UTILIZATION OF METAL-ORGANIC FRAMEWORKS FOR GAS SEPARATIONS AND CATALYTIC OXIDATION

By

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemistry).

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Metal-organic frameworks (MOFs) and their applications have been a rapidly growing area of research in recent years. The seemingly endless combinations of metal ions or clusters with various possible organic linkers, along with the methods of post-synthesis modification, has resulted in approximately 20,000 different MOFs to date. With such potential for variation, MOFs have shown to be useful in a whole host of applications.

One such application of MOFs is the separation of natural gas. Currently, these separations require expensive methods, such as amine absorptions and cryogenic distillation. Polymers, such as polyimide, have been investigated, but the necessary high temperatures lead to plasticization and poor separation performance. Alternatively, ZIF-8 (zeolitic imidazolate framework 8), a member of the ZIF class of MOFs, is a viable option due to its inherent pore size and preferential adsorption of carbon dioxide. Microporous carbon membranes have shown increased chemical and thermal stability. By converting the microporous ZIF-8 to a carbon membrane, the resulting membrane can be expected to maintain the separation properties of the parent ZIF-8 while gaining additional stability provided by carbon. Unfortunately, synthesizing this material is a challenge to reproduce due to the wide variety of methods for ZIF-8 synthesis and the limited study of the effect of carbonization on the parent material.

A second application of MOFs is as heterogeneous catalysts. Cu-BTC, or HKUST-1, is used for the oxidation of benzyl alcohol to benzaldehyde, a chemical commonly used in perfumery and pharmaceuticals. However, the use of copper requires the presence of TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) as it is needed to deprotonate the alcohol. Unfortunately, TEMPO can interrupt the framework structure of Cu-BTC and poisons the catalysts. In order to help combat this problem, layer by layer synthesis of Cu-BTC was used to incorporate the MOF into the pores of a functionalized mesoporous silica nanoparticle (MSN). However, this incorporation did not protect the Cu-BTC, as the pores size of the protective MSN was insufficient to prevent TEMPO access. Additionally, only a small amount of Cu-BTC was synthesized within the pores, which magnified the effects of TEMPO poisoning.
# TABLE OF CONTENTS

**ABSTRACT** .................................................................................................................................. iii

**LIST OF FIGURES** ....................................................................................................................... vi

**LIST OF TABLES** ........................................................................................................................ vii

**ACKNOWLEDGMENTS** ........................................................................................................... viii

**CHAPTER 1 INTRODUCTION TO THE MATERIALS** ..............................................................1

1.1 Metal-Organic Frameworks ........................................................................................................ 1

1.1.1 Synthesis of MOFs ....................................................................................................... 2

1.1.2 Applications of MOFs ............................................................................................... 3

1.2 Mesoporous Silica Nanoparticles ........................................................................................ 5

1.2.1 Synthesis of MSNs .................................................................................................... 5

1.2.2 Applications of MSNs ............................................................................................... 7

1.3 References ........................................................................................................................ 8

**CHAPTER 2 ZIF-8 BASED CARBON MEMBRANES FOR NATURAL GAS SEPARATIONS** ...............................................................12

2.1 Natural Gas Separations with Membranes ........................................................................ 12

2.2 Methods .................................................................................................................................. 13

2.2.1 ZIF-8 Membrane Synthesis ..................................................................................... 13

2.2.2 Membrane Carbonization ........................................................................................ 14

2.2.3 Gas Separations Testing .......................................................................................... 14

2.2.4 Additional Carbon Techniques ................................................................................ 14

2.2.5 Characterization ...................................................................................................... 15

2.3 Results and Discussion ..................................................................................................... 15

2.4 Conclusions ....................................................................................................................... 20

2.5 References ....................................................................................................................... 20

**CHAPTER 3 Cu-BTC INCORPORATED INTO FUNCTIONALIZED MSN-10 AS A HETEROGENEOUS CATALYSIS FOR THE OXIDATION OF BENZYL ALCOHOL** ...........................................................................................................23

3.1 Introduction ......................................................................................................................... 23

3.2 Methods .................................................................................................................................. 25

3.2.1 MSN-10 Synthesis ................................................................................................... 25

3.2.2 Functionalized MSN-10 synthesis .......................................................................... 25

3.2.3 MOP-CuSO₃ Synthesis .......................................................................................... 26
LIST OF FIGURES

Figure 1.1 Application of metal-organic frameworks ................................................................. 3
Figure 1.2 Mechanism for the formation of MSNs ...................................................................... 5
Figure 2.1 Schematic of membrane preparation ........................................................................ 13
Figure 2.2 SEM images of ZIF-8 powders ................................................................................ 17
Figure 2.3 XRD spectra of ZIF-8 powders .............................................................................. 17
Figure 2.4 Nitrogen sorption of ZIF-8 powders ....................................................................... 18
Figure 2.5 SEM images of 2-layer ZIF-8 membrane ................................................................. 19
Figure 3.1 MSN Characterizations ......................................................................................... 29
Figure 3.2 Nitrogen isotherm of Cu-BTC ................................................................................. 31
Figure 3.3 Nitrogen sorption analysis of impregnation method ................................................ 32
Figure 3.4 Nitrogen sorption analysis of synthesis method ..................................................... 33
Figure 3.5 Isotherms of mixed MSN with Cu-BTC ................................................................. 34
Figure 3.6 Nitrogen sorption analysis of layer by layer method ............................................. 35
Figure 3.7 XRD of layer by layer method materials .............................................................. 36
Figure 3.8 SEM image of Cu-BTC@MSN-OP via layer by layer method ............................... 37
Figure 3.9 EDS of Cu-BTC@MSN-OP .................................................................................. 38
Figure 3.10 XRD of PostRxn .................................................................................................. 39
Figure 3.11 PostRxn Cu-BTC@MSN-OP .............................................................................. 40
LIST OF TABLES

Table 1.1 Methods of Pore Size Control ......................................................................................... 6
Table 2.1 Membrane Separations Data .......................................................................................... 16
Table 3.1 Textural Properties of MSNs ........................................................................................ 30
ACKNOWLEDGMENTS

Thank you to all of the people who have provided support and guidance along my journey. Without you, I could not have made it this far.

I would like to thank my advisor Dr. Brian Trewyn for his guidance and assistance over the years. Your high expectations and support were a valuable experience that helped me to realize and become the scientist I have always envisioned. My thanks also go to my committee members: Dr. Moises Carreon, Dr. Ryan Richards, and Dr. Svitlana Pylypenko for the time you have given to help me make it to this point. A special thanks to Dr. Moises Carreon for your additional guidance in understanding the workings of membranes and metal-organic frameworks. It helped me get an essential understanding of my work.

Thank you to all my group members, past and present, for your assistance both in and out of the lab. An extra thanks to Dr. Megan Moyer. I will always be thankful for your assistance getting me started in the lab and for helping me understand all things mesoporous silica. Thank you to my membrane collaborators: Ting Wu and Dr Moises Carreon for your feedback and work testing all of the membranes I created.

I also like to thank all the people who supported and commiserated with me over my time spent here, especially: Dr. Patrizia Smith, Ms. Marisa Adams, Mrs. Kendall Rothenberg, Mrs. Jordan Gribben, and Mrs. Megan Rose.

To my family, especially my parents, Morgan and Vicki Evans, and grandparents, Howard and Judy Evans. You never stopped believing in me, even when I thought it was impossible. I know your love and support, even from afar, has shaped me into the person I have become.

Finally, thank you to Thomas Deisz, who has been more supportive and patient than I could have imagined. You have been my rock through it all, and I am forever appreciative of all you have done.
CHAPTER 1
INTRODUCTION TO THE MATERIALS

1.1 Metal-Organic Frameworks

Metal-organic frameworks, MOFs, are part of the metal-organic materials (MOM) family. These materials are made of metal ions or metal clusters along with organic molecules held together via coordination bonds. MOFs are also closely related to metal organic polyhedral (MOPs), which are also self-assembled metals with organic linkers. MOPs differ from MOFs in a few key ways. MOPs are three-dimensional, finite supramolecules that are soluble such that they can exist in equilibrium within a solution. Upon removal of the solvent, they can reassemble to leave behind a solid, powder-like material. MOFs on the other hand, are infinite coordination networks that can be one, two, or three dimensional depending on the composition of the material. Additionally, they are insoluble, crystalline solids. As of a 2007 review, there are approximately 20,000 different MOFs for a wide variety of applications. This great versatility arises from the seemingly endless combinations of metal components with organic linkers. With such variation comes excellent structure features including; high thermal and chemical stability, low density, various pore sizes with ultrahigh surface areas, and the possibility of luminescence and electric properties.

