Examining the Crystal Morphology of a Cobalt-Based Metal-Organic Framework

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By

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ABSTRACT

The increase in atmospheric carbon dioxide concentration has been a growing concern since the second half of the twenty-first century. This potential greenhouse gas has contributed to rising global temperatures and climate change. The switch to renewable energy sources cannot happen instantaneously, and so the development of technology for carbon dioxide capture and storage has become increasingly important. Porous solid materials are very good candidates for this application due to their quicker and cheaper regenerative ability as compared to existing methods.

Metal organic frameworks (MOFs) are a rapidly growing class of crystalline nanoporous materials, which have received much attention in the past decade for their very desirable properties including high surface area, high uniformity and pore volume. In addition, these materials can be tailored to specific applications by modifying the building blocks that comprise them. MOFs consist of both organic and inorganic materials in the form of metal ions / clusters which are connected by organic ligands to generate a large open framework. Selection of different ligands such as carboxylates, imidazolates, or any molecule with anionic oxygen, along with metal ions such as transition metals allows for the creation of infinitely many MOF configurations.

The goal of this study is to synthesize and further understand the crystallinity of a new series of metal organic frameworks containing simple molecules that can be modified and tuned according to demands. Specifically, two frameworks are investigated, one with ethylenediamine as a linker group (NEU-1) and the other with 1,6-hexanediane as the linker group (NEU-3).
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS.................................................................................................................. ii
ABSTRACT...................................................................................................................................... iii
TABLE OF CONTENTS....................................................................................................................... iv
LIST OF FIGURES .............................................................................................................................. v
LIST OF TABLES ............................................................................................................................... v

1.0 INTRODUCTION .......................................................................................................................... 1

2.0 CRITICAL LITERATURE REVIEW ................................................................................................. 2
   2.1 Current CO₂ Capture Methods ...................................................................................................... 2
   2.2 Metal-Organic Frameworks .......................................................................................................... 3

3.0 EXPERIMENTAL .......................................................................................................................... 5
   3.1 Synthesis of Metal-Organic Frameworks ....................................................................................... 5
   3.2 Modified Procedures and Scaled-Up Synthesis ............................................................................ 6
       3.2.1 Pre-mixing Solution ............................................................................................................. 6
       3.2.2 Various Reaction Vessels .................................................................................................. 7
       3.2.3 Reaction Time ................................................................................................................... 7
   3.3 Characterization ........................................................................................................................ 8
       3.3.1 X-Ray Diffraction ............................................................................................................. 8
       3.3.2 Scanning Electron Microscopy (SEM) .............................................................................. 9

4.0 RESULTS AND DISCUSSION ....................................................................................................... 9
   4.1 Varying the Diamine of the MOF ............................................................................................... 9
   4.2 Ethylenediamine as the Linker (NEU-1) .................................................................................... 13
   4.3 Hexanediame as the Linker (NEU-3) .......................................................................................... 16
   4.4 Crystal Growth and Effect of Time ............................................................................................ 20

5.0 CONCLUSION .............................................................................................................................. 23

6.0 RECOMMENDATIONS ................................................................................................................. 24

REFERENCES ...................................................................................................................................... 25
LIST OF FIGURES

