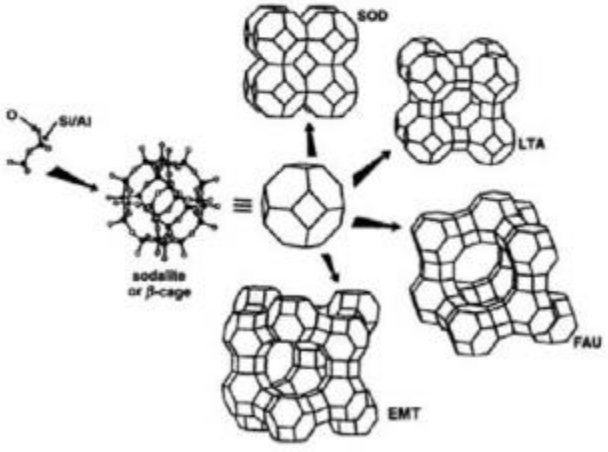

Figure 2. Examples of several zeolites showing the structures of pores resulting from covalent networks between oxygen atoms and silicon or aluminium atoms, represented by vertices in the structures shown. [7]

2.3. Metal Organic Frameworks (MOFs)

Metal-organic frameworks, or MOFs, were discovered within the last 20 years, and are an emerging class of porous solids. MOFs are self-assembling crystalline coordination complexes that form ordered polymers. They consist of metal ions of clusters that bind to bi-, tri-, or polyfunctional rigid organic ligands. The resulting molecules coordinate into one, two, or three dimensional frameworks. MOFs have large uniform channels that penetrate the structure allowing for the existence of large surface areas (3000-4500 m^2/g).[8] The physical and chemical properties of these materials can be adjusted by modifying the structures and functionality of organic ligands in the structure of the MOFs, as demonstrated by Omar Yaghi.

Yaghi first reported a highly porous and stable MOF with a cubic structure in 1999. This MOF is called isoreticular MOF-5 (IRMOF-5) and has served as a standard to which the properties of the pores of other MOFs are compared.[8] We refer to IRMOF-5 as MOF-5 throughout this report. MOF-5, depicted in Figure 3, consists of benzenedicarboxcylic acid (BDC) ligands that are coordinated to tetrahedral clusters of four zinc (II) ions. These components self-assemble into a cubic structure that has 12.9 Å by 12.9 Å channels (Figure 4) and void volumes of 52% of the total volume. MOF-5 forms in such a way that the inside of the channels is largely hydrophobic due to the benzene ring of the ligand that form the rigid linking arms of the framework. We hypothesized that the outside of particles of MOF-5 would be relatively more hydrophilic due to the presence of free, uncoordinated carboxylic acid groups of benzene-1,4-dicarboxylic acid projecting outward from the surface of the MOF-5 framework, thereby allowing for differential intermolecular interactions inside and outside of the MOF.

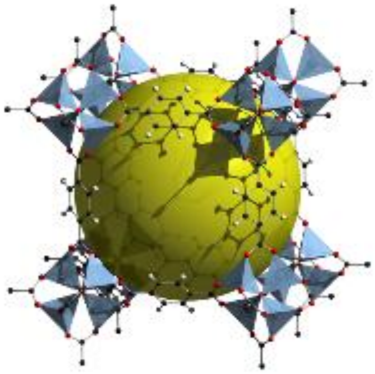

Figure 3. A ball-and-stick model showing the cubic arrangement formed by coordination of benzene-1,4-dicarboxylic acid ligands to tetrahedral clusters of four Zn(II) ions (blue) in the crystal structure of MOF-5. Void space within one cubic repeat unit of MOF-5 is represented by the yellow sphere.

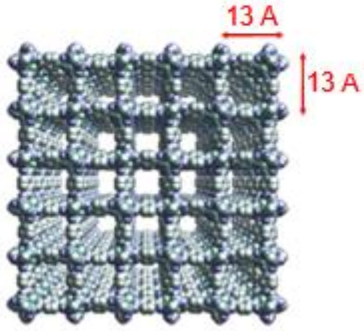

Figure 4. A space-filling model showing the repeating cubic arrangement and the corresponding 13 Å x 13Å channels formed by the coordination polymer in the crystal structure of MOF-5.