MOF materials are often compared to zeolites, especially when in reference to their applications as catalysis. This is not because MOFs and zeolites are seen as true competitors, but rather MOFs may better fill the needs of industry where zeolites are less than ideal. A subclass of MOFs, known as ZIFs (zeolitic imidazolate frameworks) has close ties to the structure of zeolites. ZIFs are based on the crystalline structure of a zeolite. The atoms located at the T-site within the zeolite are replaced with a transition metal such as zinc or cobalt. Similarly, the bridging oxygens are replaced by imidazolate. Although ZIFs and zeolites have a lot in common, there are some distinctive differences. The porosity of ZIFs is substantially higher leading to higher surface areas. ZIFs have more chemical diversity and the possibility of flexible pores. Finally, the synthesis is simplified as there is no need to remove the template.

With such variability in the components used to assemble MOFs a new class has appeared the Bio-MOF or also MBioFs. This new group is defined as a MOF that is synthesized from at least one biomolecule, usually the organic linker. Simple biomolecules such as amino
acids, nucleobases, and sugars are naturally available in quantities that make bulk synthesis feasible. Using biomolecules makes the resulting material more biologically compatible, and many of them can be synthesized with biocompatible metal units as well. Bio-MOFs have shown to be less stable than traditional MOFs. However, some level of instability is acceptable. This newer class of MOFs is heavy investigated for drug delivery and other biomedical applications, so as long as the material is stable enough to complete its intended mission, it can then break down and be processed by the body.

1.1.1 Synthesis of MOFs

Despite having such high amounts of variation in the final product, the synthesis of MOFs is relatively standard. It is most often done via solvothermal methods with the organic ligand and the metal source are dissolved in a polar solvent. The critical parameters are temperature, concentration and solubility of the reagents, and the pH of the solution. There have been some preliminary investigations into the use of microwave methods to reduce the length of time required and increase the control of the particle sizes. The resulting structure is dependent upon both the metal and the ligand. Metal ions determine the overall geometry of the crystals. In some cases, a metal cluster is used such as the dimetal paddlewheel which is used in the Cu-BTC explored in Chapter 3. These clusters are referred to as secondary building units (SBU). As the linkers then coordinate with the metal ion or cluster, it determines the direction of the resulting framework. In general, the higher the connectivity of the ions and the paired ligands, the higher the dimension of the final product, ranging from one to three-dimensional.

Much like the previously discussed MSNs, MOFs can also be further modified. This capability allows for more complex structures, greater system control, and increase functionality. All modifications are done post synthesis and fall into three classifications; ligand exchange or modification, metal exchange, and stratified synthesis. Ligand modification involves using organic synthesis methods to add or alter the functional groups present on the linker. Some modifications can be a complex process as care must be taken not to alter the functional groups involved in the coordination bond, or else the MOF structure is damaged. Adding more functional groups is often done to fine-tune the material for the desired application. Similarly, the ligand can be completely exchanged by soaking the pre-synthesized material in a solution containing the desired linker. This process maintains the porosity, and when the new ligands are chosen carefully, the new material will have similar textual properties such as pore size and
surface areas.\textsuperscript{31} The metal exchange is done in a method much like ligand exchange. However, it tends to require some solvothermal treatment.\textsuperscript{32} The stratified synthesis results in a heterogeneous material. Most commonly, this result is accomplished via partial ligand exchange such that the outermost ligands are different from those located in the center region of the particle.\textsuperscript{33}

1.1.2 Applications of MOFs

Due to the extensive variation in MOF materials, they have been investigated for a broad range of applications including gas storage and separations, catalysis, and energy production. Figure 1.2 shows the extensive areas of MOF applications, which have been extensively reviewed.\textsuperscript{17-18, 21, 25, 29} As such, only the three applications that apply the work presented here will be discussed.
The high surface areas and controllable ligands make MOFs good candidates for gas storage and separations. One study compared the capabilities of a series of IRMOFs (isoreticular); IRMOF-1, -6, -11, -20 and MOF-177 to store hydrogen gas. The surface areas of the materials ranged from 2340 – 5640 m$^2$g$^{-1}$ and found that the highest surface area resulted in the most significant amount of gas storage. In contrast, another material PCN-14, which was made of copper paddlewheels and an anthracene derivative, was investigated as a method of methane storage. With lower surface area than the previously discussed work, at 2176 m$^2$g$^{-1}$ it still held some methane gas due to the open coordination site of the copper. However, upon altering the organic linker post-synthetically, the methane adsorption increased to 22% higher the target set by the US Department of Energy.

Gas separations are an application related to gas storage. This is because the adsorption property associated with a particular material can be part of the separation mechanism. For example, a manganese formate material was found to selectively adsorb hydrogen and carbon dioxide gas over nitrogen, argon, and methane. The selective adsorption was partly due to the adsorption properties of the materials, and partly due to the pore sizes acting as molecular sieves. Other MOF materials used in separations make use of competitive adsorption, molecular sieving, and differences in diffusivities. A ZIF-8 membrane that was used to separate a mixture of Kr and Xe gases demonstrated all three of these separation mechanisms. Utilizing molecular sieving with competitive adsorption properties of ZIF-8 was utilized in natural gas separations in chapter two.

MOFs have also been heavily investigated for use in heterogeneous catalysis as the reactive site can be located on the metal, on the ligand, or both. A MOF made of copper paddlewheels and an organic linker containing carboxylate, pyridine, and amide groups was found to be an effective tandem catalyst as well as selectively adsorb carbon dioxide. The presence of a Lewis acid site on the open sites of the Cu$^{2+}$ ion, paired with the Lewis base of the pyridine and amide groups, made the material and excellent tandem, one-pot catalysts in the sequential deactalization and Knoevenagel condensation reaction. Finally, HKUST-1 also known as Cu-BTC, was deposited with gold clusters and found useful in the oxidation of alcohols. This particular MOF was further investigated in the same reaction in chapter three.
1.2 Mesoporous Silica Nanoparticles

Mesoporous silica nanoparticles (MSNs), a mesoporous form of silica, have several structural features making them ideal candidates for a variety of applications. Such features are chemical, thermal, and mechanical stability; ordered, controlled, and tunable pore morphology, large surface areas; and functionalizable surfaces, both inside and out. Two groups in the early 1990s synthesized MSNs.\(^1\) Two works utilized both inorganic and organic species to which allowed the organization of the silica polymer to directed by cationic alkyltrimethylammonium micelles, which will be discussed in more detail in the next section. The work by Kresge and coworkers called this new family of particles MCM-41 (Mobil Crystalline Materials). By controlling the precursor materials, the resulting particles can vary in morphology from spheres to rods and have a pore size range of 2 – 30 nm.\(^2\)\(^-\)\(^3\) About six years later, a group led by Zhao at the University of California, Santa Barbara published work showing rod-shaped silica nanoparticles with larger pores, 5 – 30 nm.\(^4\) This material was named SBA-15 (Santa Barbara Amorphous material) and utilized a triblock copolymer as the template in place of the cationic alkyltrimethylammonium. Then in the early 2010s, another large pore mesoporous silica nanoparticle entered into literature named MSN-10.\(^5\)\(^-\)\(^6\) This material used a nonionic surfactant like SBA-15 and had hexagonally arranged pores, but rather than rod-shaped the particles were hexagonal cylinders. The area of MSNs expends far beyond just MCM-41, SBA-15, and MSN-10 but these are representative of the related history leading up to the creation of material used in this thesis work, MSN-10.

1.2.1 Synthesis of MSNs

Mesoporous silicas result from the hydrolysis and condensation of silica precursors that is directed by a liquid crystal array of surfactant micelles, visualized in Figure 1.1.\(^7\) Variations in the synthesis conditions, such as pH, temperature, molar ratios, and templates results in a variety of mesophases.