Figure 1. Various diamines and other amines used as constituents for MOFs. Different molecular lengths and sizes were used to see the effects on the generated MOF. 10
Figure 2. XRD patterns of various crystals synthesized with different amines. These materials exhibited sharp peaks and enough crystallinity for consideration for additional testing. 11
Figure 3. a) XRD of the resulting crystal when synthesized with a high concentration, 210 mM of ED and a low concentration, 70 mM of ED, b) SEM micrograph of a crystal synthesized with 210 mM of ED, and c) synthesis with 70 mM of ED 14
Figure 4. SEM micrographs of NEU-1 crystals at various magnifications of a) 1 kx, b) 3 kx, c) 9 kx, and d) 15 kx. a) The rectangular rods of NEU-1 are present, but there is another phase that exists. b) The second phase is very clear and appears everywhere on the sample, even on the rod like crystals. c) and d) The rectangular rod and crystal structure can be seen in these two micrographs. 15
Figure 5. XRD patterns of crystal made with HD (NEU-3) with the standard one-pot procedure (in black) and the pre-mixed procedure (in gray). 17
Figure 6. XRD patterns of the crystals created when varying the main components of the MOF, hexanediamine (HD) and terephthalic acid (TPA) 18
Figure 7. Varying terephthalic acid (TPA) amounts in the synthesis of NEU-3 19
Figure 8. SEM micrographs of NEU-1 at various time points during the synthesis. a) 0 hours, b) 3 hours, c) 6 hours, and d) 8 hours. 21
Figure 9. SEM micrographs of NEU-1 at various time points during the synthesis. a) 17 hours, b) 24 hours, c) 48 hours, and d) 120 hours. 22
Figure 10. XRD patterns of NEU-1 at various times during the reaction 22

LIST OF TABLES

Table 1. Physical properties of the various amines used in different syntheses 12
Table 2. Final pH of the solution depending on the concentration of HD 16
1.0 INTRODUCTION

Rising global temperatures and climate change can be attributed to increased carbon dioxide concentration in the atmosphere caused by anthropogenic sources. Since the process of switching to cleaner energy alternatives cannot happen instantaneously and will be an ongoing work, it is necessary to either decrease emissions or reduce the harmfulness of these emissions by CO$_2$ capture and sequestration (CCS) from the sources, with one of the largest being coal-burning power plants. In order to feasibly collect and store CO$_2$, methods that are energy efficient and environmentally friendly must be developed. There are various stages where this CO$_2$ capture can take place, but one specifically, post-combustion capture, has demonstrated high effectiveness among these techniques.

Typically, aqueous alkanolamine absorbents have been used to remove CO$_2$ from flue gas. Unfortunately, these aqueous solutions require high energy for heating to regenerate the absorbent; but because they are relatively unstable towards heating, this can result in decomposition and decrease in useful lifespan.

Solid nanoporous materials such as zeolites, activated carbons, and metal-organic frameworks (MOFs) can be used to capture carbon dioxide without the disadvantages of aqueous solutions. This study focuses on the characterization and formulation of layered MOFs. These MOFs are a class of hybrid materials that comprise inorganic and organic constituents to form a crystalline material.
In this paper, the growth and formation of crystals and morphology of the MOFs is examined. Specifically, the synthesis of a class of MOFs is examined for tunability of desired physical and chemical properties.

2.0 CRITICAL LITERATURE REVIEW

2.1 Current CO\textsubscript{2} Capture Methods

The current widely accepted method for carbon dioxide capture is the use of aqueous alkanolamine absorbents.\textsuperscript{\textsuperscript{7}} However, these solutions have many limitations for scaling up CO\textsubscript{2} capture. The solutions are not stable at high temperatures, which limits their full regenerative ability. Over long time spans and many cycles, the aqueous solutions will decompose, resulting in a decrease in the effective life span of the material.\textsuperscript{\textsuperscript{8}} In addition, the amine solutions are corrosive towards their holding vessels. This corrosiveness places lower limitations on the concentration of alkanol amines in solution. Since water has such a high heat capacity, the amine solutions require very high energy input for regeneration. Porous solid adsorbents can make up for the drawbacks of the amine solutions.

Porous solids have been studied for many different uses and applications such as catalysis, gas separation, gas purification, and photovoltaic materials. Their low heat capacities are a large reason why porous solids are promising as an alternative to the aqueous solutions. Zeolites are one of these solid adsorbents that require low energy for regeneration; however, their sensitivity to moisture is a big limitation.\textsuperscript{\textsuperscript{5}} Activated carbons are also another option for CO\textsubscript{2} capture. They also require very low energies for regeneration, and they have better efficiencies in humid conditions than zeolites.\textsuperscript{\textsuperscript{9,10}} Even though activated carbons have very high surface areas for adsorption of CO\textsubscript{2} at high
pressures, they do not perform well at low pressures because of their low enthalpies of adsorption.\textsuperscript{11} There are many other porous solids that have been studied, such as metal oxides, hydrotalcites, and “molecular baskets”, each with their own advantages and downsides. One that has recently accumulated much momentum is the metal-organic framework, a very versatile and tunable porous solid.