3. Experimental

3.1. Materials and Methods

Materials were all used in their original condition. Silica gel was obtained from Sorbent Technologies with a porosity of 60 Å and a particle size of 32-63 um. The binder of calcium sulfate (Plaster of Paris) was obtained from a local craft store. VWR Micro Slides were used as a base for the TLC plates. In order to create MOF-5 terephthalic acid (benzene-1,4,-dicarboxcylic acid) obtained from acros, was combined with zinc nitrate hexahydrate from alfa aesar, reagent grade dimethylformaide from pharmco-aaper, and triethylamine from sigma aldrich.

3.2. Making TLC plates with Silica Gel

The process of making TLC plates was created based on the procedures and videos found online.[10] [11] TLC plates were tested with varying percentages (10%, 15%, and 20%) of binding agent to test adhesion and ability to separate materials. The plates that were the most stable were the 20% binder by mass. Plates made from different percentages by mass of binder were all created using the same basic procedure. The 10% binder by mass consisted of 3.5 g of silica gel, 1.5 g of plaster of Paris, and 10 mL of water. The plates with 15% binder by mass had 2.75 g of silica gel, 2.25 g of plaster of Paris, and 10 mL of water. Finally the 20% binder by mass were made using 2 g of silica gel and 3 g of plaster of Paris with 10 mL of distilled water. The three components were shaken in a sealed jar for 1 minute until a slurry formed. Within 5 minutes of the slurry being formed the resulting slurry was then applied via syringe to nine clean unused glass microscope slides using just enough slurry to cover each plate. After the slurry was applied to each plate that plate was picked up by the edges and tilted to allow the slurry to gently spread across the plate. In order to increase adhesion the microscope slides were heated in an oven at 110 °C for 30-45 minutes prior to the application of the slurry. After slurry was applied to the slides they were left out overnight to fully dry. Prior to testing any dyes on the plates the, firmness of the plates were tested. Plates from every percentage were moved around and lightly poked with a gloved finger. The plates with only 10% binder were soft enough that an indent was left and some of the particles from the surface were easily brushed away. The 15% plates were also sensitive to physical contact, but only when handled roughly. Once dyes started to be tested on the plates the 15% binder plates were more likely to fall apart after coming in contact with the mobile phase. Plates with 20% binder were the only ones that were stable enough to be spotted and run TLC.

3.3. Running Thin Layer Chromatography on Silica Gel Plates

A variety of dyes of various sizes and polarities were selected as test compounds to assess and compare chromatographic separation on TLC plates of MOF-5 and silica gel. Dyes were selected due to the fact that they will be visible without the need to expose the plates to light or additional substances that may react with MOFs. The dyes selected to use were red food coloring, yellow food coloring, green food coloring, blue food coloring, ferrocene, diacetyl ferrocene, rhodamine B, crystal violet, and porphyrin. Each dye was prepped in a solvent that it was soluble in. In order to test each dye three small spots of a given dye were placed on the plate about 1cm from the bottom of the plate using 0.4 mm diameter and 75 mm length precision capillary tubes by Drummond capillary tubes. Development jars were set up by pouring a small amount of the mobile phase into a TLC jar (less than 1 cm high) and placing a small piece of filter paper vertically inside the jar to allow the environment to be more saturated with the solvent vapor to inhibit evaporation of the mobile phase from the surface of TLC plates. The spotted TLC plate was then put into the jar, spotted side down, so that the mobile phase comes beneath the spots and the top of the development chamber was put in place. The plates were left to sit in the jar as the mobile phase traveled up the plate until the solvent line was near the top. Once the solvent line was near the top, the plate was removed and the solvent line was measured in centimeters from the initial spots. The distance that the spots traveled was also measured. These two measurements were used to calculate the R_f value.

3.3.1. Food Coloring

Solutions of red, yellow, green, and blue liquid commercial food coloring were prepared by adding three drops of a given dye to 3 mL of ethanol. The initial solvent system used to run TLC with the food dyes was 30:5:5:7 n-butanol, water, ethanol, and ammonium hydroxide. This was adjust to a 10:5:5:2 by increasing the relative amounts the components.

3.3.2. Ferrocene

A solution of ferrocene was created using 0.0030 g of ferrocene and dissolving it in 1 mL of acetone. The intensity of the color was tested by spotting a small amount onto a piece of filter paper. The intensity of the spot was increased by adding ferrocene in small amounts (0.0030 g) until it was easily visible, total ferrocene 0.0090 g in 1 mL of acetone. Ferrocene solution was first tested in 1% methanol in dichloromethane (DCM) solvent which was systematically altered by decreasing the polarity of the mobile phase until pure hexanes was settles on.