![Figure 1.2 Mechanism for the formation of MSNs\(^7\)](image-url)
In general, a synthesis involves the aqueous hydrolysis and condensation of a silica precursor, typically tetramethyldihydrosilicate (TMOS) or tetraethylorthosilicate (TEOS) in the presence of the structure directing agent, or surfactant. These materials are combined in a basic solution when using a cationic surfactant such as N-alkyl trimethylammonium bromide (CTAB) for the formation of MCM-41, or in acidic conditions when using a nonionic surfactant such as Pluronic P104 for MSN-10. A couple of mechanisms for the surfactant aggregation and subsequent porous silica formation have been proposed. In one theory, the addition of the silica precursor and its subsequent condensation activates the formation of the micelle array. However, the liquid crystal mechanism states (Figure 1.1) that the solution must be at or above the critical micelle concentration where it then forms a liquid crystal structure before the addition of a silica precursor. After the required hydrothermal treatment time, the organic surfactant is removed to open the pore structure. The removal can be done either by high-temperature calcination or via acidified alcohol wash, depending on the synthesized material and the planned applications.

One of the many benefits to MSNs is the ability to alter pore size and apply surface functionalization in a controlled manner. Pore size control is achieved by the surfactant or with pore swelling agents. Table 1.1 presents a summary of the methods used to control pores size. With cationic surfactants, the pore size is adjusted by changing the length of the alkane chains, longer chains leading to larger pore sizes. In the case of nonionic polymer surfactants, increasing the molecular weight of the hydrophobic regions has the same effect on the resulting pore size. Additionally, the pore can be expanded with the addition of size mediators such as DMHA (N, N-dimethylhexa-decylamine) or TMB (trimethylbenzene). These mediators work by integrating into the micelle formation with the surfactant to create a larger micelle.

<table>
<thead>
<tr>
<th>Pore Sizes (nm)</th>
<th>Compounds Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 – 5</td>
<td>cationic surfactants with varying chain lengths</td>
</tr>
<tr>
<td>4 – 7</td>
<td>long-chain cationic surfactants</td>
</tr>
<tr>
<td>5 – 8</td>
<td>charged surfactants with swelling agents</td>
</tr>
<tr>
<td>2 – 8</td>
<td>nonionic surfactants</td>
</tr>
<tr>
<td>4 – 20</td>
<td>triblock copolymers</td>
</tr>
<tr>
<td>10 – 27</td>
<td>high molecular weight block copolymers with and without swelling agents</td>
</tr>
</tbody>
</table>
Also, the altering the pore size, the surface of the MSN can be functionalized to aid in the application, such as containing a homogeneous catalyst or tethering a biomolecule. The first and more popular method is post-synthetic grafting. In this process, the desired functionality is covalently added to the already synthesized MSN via silylation in a moisture free environment. The original material remains intact, but where the functionalization occurs is mainly dependent on the pore size and the ability of the functional group to diffuse into the pores. Typically this, this post-synthetic process places a majority of the added functional group on the outer surface and near the pore entrances. Alternatively, using the in situ co-condensation method results in a more homogeneous functionalization of the MSN surfaces. This process is done by adding the desired functional group to the template formation with the TEOS or TMOS. Then the silanes present condenses simultaneously (co-condense) leading to the uniform distribution of the additional functional group. Through the use of pore expansion and surface functionalization, MSNs are a versatile material with a variety of applications.

1.2.2 Applications of MSNs

The structural properties of MSNs, in particular, the relative ease with which the pore sizes and surface functionality can be altered, make these particles useful in several applications including protein and drug delivery, chemical detection or sequestrations, and catalysts. A few examples are briefly presented in this section to provide an overview of some commonly investigated applications.

Protein delivery has been investigated both with pore expanded MSN and with surface functionalized MSN. Concanavalin A was dissociated into dimers and loaded into pore expanded MCM-41 type. The dimers were small enough to fit into the pores, while the fully associated protein could not. After the release, the dimers re-associated into the active protein. Similarly, the enzyme, carbonic anhydrase was released only within the cell by functionalizing the surface of the MSN particles with a thiol group which then covalently attached to the enzyme. Enzyme release relied on the redox conditions within the cell, specifically the increased concentration of glutathione. Although that example made use of the cells redox chemistry, the field of stimulus-response release continues to grow. In one case, nitric oxide molecules stored in MSN particles coated with calcium phosphate are used to heal cornea wounds. Light irradiation and subsequent acid formation result in the removal of the coating and release.
Just as the MSNs can be used to store materials for release, they can also be used to collect or separate. Through the use of post-synthetic grafting of several different organoalkoxysilanes were attached to the surface of the silica, allowing the collection of free fatty acids from microalgal oil.\(^6\) Alternatively, the collection and removal of mercury (Hg\(^{2+}\)) ions was done by synthesizing the MSN around Fe\(_3\)O\(_4\) particles to create a core-shell type material. The surface of the silica was then functionalized with an amine and carboxylic acid groups which allowed the attachment of thymine rich DNA. In the presence of Hg\(^{2+}\), the DNA is duplexed resulting in a measurable fluorescence signal, the detection and collection process. Finally, the particles, now containing the Hg\(^{2+}\), can be gathered and removed via magnet due to the Fe\(_3\)O\(_4\) core.\(^{14}\)

MSN particles are also commonly used in heterogeneous catalysis as a way to either convert a homogeneous process or to protect the catalyst from deactivation. In one example, diaqua and dichloro Pt\(^{II}\) complexes are catalysts used in the aerobic epoxidation of olefins. By functionalizing the surface of MSN with ligands used to support the Pt\(^{II}\) complexes, the catalyst becomes protected from bimolecular deactivation and thus making the catalyst reusable.\(^{15}\) Comparatively, bimetallic Pd-Au MSN particles were created by impregnation of the metals. This created a homogeneous distribution of the metals that greatly reduced aggregation and was ultimately used in the esterification of benzyl alcohol.\(^{16}\)

1.3 References


CHAPTER 2
ZIF-8 BASED CARBON MEMBRANES FOR
NATURAL GAS SEPARATIONS

2.1 Natural Gas Separations with Membranes

While natural gas is an important energy source within the U.S., a significant number of deposits cannot be used economically to produce natural gas due to contaminants, such as carbon dioxide and nitrogen. These impurities reduce the energy efficiency of the gas and, in the case of CO₂, can interact with moisture to produce carboxylic acid which degrades the infrastructure and processing facilities. The amount of CO₂ can reach up to 70%, and exceed 4% of N₂. Current U.S. pipeline specifications require contamination to be less than 3% of non-methane gas, necessitating costly treatment methods such as amine absorptions and cryogenic distillation.¹ Membrane separations technology, however, represents a scalable and less expensive alternative.²⁻³

In terms of membrane materials, cellulose acetate and polyimide are often selected for natural gas cleanup, but these polymers have low thermal stability and are therefore prone to plasticization, resulting in low permeabilities and low separation selectivities.⁴⁻⁶ Metal-organic frameworks (MOFs), on the other hand, are a promising alternative, as they are more stable under high temperatures and pressure, and allow for increased chemical stability. In addition, MOF synthesis grants the ability to control pore size and to functionalize the surfaces.⁷⁻⁸ ZIF-8 (zeolitic imidazolate framework 8), a member of ZIFs class of MOFs, has been studied for gas separations as its inherent pore size is smaller than methane but larger than CO₂, and the 2-methylimidazole linkers preferentially adsorb CO₂.⁹⁻¹⁰ Microporous carbon represent another membrane material that due to its unique properties can improve the membranes in terms of their thermal and chemical resistance, while having high permeance and increased selectivity.¹¹⁻¹² A study by Koros et al. investigated the pyrolysis of a commercial polyimide film, Matrimid® for N₂/CH₄ separation and found it to surpass the limitations of the polymer alone.¹³

Another study performed an investigation of a combined polymer and MOF membrane using ZIF-L (a leaf-shaped ZIF) with a polymer precursor to create a carbon membrane on
porous alumina disks which demonstrated high H$_2$ permeance when compared to the polymer alone.\textsuperscript{14} These examples illustrate that a combination of materials may be beneficial in terms of optimizing the properties of membranes used for gas separation. Furthermore, current literature lacks reports of a microporous carbon membrane made solely from MOFs for the use of natural gas purification.