2.2 Metal-Organic Frameworks

Metal-organic frameworks (MOFs), also referred to as porous coordination polymers (PCPs), are a relatively new class of porous materials that have gained much interest and traction in the past few decades.\textsuperscript{12} These materials have a very high porosity and surface area, which lend to their usefulness in gas capture and storage. In addition, the field of MOFs has grown significantly because they are very structurally and chemically tuneable.\textsuperscript{13} Since the discovery of MOFs in the 1990s, reviews on the material and number of publications have increased significantly each year.\textsuperscript{14}

MOFs are composed of a three-dimensional network of metal ions that are linked to organic ligand molecules to form coordination bonds. The underlying principle to create these structures is that the metal ion sites are able to coordinate to more than one ligand and the ligands are able to bond to more than one metal ion site. Reticular chemistry describes the subunits of the MOF as secondary building units (SBUs).\textsuperscript{15} The cationic metal sites, which can be composed of various nodes, clusters, or chain layers, act as the inorganic SBUs of the MOFs. The organic components are typically polycarboxylates, imidazolates, and other ligands that have anionic oxygen or nitrogen ends.\textsuperscript{6} As with most porous nanoscale materials, MOFs are formed via self-assembly
under carefully controlled conditions to create the coordination bonds between the organic ligands and the metal sites.¹⁵

The properties of MOFs that make them very desirable are their very high and permanent porosity, large surface areas, high pore diffusion rates, and chemical tunability. The measured Brunauer-Emmett-Taylor (BET) surface areas range anywhere from 1000-3000 m²/g. Many factors affect the resulting crystal structure and quality of MOFs. The metal centers, organic ligands, and functional groups all have a large effect on the outcome of the final physical MOF network and gas capture performance.¹² The sheer number of possible arrangements and combinations adds another reason why these materials are so widely studied today. The versatility that these MOFs can provide is extremely beneficial to targeting specific applications and situations.

Metal-Organic framework synthesis is extremely sensitive to the conditions in which the components are reacted. Factors such as temperature, solvent composition, reagent concentrations and ratios, pH, reaction time, and agitation conditions all affect the output of the crystal that you will attain.³ In addition, the formation of by-products, such as metal oxides and unwanted phases, may have to be considered. Temperature of the reaction can affect crystal nucleation as well as coordination of the metal sites. The starting concentrations play a role in arrangement of the ligands as well as reaction rate. The ratios of the starting materials can affect the different phases that are generated during the formation of the network. The selection of the metal ions and their acidity or basicity affect the resulting structure as much as the organic ligands and in some cases, more than the ligands. They also affect the various adsorption properties at low or high pressures.¹⁶
MOFs can also be modified post-synthesis. This change allows for greater tunability to account for some of the drawbacks of certain MOF structures, such as moisture sensitivity. It has been reported that amine functional groups can be used for impregnation and infiltration of various nanoporous solids. These additions can increase the stability, selectivity, capacity, and capacity retention of the MOF.