3.3.3. Diacetyl Ferrocene

Diacetyl ferrocene was made into solution by dissolving a small amount (0.002 g) in 1 mL of acetone. The initial mobile phase that the diacetyl ferrocene was tested in was a 1% methanol in DCM. This mobile phase was adjusted up to a final solution with 3% methanol in 1% increments.

3.3.4. Rhodamine B

A solution of rhodamine b was created using 0.0008 g of rhodamine and dissolving it in 6 mL methanol. A 1:1 hexanes: ethyl acetate mobile phase was initially created and used to test the rhodamine b. The polarity of the system was systematically increased to until a 10% methanol in DCM solution gave good separation and well defined spots.

3.3.5. Crystal Violet

Crystal violet (0.0005 g) was dissolved in 6 mL of ethanol. The mobile phase to move the crystal violet was initially selected to be a 1:1 hexanes: ethyl acetate, but was adjusted to a higher polarity first using pure ethyl acetate, 1% methanol in DCM, 5% methanol in DCM, then increased from the 5% methanol to a final mobile phase of 9% methanol in 1% increments and testing on at least 3 different plates.

3.3.6. Porphyrin

Porphyrin (0.0008 g) was added to a 3 mL sample of DCM in order to create the aqueous solution. The original mobile phase used was a 1:1 hexanes: ethyl acetate. The polarity of the mobile phase needed to be decreased to a 10:1 hexanes: ethyl acetate for proper spot development.

3.4. Synthesis of MOF-5

MOF-5 was synthesized using the method reported by Yushan Yan. [12] Zinc nitrate hexahydrate (7.14 g, 24 mmol)) and benzene-1,4-dicarboxcylic acid (BDC) (2 g, 12 mmol) were dissolved in 240 mL of dimethyl formamide (DMF) with stirring in a 500 mL round bottom flask. Triethylamine (TEA) (13.38 mL) was added to the solution. Upon addition of the TEA, a white precipitate started to form. The reaction was stirred for 1 hour then left in the sealed flask overnight to yield a white precipitate. The precipitate was recovered by vacuum filtration and rinsed with acetone. The MOF was stored wet in a sealed jar prior to characterization then was kept unsealed for 5 days to allow the MOF to dry out.

3.5. Characterization of MOF-5

3.5.1. Characterization using Powder X-ray Diffraction (PXRD)

The PXRD was collected on a Bruker-AXS D8 Advance diffractometer using Cu-Kα radiation with X-rays generated at 40 kV and 40 mA. Samples of the MOF powder taken in their wet form from the jar and placed in the well of a plastic sample holder and scanned at RT from 3-40 ° in 0.05 ° steps at a scan rate of 2 °/min.

3.5.2. Characterization of MOF-5 by Thermogravimetric Analysis (TGA)

Porosity of the MOF was measured on the TA instrument, Hi-Res TGA 2950 Thermo Gravimetric Analyzer heating at a rate of 10 °C/min over a range from room temperature to 550 °C in a nitrogen atmosphere. The platinum pan for the TGA instrument was treated by heating it in an open flame. After preparing the pan, the instrument was tared using the clean pan. As the tare was being performed, a small amount of wet MOF was taken from the jar and pressed dry on filter paper. Approximately 5 mg of dry MOF sample was loaded into the platinum pan and run in the TGA instrument.

3.5. Preparation of TLC Plates with MOF

Two different types of MOF-5 based TLC plates were prepared. Microscope slides were prepared to have the TLC slurry applied by heating at least 9 plates in an oven set to 110 °C for 30-60 minutes. One type of plate was prepared by combining 2 g of wet MOF-5 with 3 g of plaster of Paris and 10 mL of distilled water in a sealable jar. Once all components were added to the jar it was sealed and shaken vigorously for one minute. The resulting white slurry was then removed via syringe and applied to all 9 of the prepared microscope slides within 5 minutes of the slurry being made. The other types of plate was created by allowing the created MOF-5 to air dry in an open container for 5 days then heating at least 9 microscope slides in an oven at 110 °C for 30-60. During the heating process 2 g of dried MOF-5 were combined with 3 g of plaster of Paris in a sealable jar. Once the plates were taken out of the oven the 10 mL of water were then added to the jar and it was sealed. The jar was then shaken for 1 minute to allow a slurry to form. The resulting slurry was then applied to 9 microscope slides via syringe and spread across the slide by lifting the slide by the edges and gently tilted until an even layer of slurry was on each slide.