With this in mind, the goal of this work is to combine the properties of MOFs and mesoporous carbon membranes to improve gas separation notably. Specifically, a continuous ZIF-8 membrane will be created which can then be pyrolyzed to create a carbon membrane with unique properties which differ from the polymer derived versions. This will be achieved through the method illustrated in Figure 2.1.

![Figure 2.1 Schematic of membrane preparation](image)

2.2 Methods

2.2.1 ZIF-8 Membrane Synthesis

The preparation of the ZIF-8 membranes was done in a Teflon lined Parr reactor on tubular alpha-alumina supports with 100 nm pores. The support was wrapped in a double layer of Teflon tape and submerged in the ZIF-8 solution and held in the center of the liner with a Teflon support. The ZIF-8 solution was prepared using one of two recipes.

In the first recipe, 0.4 g of zinc chloride and 1.07 g of sodium formate were dissolved into 15mL methanol. A second solution containing 1.95 g of 2-methylimidazole also dissolved in 15mL of methanol is added to the first and allowed to stir for 20 minutes. The second recipe follows the same procedure. However, the zinc chloride amount is increased to 0.5 g and the sodium formate is reduced to 0.5 g. After the ZIF-8 solution is prepared, the support is inserted
vertically with the centering support. The sealed reactor was then placed in a preheated oven at 120°C for five hours. When finished the reactor was allowed to cool, the support was removed and rinsed gently with fresh methanol and left to dry in air. This process can be repeated for additional layers.

2.2.2 Membrane Carbonization

A ZIF-8 membrane with acceptable separation performance was then carbonized in a tube furnace. Initially, the tube was purged with nitrogen for 24 hours. With the nitrogen still flowing, the furnace was heated to 800°C slowly in a three-step process. First, it is heated to 250°C at a rate of 3°C per minute, then to 300°C at 0.8°C per minute. A final rate of 0.25°C per minute is used to reach the final temperature of 800°C, which is held for one hour. The furnace was then cooled back down to room temperature at a rate of 0.8°C per minute.

2.2.3 Gas Separations Testing

All membranes were tested using the same process through collaboration with Dr. Moises Carreon’s research group.\textsuperscript{8, 15} A 50:50 mixture of CO\textsubscript{2}/CH\textsubscript{4} was tested at a pressure of 20 psi. The membrane was placed in a stainless steel setup and sealed with an O-ring on each side. The gas was then fed in one side at a rate of 70 mL/min. After attaining a steady state, feed, retentate, and permeate stream compositions were measured using a gas chromatograph (SRI instrument, 8610C) which was equipped with a HAYSEP-D packed column and a thermal conductivity detector.

2.2.4 Additional Carbon Techniques

In an effort to create a continuous membrane, two techniques were used to provide an additional carbon source to the base ZIF-8 membranes. The first involved adding 15 mg of OMC to the ZIF-8 synthesis solution. OMC was synthesized through a hard templating method using MSN-10 that has been previously published.\textsuperscript{16} In short, 1 g of MSN-10 was combined with sucrose, sulfuric acid, and water. After stirring for 7 minutes, the mixture was heated to 100°C for 6 hours then at 160°C, each for an additional 6 hours. This process was repeated four times, ensuring the material was powdered between each cycle. A final heating step was done in a tube furnace at 900°C in a nitrogen atmosphere for 5 hours. The MSN-10 template was removed with 10% HF overnight and washed with copious amounts of water.

The second method was a pretreatment to coat the tubular support in polydopamine. Polydopamine is a collection of oligomers that pi-stack resulting in a surface coating.\textsuperscript{17-18} To
form this coating, dopamine was added to a TRIS buffer which had been adjusted to a pH of 8.5. The tubular supports were wrapped in Teflon tape to prevent a coating from forming on the outside surface of the support and suspended horizontally in the stirring solution. The supports were then removed at the desired time point and allowed to dry at room temperature.

2.2.5 Characterization

All nitrogen adsorption-desorption data was measured and collected using a Micrometrics TriStar II surface area and porosity analyzer. Samples were degassed with nitrogen at 100°C for six hours before analysis. X-ray diffraction measurements were collected using the Panalytical PW3040 with a copper tube. Scanning electron microscope images were captured on a JEOL JSM-770F Field Emission SEM or an FEI Qunata 600I Environmental SEM in high vacuum mode. All SEM samples were treated with a gold sputter coating with a Hummer IV Sputtering System.

2.3 Results and Discussion

Several ZIF-8 membranes were synthesized; however only a few were able to hold enough pressure to be tested. Only those that could withstand both a minimum pressure of 20 psig and have measurable separations were then carbonized. All of the testable membranes are listed in Table 2.1.

The first successful membrane (M1) was two ZIF-8 layers with 0.5 wt% OMC (based on the weight of methanol used) incorporated into the ZIF-8 synthesis solution for both layers. M1 showed the best performance of all the membranes synthesized during this project with a selectivity of 1.61. Due to its promising performance, it was then carbonized and tested again, shown in Table 2.1 as CM1. After carbonization, the membrane could not withstand as much pressure, and the selectivity decreased. Although this membrane showed some promise, it proved to be irreproducible. ZIF-8 membranes are notoriously difficult to reproduce, particularly on a tubular support versus a flat disk. However, the collaborators of this work successfully synthesized reproducible ZIF-8 membranes for Kr/Xe separations. A few of these membranes were treated with carbonization, but they could not hold enough pressure to be tested for natural gas separations.
Some investigation was done on the carbonization of ZIF-8 in an effort to improve the method. To do this, ZIF-8 powders were also exposed to the carbonization process to help elucidate how the treatment altered the material. SEM images (Figure 2.2) of the powders before and after carbonization show a change in morphology from small homogeneous shapes to a heterogeneous web-like material suggesting the loss of the crystalline structure. Through the use of XRD analysis, in Figure 2.3, it was noted that the crystalline structure of the original ZIF-8 material was completely lost after the carbonization process. The crystalline pattern is confirmed by literature\textsuperscript{20} while the pattern resulting from the carbonization process not only shows the loss of the crystallinity but also characteristics of amorphous carbon by the shallow hump between 20 and 30\textdegree.\textsuperscript{21} The sharp peak present at 44\textdegree was the in-plane reflections of carbon materials.\textsuperscript{22-23}

The change in the XRD spectra suggests that while temperature programming of the carbonization process removed the zinc, it also collapsed the ZIF-8 structure. Loss of some porous structure was also shown in the nitrogen adsorption-desorption isotherm (Figure 2.4). Surface area dropped significantly after carbonization, from 1,366 m\textsuperscript{2}/g to 639.7 m\textsuperscript{2}/g, as well as the pore sizes shifting down (Figure 2.4 inset). Even with reproducible ZIF-8 membranes, the carbonization process produces defects that destroy the membrane’s ability to hold pressure.

Table 2.1 Membrane Separations Data

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sample</th>
<th>CO\textsubscript{2} permeance (mol/m\textsuperscript{2}sPa)</th>
<th>CH\textsubscript{4} permeance (mol/m\textsuperscript{2}sPa)</th>
<th>Selectivity</th>
<th>Feed pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>2 layered ZIF-8 + 0.5 wt % OMC</td>
<td>1.23 X 10\textsuperscript{-8}</td>
<td>7.66 X 10\textsuperscript{-9}</td>
<td>1.61</td>
<td>60</td>
</tr>
<tr>
<td>CM1</td>
<td>2 layered ZIF-8 + 0.5 wt % OMC Carbonized</td>
<td>1.52 X 10\textsuperscript{-7}</td>
<td>1.40 X 10\textsuperscript{-7}</td>
<td>1.08</td>
<td>20</td>
</tr>
<tr>
<td>M2</td>
<td>0147</td>
<td>2.32X10\textsuperscript{-9}</td>
<td>2.32X10\textsuperscript{-9}</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>M3</td>
<td>0150</td>
<td>1.05X10\textsuperscript{-9}</td>
<td>1.03X10\textsuperscript{-9}</td>
<td>1.0</td>
<td>20</td>
</tr>
<tr>
<td>M4</td>
<td>0210</td>
<td>8.00X10\textsuperscript{-9}</td>
<td>1.01X10\textsuperscript{-9}</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>M5</td>
<td>0211</td>
<td>1.61X10\textsuperscript{-7}</td>
<td>2.01X10\textsuperscript{-7}</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>M6</td>
<td>0226</td>
<td>2.30X10\textsuperscript{-8}</td>
<td>2.30X10\textsuperscript{-8}</td>
<td>1.0</td>
<td>20</td>
</tr>
</tbody>
</table>
Figure 2.2 SEM images of ZIF-8 powders (A) and carbonized ZIF-8 (B). Scale 1 μm.