3.0 EXPERIMENTAL

3.1 Synthesis of Metal-Organic Frameworks

The synthesis conditions of the MOFs were based on previously reported procedures and modified accordingly. Dimethylformamide (DMF) (18 mL, Fisher Scientific) was added to a 100 mL glass beaker with a Teflon stir bar spinning at a speed of 175 RPM. Acetonitrile (CH₃CN) (6 mL, Fisher Scientific) was then added to the beaker, followed by Ethylenediamine (0.3034 g, Fisher Scientific). When the solution was homogeneous, Co(NO₃)₂·6H₂O (0.1314 g, Fisher Scientific) was added. After the cobalt (II) nitrate hexahydrate dissolved, terephthalic acid (TPA or H₂BDC) (0.0273 g, Fisher Scientific) was added to the solution. The solution was allowed to stir for one hour to ensure complete mixing, then transferred to a Teflon liner and placed into a Parr reactor (75 mL). The reactor was placed in a temperature controlled oven for five days at 80 °C. After the reaction was complete, the reactor bomb was removed from the oven and allowed to cool to room temperature. The resulting solution was aerated with a glass Pasteur pipette to break up the crystals. The solution and precipitate were vacuum filtered through a Fisherbrand filter paper (P2, porosity: fine, flow rate: slow) with a Buchner funnel and flask. The powder that was collected on the paper was rinsed with dimethylformamide (60 mL). The powder was kept on the filter paper for at least one day.
until the bulk of the solvent had evaporated. The resulting powder varied in color, ranging from yellow to purple to brown.

Changes in the synthesis conditions were made to attempt to optimize uniformity of the reaction and crystal formation. These modifications will be discussed in the results section.

3.2 Modified Procedures and Scaled-Up Synthesis

3.2.1 Pre-mixing Solution

Different steps were taken to ensure mixing uniformity. The “one-pot” solution that was described in the previous section did not result in the most homogeneous solutions. To account for this, the initial solution was divided into two solutions. The first solution (linker solution) consisted of 16 mL of a 3:1 DMF/CH$_3$CN solution in a 100 mL glass beaker (Fisherbrand). The second solution (layer solution) consisted of 8 mL of the 3:1 DMF/CH$_3$CN solution in a 20 mL scintillation vial (Fisherbrand). The linker solution was stirred in a beaker and had the diamine added and mixed for one day at 175 RPM. Co(NO$_3$)$_2$·6H$_2$O was charged and dissolved into the layer solution had the Co(NO$_3$)$_2$·6H$_2$O before adding TPA (both dissolved relatively quickly in less than 10 minutes). After both the linker solution and the layer solution were homogeneous, the layer solution was added dropwise to the 100 mL beaker containing linker solution. The combined solution was allowed to stir for an additional 60 minutes before being placed in a reactor vessel.
3.2.2 Various Reaction Vessels

The autogenous pressure was low enough for the use of smaller glass vials because the reaction occurs at a specific temperature of 80 °C. The resulting fully mixed solution was divided evenly into four 20 mL scintillation vials with rubber caps, each containing 6 mL of the solution. The caps were secured with Teflon tape to ensure a good seal.

Larger solutions were generated by keeping a constant ratio of liquid volume to reactor volume. The desired ratio was 0.32, based off of an 8 mL liquid volume to a 25 mL reactor volume. Therefore, the small 20 mL scintillation vials required 6.4 mL of liquid, the medium 75 mL Parr reactor required 24 mL of liquid, the larger 125 mL Parr reactor required 40 mL of liquid, the 250 mL glass Pyrex bottles required 80 mL of liquid, and the 500 ml glass Pyrex bottles required 160 mL of liquid.

Different types of scale-up were utilized, including large mixed solution reacted in the small 20 mL vials and large mixed solution reacted in a large bottle.

3.2.3 Reaction Time

In order to understand the effect of reaction time on the formation of MOFs, different timed experiments were conducted that varied the amount of time that the MOF solution was allowed to react at the temperature in the oven. The initial mixing phase of this experiment followed the pre-mixing solution procedure outlined in section 3.2.1. After the solution was divided into four vials, they were placed in the oven to react. One single vial was removed at each desired time point and allowed to cool down to room
temperature. The individual vial was then aerated with a Pasteur pipette and then filtered with a Buchner funnel and flask. The crystals were rinsed with DMF (15 mL).