3.6. Running TLC on MOF-5 Plates

TLC was run in the same manner as the silica gel plates. Each dye was to be tested using the final mobile phase as silica gel TLC then adjusted to find the ideal mobile phase for MOF based plates. After running some samples on both the pre dried plates and the non-pre-dried plates it was determined that the pre-dried plates gave better spotting so future tests would only be carried out on the pre dried plates. The non-pre-dried MOF did not dissolve as well in the water to make a uniform slurry. When applied to microscope slides there were clumps of MOF-5 disrupting the smooth surface of the TLC plates. These clumps interfered with the running of dyes on the plates, giving inconsistent results when tests were run.

3.6.1. Food Coloring

The food coloring samples were not able to be tested on the MOF plates due to time restrictions.

3.6.2. Ferrocene

Ferrocene was made into solution by adding 0.0030 g of ferrocene to 1 mL of acetone. The visibility of the spot was tested by spotting it with a capillary tube on filter paper. Ferrocene was added in increments of 0.0030 g until it was easily seen at 0.0090 g of ferrocene in 1 mL of acetone. Ferrocene solution was tested using pure hexanes as a solvent system.

3.6.3. Diacetyl Ferrocene

The sample of diacetyl ferrocene was put in solution by adding diacetyl ferrocene (0.002 g) to 1 mL of acetone. This solution was tested on MOF plates using a mobile phase of 3% methanol in DCM.

3.6.4. Rhodamine B

Rhodamine b (0.0008 g) was added to 6 mL of methanol to create a solution. A MOF-5 TLC plate was spotted with rhodamine b and run in 10% methanol in DCM mobile phase.

3.6.5. Crystal Violet

Crystal violet was turned into solution by adding 0.0005 g of crystal violet to 6 mL of ethanol. This was first tested with the 9% methanol in DCM. Less polar solvents were systematically tested by decreasing the amount of methanol in 1% intervals until a 1% methanol in DCM, then switched to 1:1 hexanes: ethyl acetate, followed by 5:1 hexanes: ethyl acetate then pure ethyl acetate.

3.6.6. Porphyrin

Porphyrin was not tested on the MOF-5 plates.

4. Results and Discussion

4.1. Synthesis and Characterization of MOF-5

While conducting this project it was necessary to ensure that the precipitate formed was actually MOF-5 prior to attempting to create TLC plates. During synthesis of MOF-5, there was no noticeable reaction happening while the zinc nitrate hexahydrate, BDC, and DMF were being mixed. As soon as the TEA was added a white precipitate started to from. This precipitate needed to be tested using methods that are standard to this type of powdered solid. Both thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) were taken on the solid either immediately after separation or after it had been stored in a sealed jar for one day, due to time constraints preventing analysis being performed immediately.

TGA is a test that measures the percentage of weight loss of porous solids as guest solvents escape from the pores of the solid. It is often used to confirm the porosity of materials. If a solid is nonporous then there will be no loss of mass in the TGA until higher temperatures, where the material decomposes. In this experiment it was used both to confirm porosity and to determine the thermal stability of the MOF. It is typical for MOF-5 to lose 40-55% of its mass when heated in TGA and to remain thermally stable up to 450 °C. TGA data of the precipitate can be seen in Figure 5. The initial loss of 55% mass of the solid from room-temperature to 150 °C shows a loss of DMF (boiling point 153 °C). The additional 5% mass lost would be from excess TEA (boiling point 89 °C). The system shows stability from 200 °C to 460°C. The final loss of mass above 460 °C is indicative of MOF-5 decomposing. The trends in the TGA are consistent with the expected thermal behavior of MOF-5 that has not been activated through heating or removal of DMF through vacuum.