Figure 2.3 XRD spectra of ZIF-8 powders (A) and carbonized ZIF-8 (B)
Several attempts were made to reduce the number of defects by providing additional sources of carbon to the starting ZIF-8 membranes. Using OMC particles resulted in the only working carbon membrane, even though this method proved to be undependable. Figure 1.5a shows the crystals of M1 while Figure 1.5b shows CM1. The SEM image of CM1 shows a mostly continuous membrane with few large defects. This lack of defects was what enables the membrane to hold the needed pressure to perform. Another carbon source, polydopamine, improved the ability to reproduce the ZIF-8 membranes by reducing the number and size of defects. By allowing the polydopamine to coat for 20 hours before adding two layers of ZIF-8; M2, M5, and M6 resulted in similar gas separations. Similarly, M3 and M4 were comparable and contained only a 3-hour coating. Although the polydopamine seemed to aid in the reproducibility of the starting ZIF-8 membrane, none of the membranes could hold the needed pressure after carbonization.
Several reports have investigated the thermal stability of ZIF-8 beyond the simple thermal-gravimetric analysis and found the powders degrade between 400 and 550°C. However, there are limited studies on the isothermal stability.\textsuperscript{24-25} Lin and coworkers tested the stability and separation characteristics for H\textsubscript{2} and CO\textsubscript{2} as a function of temperature from 25 - 300°C. This work showed that in a mixed gas test the selectivity improves with temperature until approximately 225°C at which point the membrane selectivity decreases drastically.\textsuperscript{25} At extended temperature exposure (24 hours) the ZIF-8 membrane only maintains its pore structure at temperatures below 150°C.

As detailed above, the method used in this work increases the temperature slowly with an hour spent at 800°C before slow and controlled cooling. Direct carbonization of ZIF-8 particles with removal of the zinc has been demonstrated in literature by heating to 800°C, however, more time must be spent at the maximum temperature, and this was followed by a wash with HCl solution.\textsuperscript{26} A similar alteration to the carbonization process was investigated, but the hold time was only increased to 2.5 hours in comparison to the published 5 hours. Additionally, any kind of wash post-carbonization was determined to be damaging as it was observed that the membrane would flake off after the smallest of motions.
In an effort to both provide additional carbon source and more firmly attach the membrane to the support, the support was modified with a silane.\textsuperscript{27} The blank support was modified with IPTES (3-(2-imidazolin-1-yl)propyltriethoxysilane), and IPTES combined with TMOS through the use of microwave irradiation. After the alteration to the support, layers of ZIF-8 were synthesized the same way as all the other membranes. This method did not outperform the membranes created with polydopamine, however, after three layers of ZIF-8, the membrane could hold some pressure, but not enough to be tested. Upon the addition of a fourth layer, however, the membrane’s ability to hold pressure began to drop. This was believed to result from the increased molar ratio of Zn\textsuperscript{2+} to methanol in the solution as more layer results in more zinc. This increase also creates large particles which result in more defects in the overall membrane.\textsuperscript{20}

2.4 Conclusions
This work succeeded in making a few testable ZIF-8 membranes through several different methods. Inclusion of an additional carbon source is essential to creating a membrane capable of withstanding the required pressure levels for testing. Although each variation resulted in a testable membrane, very few of these methods gave reproducible results making it challenging to optimize the carbonization process. XRD and nitrogen sorption showed that upon carbonizing the original ZIF-8 material the crystalline structure and some of the pore structure was lost. Future directions of this work involves a screening process of all of the different ZIF-8 synthesis to find one that consistently makes a testable membrane, while also maintaining the porous structure after carbonization.

2.5 References


3.1 Introduction

Benzaldehyde is an industrially useful aromatic aldehyde. It is used as an intermediate in several industries including perfumery, dyestuff, agrochemical, and pharmaceuticals.\textsuperscript{1-4} Although several synthetic methods to make benzaldehyde have been explored by industry in the past, the two main processes currently used are air-oxidation of toluene and hydrolysis of benzyl chloride. These methods have several drawbacks such as complexity, high temperatures and pressure requirements, low yields, and large amounts of acidic waste that is costly to treat.\textsuperscript{1-2} As an alternative, the aerobic oxidation of benzyl alcohol with molecular oxygen or air has gained interest as water is the only by-product. In this regard, several heterogeneous catalysts using transition and noble metals have been reported.

Palladium nanoparticles have shown significant promise for benzyl alcohol oxidation. Studies have used a variety of supports with water as a solvent.\textsuperscript{2,4-5} Having the Pd\textsuperscript{0} nanoparticles supported on hydroxyapatite was shown to have comparable yields to the industrial methods with 100\% selectivity. This process was done at a lower temperature (100°C) and atmospheric pressure.\textsuperscript{5} A later work placed Pd\textsuperscript{0} nanoparticles on a phosphorous-doped porous carbon framework in a continuous flow reactor system. In this situation, the catalysts maintained a high rate of conversion for 10 hours before the catalysts showed any sign of deactivating.\textsuperscript{4} Another noble metal, gold nanoparticles supported on triuranium oxide was studied for the same reaction, with a variety of solvents. This method compared no solvent, toluene, p-xylene, DMF, and DMSO. The reaction required higher temperatures and pressures than the batch reactions with Pd\textsuperscript{0}, but it did require less time. Additionally, it showed to be most effective, with high yield and selectivities, in the absence of a solvent.\textsuperscript{6} A recent work looked to combine the abilities of Au and Pd. Chen and coworkers synthesized bimetallic Au-Pd nanoparticles confined with SBA-15. This bimetallic was compared to the individual metals alone and found to outperform both while requiring no solvent and only atmospheric pressure of oxygen.\textsuperscript{7}
Although these noble metals have proven to be beneficial in lowering the required temperatures and reducing wastes by requiring no additional solvents, they present additional problems including toxicity and expense. In response, research has started to focus on other transitional metals. A few metal tosylate complexes were tested for oxidation of benzyl alcohol, including iron(III), cobalt(II) and nickel(II). Of the three, only Fe(III) was found to react with hydrogen peroxide to produce benzaldehyde in both acetonitrile and chloroform; however, using the later resulted in a lower yield and further oxidized the product to benzoic acid.\textsuperscript{8} Copper nanoparticles on a reduced graphene oxide support have also demonstrated selectivity towards the oxidation of benzyl alcohol to benzaldehyde. The temperature requirements for Cu catalysts are lower than the noble metals, between 60 - 80°C.\textsuperscript{9-10} Although copper is a promising, inexpensive alternative to the noble metals, it does require additional components.