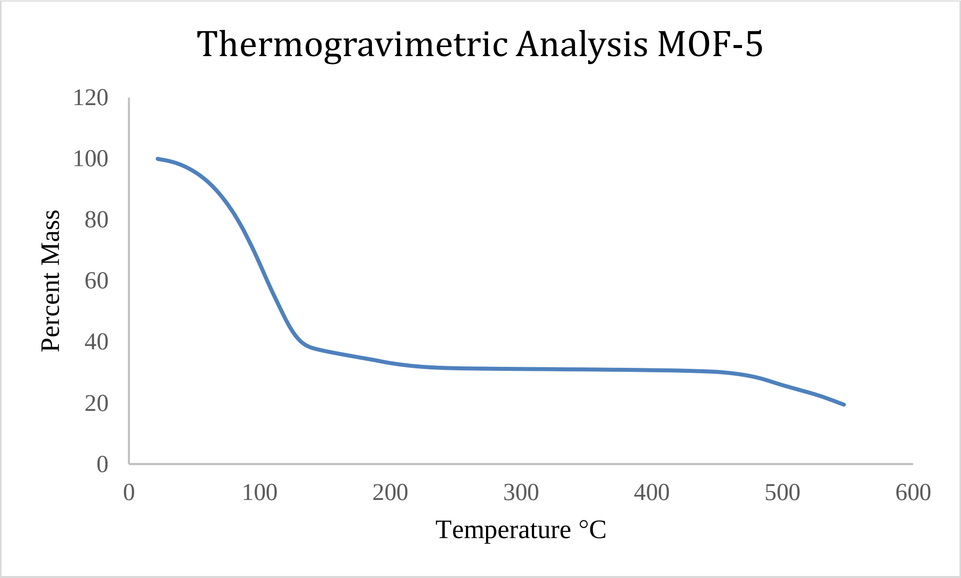

Figure 5. TGA Data collected on MOF-5 sample.

PXRD is used as a method to characterize crystalline materials. Since there are PXRDs already in existence for MOF-5, such as the one in Figure 6 from Yan et al, we were able to run PXRD under the same conditions and directly compare the results. The PXRD data gathered on the precipitate formed during this experiment has been lost and cannot be shown.

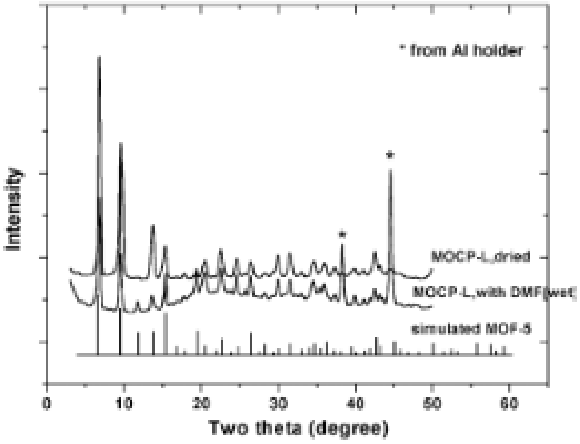

Figure 6. PXRD of MOF-5 from procedure created by Yan et al.

4.2. Creating TLC Plates Using MOF-5

TLC plates using MOF-5 as the stationary phase were able to be created. Before creating plates with MOF was attempted, a reliable method to make silica gel plates was created. Since making TLC plates with silica gel is fairly common, we just needed to adjust some procedures to make sure that the components we had in the lab would work. Most procedures found tended to use gypsum or plaster of Paris. Gypsum is calcium sulfate dihydrate whereas plaster of Paris is calcium sulfate hemihydrate. Since the materials were so similar and going to be mixed in water as a solvent, plaster of Paris was used because it was easier to obtain. As discussed above it was necessary to determine what percent binder by mass the silica gel plates should be, 10%, 15%, or 20%. Whatever was decided to be the best ratio based on hardness and how well TLC can run on the plate would be used as the ratio for the MOF plates as well. Since the 20% binder by mass was the best most stable phase because the others were too soft to be used MOFs were made with 20% binder with not testing of lower percentages.

Throughout the process of making TLC plates with MOF-5 the biggest trouble encountered was difficulty adhering the dried slurry to the glass substrate. This was only a problem that occurred with the MOF plates. The MOF and plaster of Paris would bind to each other but on occasion some of the plates created in a batch of 9 would have the dried slurry slide off the of the glass substrate in one cohesive piece. It was believed that the issue arose due to contaminants on the surface of the plates. We was theorized that residual contaminants introduced during the manufacturing process or in the lab might be responsible for the poor binding of the MOF slurry. In order to attempt to lessen this issue plates were rinsed with acetone, as standard way to clean glass substrates. This method did not make any difference in the adhesion of the slurry to the glass substrate. Two other methods were attempted to give better adhesion. The first method was to rinse with acetone (boiling point 56 °C) then heat the plates in an oven at 110 °C before the slurry was applied. This method hoped to remove any contaminants with the acetone rinse then heat any remaining acetone off with the hope that it would leave the dangling bonds on the surface that the binding agent could then bond with. The second method was just to heat the plates before applying the slurry in the oven at 110 °C for 30 minutes. This was done under the assumption that water was on the surface, and would be driven off when heated above the boiling point. Both of these methods gave better adhesion, but there was no evidence that one was better than the other so going forwards it was decided to just heat at 110 °C for 30 - 60 minutes before the slurry would be applied. The best timeline for creating the plates was to heat the glass substrate in the oven for 30-60 min, during that time the solid components to the slurry were measured out, once the substrate was done being heated it would be removed from the oven, after that the slurry would be mixed then immediately applied to the glass substrate, they would then be left to air dry to a day. The plates needed to be air dried to allow for the binding agent to set properly. The plates came out as seen in Figure 7 and were stored in a petri dish in open air when not in use. Prior to them being used they would be placed in an oven at 110 °C for 30 minutes to drive off any additional water that would interfere with the running of TLC. This was a method used for both the MOF plates and the silica gel plates and did allow for better spotting and running of TLC than if they had not been pretreated with heating in the oven

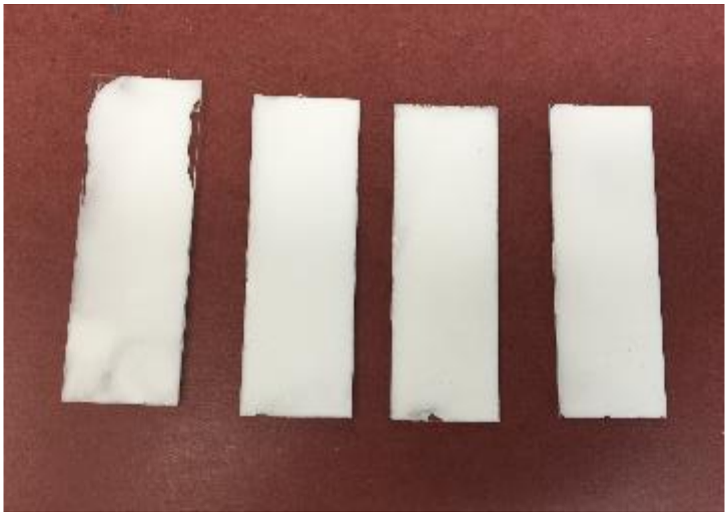

Figure 7. TLC plates after drying overnight made with MOF-5, plaster of Paris, and water.

4.3. Examining chromatographic behavior of dyes on MOF based TLC plates

In order to test how well MOF-5 functioned as a stationary phase in TLC substances that could be visualized needed to be selected to test. Often times in TLC performed on silica gel plates are visualized due to the presence of a fluorescent indicator in the plate itself which glows green under 254 nm light. This light is quenched by pi bonds that are in contact with the indicator showing dark spots where compounds are located. This method was not tested with MOF based plates due to the fact that MOF-5 contains benzene-1,4-dicarboxcylic acid which is an aromatic compound that contains pi bonds. Assuming that MOF-5 would immediately quench the indicator it was decided that the best method to visualize spots would be to not need any additional components and use compounds that could already be seen by the naked eye, in this case a series of dyes. The dyes were also beneficial in being selected due to the fact that they are all aromatics with large surface areas and van der Waals interactions that will allow for them to interact strongly with the aromatic benzene rings in the structure of MOF-5. Of the dyes selected it was made sure that there were a variety of sizes. This was done with the intention that we would make some TLC plates using a MOF that had a smaller channel size than the 13 Å channels in MOF-5. All of the dyes selected were small enough to fit inside the MOF-5 channels, but by running them with a smaller MOF there could have been a difference in how the TLC ran due to some dyes being able to enter the channels and some that would not. Although this was no something that was able to be tested, the size difference in dyes could still allow for differential binding to get additional separation. The final characteristic taken into account when selecting dyes was their polarity. Currently one of the most important detail that affects separation of materials in TLC is the polarity of compounds being run and how that will interact with the stationary phase and the mobile phase. The dyes selected had a variety of polarities so that the difference in how they react could be tested both on the silica gel plates and one the MOF-5 plates. The dyes that were selected for testing can be seen in Figure 8 and are listed in order of decreasing polarity: rhodamine b, crystal violet, diacetyl ferrocene, porphyrin, and ferrocene. Commercially made liquid red, yellow, green, and blue food coloring were also tested.