Hoover studied the different catalysis systems for using copper to oxidize benzyl alcohol to benzaldehyde. It was determined that when working with a Cu(II) complex, both TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) and a base are required for conversion.\textsuperscript{11} Most of these complexes are homogeneous catalysts; therefore, product collection requires an additional separations step. Converting this to a homogeneous process is an attractive alternative and can be achieved through the use of MOFs. Cu-BTC, (Cu - 1,3,5-benzenetricarboxylate), also known as HKUST-1 or Basolite C 300, has been shown to be active in the aerobic oxidation of benzylic alcohols in acetonitrile while in the presence of TEMPO. Despite this material being inexpensive and heterogeneous, the crystalline framework does not survive more than two reaction cycles. This occurs because the framework is disrupted by both the TEMPO and the over-oxidation product, benzoic acid, as both can coordinate with the Cu(II) ions.\textsuperscript{12}

In an effort to combat this disruption, this work looks to protect the framework from exposure to the poisoning chemicals by assembling Cu-BTC within the pores of MSN-10. Some poisoning is expected, as the pores of the MSN are too large to restrict access fully. Regardless, this work is one of the few examples of fabricating a MOF within mesoporous silica.
3.2 Methods

3.2.1 MSN-10 Synthesis

The general MSN-10 synthesis has been published several times. However, for simplicity, the process is explained here. In a parafilm covered Erlenmeyer flask, 7.0 g of P104 was dissolved into 224.4 mL of 1.6 M HCl by heating in an oil bath at 55°C for one hour. Next, 10.4 mL of tetramethylorthosilicate (TMOS) was added dropwise. The flask was recovered and heated while stirring for an additional 24 hours. At this point, the now cloudy solution was transferred to a large Parr reactor, sealed, and heated in an oven at 150°C for 24 hours. The resulting solid was filtered and washed with nanopure water and methanol. Finally, the surfactant was removed by heating the material to 550°C in air for six hours. This material is further referred to as MSN-10.

3.2.2 Functionalized MSN-10 synthesis

The base MSN-10 material was altered to increase the number of hydroxyl groups present on the surface in a couple of ways. In the simplest method, the MSN-10 was placed in a Parr reactor and submerged in nanopure water. It was then placed into an oven 80°C for six hours before being filtered. This modified material was named MSN-OH.

Alternatively, the surface could be modified by the co-condensation of (3-triethoxysilyl)propyl-succinic anhydride. The same procedure for MSN-10 was used, but 2.4 mL of this additional organic silane was added 30 minutes after the addition of the TMOS. In order to remove the surfactant without also removing the added functional groups, this material was refluxed in ethanol for 24 hours. Material made through this procedure contained the functional group both inside the pores and on the outer surface of the structure and was referred to as MSN-COOH. Alternatively, the functional groups can be removed from the outer surface and only contained within the pores. The same co-condensation procedure was followed with a couple of modifications before the surfactant was removed. First, the material was stirred in a 100 mL ethanol solution containing 12 g of dissolved P104 for 24 hours at ambient temperature. Second, the outside functional groups were passivated using HDMS. This step was achieved by
suspending the MSN material in 200 mL of hexanes while adding 10 mL of HDMS over several minutes and allowing the solution to stir overnight. After filtering and washing with hexanes, it was refluxed in ethanol for 48 hours. This outer surface passivated material was called MSN-OP.

3.2.3 MOP-CuSO₃ Synthesis

The metal organic polyhedral referred to as Cu-SO₃, was synthesized mostly according to the published procedure.¹⁵ In 8 mL of methanol 269 mg of the linker (5-sulfo-1,3-benzenedicarboxylic acid monosodium salt) was dissolved with stirring. Once dissolved, this solution was added to a 16 mL solution containing 1:1 of dimethylacetamide to methanol with 232 mg of Cu(NO₃)₂•2.5H₂O. These two solutions were mixed in a closed glass vial for ten minutes. Afterward, an additional 5 mL of DMA was added, and the vial was left open to air and undisturbed for 14 days. The resulting light blue solid was filtered and washed with methanol.

3.2.4 MOF-Cu-BTC Synthesis

The metal-organic framework, Cu-BTC was typically made by tripling the procedure published by Schlichte and co-workers.¹⁶ To start, 2.524 g of Cu(NO₃)₂•2.5H₂O was dissolved in 36 mL of water. Concurrently, 1.266 g of the linker (trimesic acid) was dissolved in 36 mL of ethanol. Once both were dissolved entirely, they were combined in a Teflon lined Parr reactor. The reactor was sealed and placed in a pre-heated oven at 120°C for 12 hours. After the reactor was cooled to room temperature, the resulting blue solid was filtered and washed with ethanol.

3.2.5 Methods of MOM@MSN Incorporation

3.2.5.1 Multiple Solvents

Incorporation of the metal-organic material (MOM) into the pores of the MSN through the use of multiple solvents exploited the polar pores to draw the needed materials into the pores.¹⁷ The MSN was first suspended in the non-polar solvent, and then small amounts of polar solutions containing the components of the MOM were added. Such a minuscule amount of the compounds were utilized because the volume of MOM components added needed to be less than the pore volume of the MSN material.
The polar solutions were made by dissolving 484.9 mg of Cu(NO$_3$)$_2$$ \cdot $2.5 H$_2$O in 1 mL of methanol and 420 mg of trimesic acid (Cu-BTC) or 268 mg 5-sulfonic-1,3-benzenedicarboxylic acid (Cu-SO$_3$) in 6 mL of methanol. In 10 mL of n-hexanes, 250 mg of the desired MSN material was suspended. After ten minutes, the stirring speed was increased, and 0.27 mL of the copper solution was added. This solution was stirred for another ten minutes before adding 0.27 mL of the linker solution. Finally, a drop of an inducer, 2,6-lutidiene was added as it was required to form the Cu-SO$_3$ MOP. The resulting solids were filtered and washed with hexanes. This cycle was repeated at least three times. A second set was synthesized in the same way; however, the stir times were extended to 24 hours after adding each of the MOM components to allow better diffusion as is often published for loading materials in MSN-10.

3.2.5.2 Impregnation/Evaporation

An alternative method to incorporate the MOM within the pores of the MSN-10 works like wet impregnation. First 80 mg of the fully synthesized MOM was added to a volatile solvent, specifically methanol or dichloromethane. Afterward, 120 mg of the desired MSN-10 was added, and the solution was stirred for four hours. Finally, the solvent was removed via evaporation in a drying oven overnight at either 80°C (methanol) or 40°C (CH$_2$Cl$_2$).

3.2.5.3 Silica in MOF Synthesis

For this method of incorporation, 120 mg of MSN-OP was added to a single batch synthesis of the MOM. In both cases, the MSN was added after combining the metal solution with the linker solution, and the resulting solution was stirred for an hour to complete the MOM procedure.

3.2.5.4 Layer by Layer

The layer by layer method was only used with MSN-OP since the functional groups were needed to initiate growth. Next, 200 mg of MSN-OP was added to 15 mL of a 2 mM of copper acetate in ethanol and was stirred for 24 hours. This solid was filtered, washed in triplicate with ethanol, and dried in air overnight. Next 15 mL of a 0.2 mM solution of trimesic acid in ethanol
was added to the washed material and stirred for 48 hours. The resulting solid was again filtered, washed in triplicate, and dried in air overnight. Stirring in both solutions was considered a cycle. Each sample went through three cycles to incorporate Cu-BTC into the MSN-OP.

3.2.6 Oxidation Reaction Conditions

The reaction conditions used for the alcohol oxidation of benzyl alcohol to benzaldehyde were completed using a previously published set-up.\(^ {12,19}\) Simply, the catalysts (30 mg), sodium carbonate (17 mg), TEMPO (5 mg) were placed into a flask with 3 mL of the solvent, acetonitrile, and 2 mL of benzyl alcohol. The mixture was placed under an oxygen atmosphere and heated to 75°C for 24 hours. The resulting product was extracted with acetonitrile and analyzed by GC-MS. The remaining catalyst (PostRxn) was also characterized.

3.2.7 Characterization

All nitrogen adsorption-desorption data was measured and collected using a Micrometrics TriStar II surface area and porosity analyzer. Samples were degassed with nitrogen at 60°C for six hours before analysis. Scanning electron microscope (SEM) images were captured on a JEOL JSM-770F Field Emission SEM or an FEI Quanta 600I Environmental SEM in high vacuum mode. All SEM samples were treated with a gold sputter coating with a Hummer IV Sputtering System. Transmission electron microscope (TEM) images were collected using the FEI Co. Talos F200X with 200KeV emission and four silicon drift detectors used for energy-dispersive X-ray spectroscopy (EDS) images. X-ray diffraction measurements were collected using the Panalytical Empyrean equipped with a BBHD copper source and Gallpex with FASS detector. The sample was placed on a zero background well and spinning at 2 RPM. Metal content was determined using inductively coupled plasma-atomic emission spectrometry with an ICP-AES PerkinElmer Optima 8300 after dissolving the solid in HF and aqua regia (1:2) and diluting with 5% HCl. The oxidation reaction results were analyzed by the gas chromatograph with mass spectrometer Varian 1200L GC-MS by Agilent Technologies with electron ionization.
3.3 Results and Discussion

3.3.1 MSN and MOM materials characterizations

The four MSN materials, 10, OH, COOH, and OP, were characterized before adding any MOM. Figure 3.1 displays the isotherms and pore size distributions of all four materials. All of them present with a type IV isotherm with hysteresis loop confirming the presence of mesoporous. MSN-OH (dotted line) was created from the MSN-10 (solid line) batch which accounts for the high level of similarities. Correspondingly, MSN-COOH (short dashes) was collected from the synthesis of MSN-OP (long dashes) before the passivation with HDMS.

Figure 3.1 MSN Characterizations A) Isotherms and pore size distributions (inset) of the MSN materials; MSN-10 (solid), MSN-OH (dots), MSN-COOH (short dash), and MSN-OP (long dash). B) TEM image of MSN-10 and C) TEM image of MSN-OP.
TEM images (Figure 3.1 B and C) also confirm that the functionalization process with (3-triethoxysilyl)propyl-succinic anhydride did not alter the overall morphology of the material as the hexagonally arranged pores and shape remained present. The functional group coated the pores with carboxyl groups, which are the same functional groups present in the organic linkers of Cu-BTC. When MSN-10 is functionalized via co-condensation, it will have an overall higher surface area and smaller pore volumes.\textsuperscript{20-21} This pattern can also be seen in the MSN materials made for this work, shown in Table 3.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface Area (m(^2)g(^{-1}))</th>
<th>Pore Volume (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSN-10</td>
<td>435.5</td>
<td>1.22</td>
</tr>
<tr>
<td>MSN-OH</td>
<td>402.8</td>
<td>1.29</td>
</tr>
<tr>
<td>MSN-COOH</td>
<td>505.6</td>
<td>0.79</td>
</tr>
<tr>
<td>MSN-OP</td>
<td>538.8</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The MOM materials were synthesized only for base material analysis to allow for comparison to the composite materials discussed in this chapter. Cu-BTC was a bright blue crystalline powder with high surface area, around 1500 m\(^2\)g\(^{-1}\). Commonly, Cu-BTC isotherms are collected using an instrument with the capability to measure micropores, however, for comparison purposes the isotherm, shown in Figure 3.2 was collected on the same instrument used for all the other materials in this work. The isotherm is scaled to provide a comparison to the other isotherms within this chapter.

Cu-SO\(_3\) was very similar in color to Cu-BTC, but the texture was waxier. Nitrogen sorption data was not possible because the particles agglomerate enough that the surface area was determined to be zero as there was no absorbance.
3.3.2 Unsuccessful MOF Incorporation

Several of the methods used to incorporate the MOMs only worked with CuSO₃ and not Cu-BTC. As the goal of this work was to incorporate the copper MOF material, many of these materials were not fully characterized as after one or two different analyses showed if the incorporation was successful or not.

The method of multiple solvents was first published using Cu-SO₃ and SBA-16.¹⁷ SBA-16 is a porous silica material with an interesting pore structure. It has sphere shaped pore cavities connected by small openings. By adding the building compounds in volumes less than the total pore volume, the polar solutions should be drawn into the polar pores. However, the published procedure proved difficult to replicate. To begin with, the linker solution was highly concentrated, containing nearly 500 mg of the organic salt within only 1 mL of methanol. The result was less of a solution and more similar to a paste with no feasible way to accurately add less than 1 mL. As a workaround, this solution was made in 6 mL and added multiple times for both of the different MOMs. The resulting solids for the Cu-SO₃ components were a light blue with the filtrate being clear, while on the other hand, the Cu-BTC sample remained white with the filtrate being bright blue. Since the blue is indicative of the copper ions, this lack of color implied that this method did not successfully lead to the incorporation of the MOF.
Using the impregnation method had similar results to the method of multiple solvents. Upon placing the Cu-SO$_3$ in the methanol it immediately dissolved, whereas in dichloromethane it did not. The Cu-BTC, however, did not dissolve in either solvent or any other solvents ranging from cyclohexane to water. After nitrogen sorption tests, solubility was determined to be a critical factor in the incorporation of the MOM. As seen in Figure 3.3, when the MOP was fully dissolved the resulting isotherm took on characteristics present to both starting materials and showed a drop in the overall surface area. In contrast, when the MOP did not dissolve, it aggregated together with the MSN-10 blocking access to any pores and resulting in a type III isotherm. In a study by the Zhou group, a similar method was employed with SBA-15 which showed comparable results with Cu-SO$_3$.\textsuperscript{18}

![Figure 3.3 Nitrogen sorption analysis of impregnation method. Isotherms and pore size distributions (inset) of CuSO$_3$ in methanol (solid) and in dichloromethane (dashed) and Cu-BTC in methanol (dotted) with MSN-10. Similar results were seen with other MSN materials.](image)

In applying this to Cu-BTC, the nitrogen absorption isotherm (Figure 1.3, dotted) suggested some level of incorporation as there were elements of both materials; an enhanced micropore region attributed to the MOF while maintaining the overall type IV shape of MSN-10. When looking at the pore size distribution (Figure 1.3 inset), the large presence of micropore diameters combined with the presence of the hysteresis loop showing mesopores shows that
rather than the incorporation of the MOF, the pore opening is blocked with the microporous Cu-BTC. This was further confirmed with visual observations that the MOM samples that did not dissolve appeared as different colored powders, while the CuSO₃@MSN in methanol was homogeneous in color.

Adding MSN-OP to the synthesis process of the MOM did not successfully incorporate the Cu-SO₃ and was inconclusive regarding the Cu-BTC. In the case of Cu-SO₃, the material appeared a homogeneous, barely blue color and the isotherm, shown in Figure 3.4, had no significant differences from the impregnation method of Cu-SO₃@MSN-10 in methanol, other than those attributed to the differences in MSN material. Unlike the impregnation method, however, there was no significant drop in the surface area. In addition to the visual observation that a majority of the blue color was lost in the filtrate, it was determined that the Cu-SO₃ was not incorporated into the MSN-OP.

![Figure 3.4 Nitrogen sorption analysis of synthesis method. Isotherms and pore size distributions (inset) of Cu-SO₃@MSN-OP (solid) and Cu-BTC@MSN-OP (dashes)](image)

In the case of Cu-BTC@MSN-OP via the synthesis method, nitrogen sorption analysis suggested there was incorporation, according to published work by Gaun and coworkers. They used 0.5 – 3wt% of SBA-15 based on the copper ions whereas the work discussed here used 30wt% MSN-OP. When considering the nitrogen absorption analysis (Figure 3.4), the isotherm
shows both MSN-OP characteristics with the overall type IV isotherm, but increased absorbance in the micropore region. Mesopores from the MSN are confirmed by the presence of the hysteresis loop and in the pore distribution. However, an increase in microporous character is not duplicated in the pore distribution (not shown due to the lack of peaks). The surface area increased to 750 m² g⁻¹ which merely confirms the existence of the MOF, but neither confirms nor denies incorporation. Since additional methods of characterizing, such as SEM or XRD, are also bulk methods that would not provide a definitive answer as to whether the material was Cu-BTC@MSN-OP, or a mix of the two materials, two samples known to be mixes were analyzed via nitrogen absorption (Figure 3.5).

Two samples of mixed materials, one with 30 wt% (dashes) and one with 70 wt% MSN-OP (solid) to determine if there was any significant difference. The lower weight percent is a mix comparable to that of the synthesized material and shows no significant differences in the resulting isotherms (dashed lines of Figures 1.4 and 1.5) contradicting literature. The mix containing more MSN-OP that Cu-BTC extends the trend that the isotherm will show characteristics of both materials even if they are not incorporated. Without the capabilities to analyze a representative collection of single particles, it was determined that it is unknown where

![Figure 3.5 Isotherms of mixed MSN with Cu-BTC showing more Cu-BTC (dashed) and more MSN (solid).](image-url)
the synthesis method of Cu-BTC with MSN-10 was just a mix of powders or a mix with some composites.