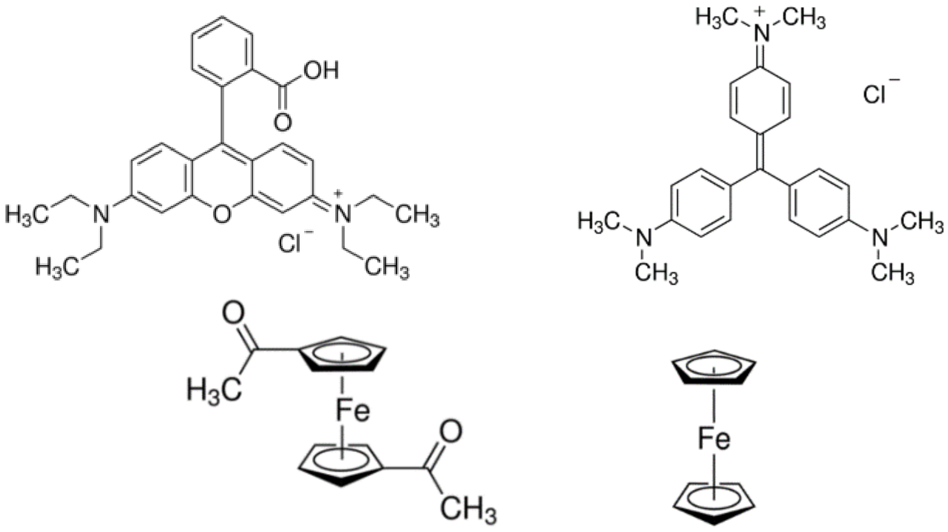

Figure 8. Structure of selected dyes used on TLC plates in relative size comparison. Dyes are in order of decreasing polarity. From left to right: rhodamine b, crystal violet, diacetyl ferrocene, porphyrin, ferrocene.

With the dyes selected it was necessary to find the mobile phase that gave the best spot for each dye. A good spot is one that is fairly concise (not a large streak) and has a retention factor (R_f) value between 0.20 and 0.40. The R_f is the distance from the initial spot to the center of the final spot divided by the distance from the initial spot to the solvent front. Mobile phases were first found on the silica gel plates then used as the starting phase for MOF plates. Rhodamine b spots when run on MOF plates had and R_f value of 0.45 and a lot of streaking as can be seen in Figure 9. Of the other dyes only crystal violet, ferrocene, and diacetyl ferrocene were able to be run on the MOF plates. In Figure 10, all three of these dyes are seen at their respective solvent fronts. The R_f value of each of these dyes came out to be 1. There was not time to find better solvent systems that would give smaller R_f values so further analysis of the chromatographic behavior was not done.

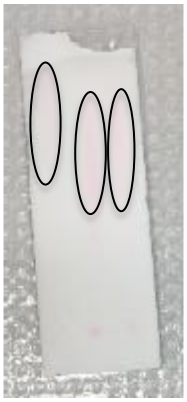

Figure 9. Rhodamine b spots run on MOF based TLC plates that was run in 10% methanol in DCM showing the streaking.

Figure 10. MOF based TLC plates with (from left to right) crystal violet run in 9% methanol in DCM, diacetyl ferrocene in 3% methanol in DCM, and ferrocene in pure hexanes.

4.4. Comparing chromatographic behavior of dyes on MOF plates versus TLC plates

The mobile phases that were determined on the silica gel plates were used on the MOF plates as a starting mobile phase in order to allow for direct comparisons between the silica gel and MOF plates using the same system. We were initially unsure on how the mobile phases might run on MOF plates so finding system that worked well on silica gave a good starting point for when adjustments needed to be made. There were a few noticeable patterns that occurred when transitioning from the silica gel plates to the MOF plates. The first difference was that the mobile phases tended to move faster when traveling up the MOF plates. This is likely due to capillary action, which is the tendency of liquids to rise or fall as a result of surface tension in absorbent material. Another pattern that was observed can be seen in Figures 11-13 and was that most of the dyes that were run on the MOF plate never left the solvent front. This would be consistent with the knowledge the MOF-5 is a less polar stationary phase than silica gel. Though both silica gel and MOF-5 have hydroxyl groups on their surfaces they are part of different classifications of materials. Silica gel has alcohol groups that appear frequently at regular intervals. MOF-5's surface has acids groups along it, at infrequent intervals. Though overall acids are more polar than alcohol groups, the frequency that the alcohol groups occur on the surface of the silica gel compared to the acids on the MOF allows for the silica gel to be more polar. MOF-5 also has a hydrophobic inside which tends towards being less polar. Should the dye diffuse into the MOF system rather than traveling along the surface, it will have a much less polar system to interact with. The only dye that did not stay at the solvent front was rhodamine b, though it did still travel further up the MOF plate than the silica gel plate as can be seen in Figure 14. The rhodamine b did also appear to streak more on the MOF plate than the silica gel. That pattern would show that the rhodamine b is the most polar compound tested on the MOF plate as well as the most likely to bond with the MOF which could be cause for the streaking. Since rhodamine b was the largest dye being tested it makes sense that it would be the most likely to interact with MOF via van der waals interactions.