3.3.3 Successful Synthesis Method of MOF incorporation

The layer by layer method proved to be the most effective at building the Cu-BTC within the pores of MSN-OP. This was also tested using MSN-10, but the MSN-OP showed more presence of Cu-BTC so only the latter was fully characterized and tested. Nitrogen absorption was collected after each cycle, however, only the final cycle is shown in Figure 3.6 (dashes). There was a slight increase in the microporous region, but this cannot be confirmed with the pores distribution as it was only calculated to 1.7 nm and the majority of the micropores fall below that width. However, the pore volume did decrease from the 0.84 cm$^3$ g$^{-1}$ of the MSN-OP to 0.69 cm$^3$ g$^{-1}$ for the Cu-BTC@MSN-OP showing that the pore interior was covered to some degree. Additionally, the pore width was unchanged showing that the MOF materials were only located within the pores and not on the entrance, as was the goal of passivating the outer surface while leaving the interior walls functionalized. The first cycle of the copper precursor was drawn in and connected to the carboxyl groups, and the remaining cycles continued to build from that first cycle.

![Figure 3.6 Nitrogen sorption analysis of layer by layer method. Isotherms of MSN-OP (solid) and Cu-BTC@MSN-OP (dashed) with corresponding pore distribution (inset).](image)
The small amount of MOF material was also confirmed in the XRD analysis. Figure 3.7 shows the overlapping patterns of the MSN-OP (dashed), Cu-BTC (dotted), and Cu-BTC@MSN-OP (solid). The large shoulder and broad peak are characteristic of amorphous silica. The major peaks of Cu-BTC at 11, 9, and 7 2θ are present in the composite material. The numerous other peaks attributed to the MOF are hidden by the MSN-OP. As with the nitrogen sorption, XRD was done on the composite after each cycle, but the pattern was no different from MSN-OP until the third cycle was complete.

It could be expected that the XRD and nitrogen absorption analysis would produce similar results if the sample was a mix of MSN-OP with a small amount of Cu-BTC added in. In order to ensure that was not the case, a couple of steps were taken. First, several mL of the ethanol solutions containing the MOF components were stirred together for 48 hours to see if anything precipitated out of the solution. After filtering, there was no solid left behind showing that without the functionalized surface to grow from; Cu-BTC would not form. Second, the resulting powder was imaged using SEM to confirm the absence of free Cu-BTC octahedral
crystals. Figure 3.8 is a representative image showing only the hexagonal plates morphology of MSN-OP.

Figure 3.8 SEM image of Cu-BTC@MSN-OP via layer by layer method

EDS imaging, shown in Figure 3.9 (page 38), was done to confirm that the copper within the pores was well dispersed throughout. Silicon was from the MSN-OP and thus found throughout. Oxygen and carbon were from both the porous silica and within the linker of the MOF. The additional carbon present in an x-shape is from the lacey carbon grid used to image the sample. ICP analysis found the copper content of the sample to 8.3 ppm.

3.3.4 Oxidation of Benzyl Alcohol

The Cu-BTC@MSN-OP from the layer by layer method was tested in the oxidation of benzyl alcohol to benzaldehyde. After the products were analyzed on GC-MS, only three peaks were present. A large peak attributed to the solvent acetonitrile, a slightly smaller peak for benzyl alcohol, and the narrow peak of benzaldehyde. Although there was no quantification done, straightforward results suggest that the catalyst was selective towards benzaldehyde but does not achieve full conversion. Interestingly there were no peaks indicating the presence of the TEMPO in the product.
Figure 3.9 EDS of Cu-BTC@MSN-OP. All scale bars are 300 nm.
There was not enough PostRxn material to perform nitrogen sorption analysis with any degree of accuracy, but Figure 3.10 shows the XRD analysis which shows the loss of the major Cu-BTC peaks. However, additional peaks are present beyond 20 2θ. These peaks may suggest where the missing TEMPO is located. As mentioned earlier, both TEMPO and benzoic acid have poisoning effects on Cu-BTC. In this work, there was no evidence to suggest the presence the benzaldehyde was further oxidized to benzoic acid, leaving only the TEMPO. If it did incorporate into the MOF, it could alter the crystal structure creating the change in XRD pattern. This is further confirmed through ICP analysis of the PostRxn catalyst. The analysis did show some loss in the amount of copper, dropping to 5ppm. The loss of copper ions shows that the crystal structure of the incorporated Cu-BTC was altered and released some copper ions. The PostRxn catalyst was also imaged to determine if the structure of the MSN-OP shell was maintained as well as the even dispersion of the copper. EDS imaging (Figure 1.11, page 39) showed that the copper was still well dispersed with no indication of aggregation.

Figure 3.10 XRD of PostRxn material (solid) compared to Cu-BTC (blue) and MSN-OP (dashed).
Figure 3.11 PostRxn Cu-BTC@MSN-OP. All scale bars are 200 nm.
3.4 Conclusions

Several methods were used in the attempt to incorporate a MOF within the pores of an MSN. In the end, the layer by layer method with a (3-triethoxysilyl)propyl-succinic anhydride functionalized MSN-10 with outer surface passivation proved successful. It was confirmed that the Cu-BTC’s crystalline structure was present within the pores and not attributed to a mix of Cu-BTC and MSN-OP particles through the use of XRD, nitrogen sorption, SEM, and elemental mapping. The resulting Cu-BTC@MSN-OP was also shown to be reactive in the aerobic oxidation of benzyl alcohol to benzaldehyde. Unfortunately, the MSN housing did not protect the MOF from poisoning by TEMPO, a required compound when using a copper catalyst. As the synthetic method was shown to be successful, future work in this project should be focused on further protecting the Cu-BTC from the effects of TEMPO. This could be done a few ways. Changing the type of MSN to one with smaller pores may restrict access to the incorporated MOF, but depending on the pore size it may also restrict the access of the desired reagent. Alternatively the outer surface of the MSN could be altered in such a way that TEMPO is repelled and pushed away from the MOF within. Finally, finding an alternative to the TEMPO that does not cordite with the incorporated MOF would eliminate the poisoning of the catalyst.

3.5 References


CHAPTER 4
FUTURE OUTLOOKS

4.1 Reproducibility of Carbon ZIF-8 Membranes

At this point, and to the author’s knowledge, there are still no reports of a carbon membrane sourced from ZIF-8 on a cylindrical support. There are several challenges that need to be studied and overcome such as reducing defects of the carbon membrane and maintaining attachment to the support. The most significant hurdle, however, is the reproducibility of the methods. The synthesis of ZIF-8 varies significantly regarding possible zinc salts, different amounts of solvent, and variable synthesis times and temperatures. With such variation in the parent material, a significant amount of time and effort is needed to determine which recipe will not only make reproducible ZIF-8 membranes but will also survive the carbonization process. One possible approach is to make ZIF-8 powders made in the same way as the reproducible membrane and use those to optimize the carbonization process. This approach grants control over the structure and properties of the resulting carbon material.

4.2 Improved Protection of the Cu-BTC Catalysts

This work aimed to both synthesize a MOF within the pores of an MSN and use that incorporation as a form of protection. The synthesis process was mostly successful, but more layers or cycles were needed to incorporate a larger amount of catalyst. There is some possibility that building of the MOF will level off after a certain number of cycles, at which point if it is determined that the pores are not completely filled; the composite material could be hydrothermally treated. Doing so would, in theory, solidify the existing MOF and potentially allow for further growth. Alternatively, increasing the concentration of the laying solutions would allow for more MOF formation within the pores. This would increase the overall conversion of benzyl alcohol to benzaldehyde.

Although the composite material was successfully synthesized, the Cu-BTC was not protected from the poisoning reagent, TEMPO. Unfortunately, the pore size of the functionalized MSN-OP was not smaller than the poisoner, so access was not restricted. This could be rectified by starting with an MSN with smaller pores, such as MCM-41. Alternatively, Cu-BTC synthesized in the presence of PEG has been shown to be more stable for the oxidation of
alcohols. By incorporating the PEG into the layer by layer synthesis, the catalyst should be able to withstand the presence of TEMPO and thus achieving protection and recyclability.