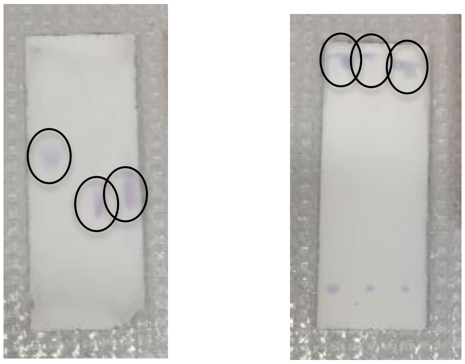

Figure 11. Crystal violet on silica gel (left) and MOF (right) using 9% methanol in DCM.

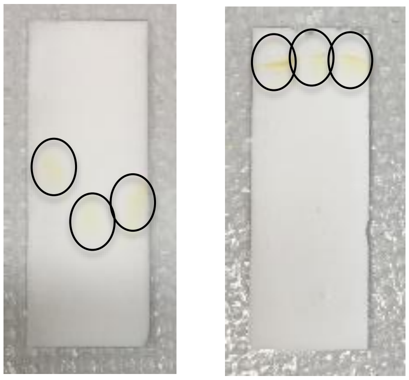

Figure 12. Ferrocene on silica gel (left) and MOF (right) using pure hexanes.

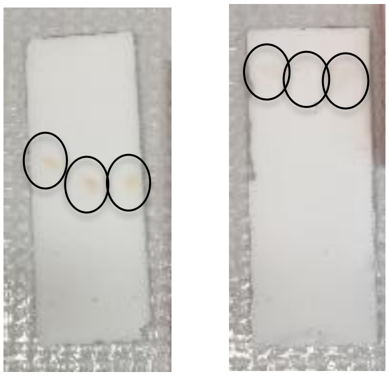

Figure 13. Diacetyl ferrocene on silica gel (left) and MOF (right) using 3% methanol in DCM.

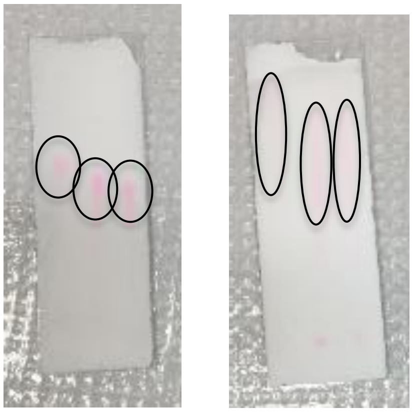

Figure 14. Rhodamine b on silica gel (left) and MOF (right) using 10% methanol in DCM.

5. Conclusions

Throughout the process of this project there were some goals that were met and some longer term goals that were not able to be met. We were able to synthesize and characterize MOF-5. The procedure provided by Yan et al was able to be performed in much less time than other MOF-5 synthesis methods, and still gave the correct MOF structure. This was shown through the TGA and PXRD analysis run on the untreated precipitate in its wet form. The MOF-5 created following Yan's procedure was able to be used in the creation of TLC plates. MOF-5 (2 g) had been combined with plaster of Paris (3 g), and distilled water (10 mL) then applied to glass substrates. The TLC plates created with MOF-5 were stable to the touch with the exception of plates that had not been treated by heating. The plates made without treating the glass substrates had poor adhesion of the slurry to the glass substrate. In order to test the MOF-5 plates that were made a library of dyes of various sizes and polarities were selected. These dyes included rhodamine b, crystal violet, diacetyl ferrocene, porphyrin, and ferrocene, as well as red, yellow, green, and blue liquid food colorings. Of these dyes only rhodamine b, crystal violet, diacetyl ferrocene, and ferrocene were able to be tested on the plates made with MOF-5. When testing these plates it was observed that they gave R_f values over 0.4, which was undesirable. Further research should be done on what solvent systems would provide the best R_f values within the 0.2 and 0.4 range. By figuring out what the best solvent system for a better look at how the dyes behave on the MOF-5 plates. Another step that should be taken is testing the remaining dyes with MOF-5 plates to see if they have any unique patterns that the ones tested here did not represent. A long term goal that was not reached was to create a MOF based TLC plate using a MOF with smaller pore sizes. By testing our library of dyes on a plate that had smaller pore sizes, the would be done to see if there was different chromatographic behavior based on some of the dye potentially not making being able to diffuse into the MOF and only having surface interactions. If size exclusion from entering MOFs during TLC does cause for different chromatographic behavior then a new avenue of chromatography can be researched more in depth.

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