3.3 Characterization

3.3.1 X-Ray Diffraction

X-ray diffraction is a very common and powerful analytical technique that is used to characterize the crystal structure of a material by analysing its atomic arrangement. The material under study is bombarded by x-rays that are spaced uniformly. The beam enters at a certain known angle, and based on the laws of specular reflection, it is reflected at the same angle. Depending on the distance between the reflecting planes, constructive and destructive interferences will occur. Constructive interference occurs when the rays of the same wavelength are in phase, and it appears as peaks on the XRD patterns. Destructive interference occurs when the rays of the same wavelength are out of phase, and it appears as flat regions on the XRD patterns. Using Bragg’s law (Eqn. 1), the distance between two parallel planes can be determined, which can be used to determine crystal structure.

\[ n \lambda = 2d_{hkl} \sin \theta \]  

(Eqn. 1)

Where:

- \( n \) = number of reflections
- \( d_{hkl} \) = distance between two parallel planes

Using a radiation source with a constant wavelength, the position is varied and the resulting intensities are recorded. The crystals will generate a unique diffraction pattern based on their crystal lattice structure.
In this study, the materials synthesized were analysed with powder x-ray diffraction. The instrument used was a Rigaku Ultima IV X-RAY diffractometer using Cu Kα radiation. The data was collected over the range of 5-40° or 5-50° with a step size of 0.1 degree and a scan rate of one degree per minute.

3.3.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a tool used to view samples under very high magnification by scanning it with a beam of electrons. An electron beam is scanned in a raster pattern, and depending on the type of detector, different kinds of signals are detected and produce an image. SEM is especially useful for viewing and analysing topography and composition of materials. The samples used in this work were not conductive, and therefore needed to be sputter coated with a 6 nm layer of platinum to increase the conductivity of the surface.

In this study, a Hitachi S-4800 high-resolution cold field emission scanning electron microscope was utilized at Northeastern University.

4.0 RESULTS AND DISCUSSION

4.1 Varying the Diamine of the MOF

It has been reported in the literature that pyridine groups can successfully be used as constituents within MOFs. It is not as common to see primary amines used for MOFs with –NH₂ end-groups. If MOFs can be made with smaller molecules that are less bulky, higher surface areas and more selective molecular sieving may be possible. Many different diamines were tested for feasibility as constituents within MOFs. Based on the work of Han et al., who created a MOF that had layers of terephthalic acid and cobalt
metal ion sites, the possibility of utilizing a similar structure with other nitrogen-containing groups was hypothesized.\textsuperscript{20}

Crystalline materials exhibit very sharp peaks on the XRD patterns; however, having sharp peaks does not completely signify the synthesis of a MOF. Comparisons to the literature as well as determination of interlayer distances using Bragg’s law are necessary to confirm that the appropriate MOF has been synthesized.

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>ethylenediamine (ED)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>1,4-butanediamine (BD)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>1,6-hexanediame (HD)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>1,12-dodecanediamine (DD)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>triethylenetetramine (TETA)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>tetraethylenepentamine (TEPA)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>para-phenylenediamine (PPD)</td>
</tr>
<tr>
<td>( \text{H}_2\text{N} - \text{NH}_2 )</td>
<td>4,4-diaminodiphenylamine (DADPA)</td>
</tr>
</tbody>
</table>

Figure 1. Various diamines and other amines used as constituents for MOFs. Different molecular lengths and sizes were used to see the effects on the generated MOF.
Figure 1 displays the different diamines that were candidates for MOF formation. Small molecules such as ethylenediamine (ED) and 1,4-butanediamine (BD) were considered along with large bulky molecules such as 4,4-diaminodiphenylamine (DADPA). Syntheses with some of the molecules demonstrated more promise than the others in terms of crystallinity.

1,12-dodecanediamine (DD) was not reacted because it did not meet the synthesis conditions. DD’s solubility in the DMF/CH$_3$CN solution was too low at the necessary concentration, so the solution would not have been completely homogeneous. In addition, synthesis with para-phenylenediamine (PPD) did not generate a clear XRD pattern upon initial synthesis attempts. Tetraethylenepentamine (TEPA) also did not result in a crystalline XRD pattern. MOF formation with these constituents may be possible, but the reaction conditions would have to be modified to achieve a feasible crystal structure.

Figure 2. XRD patterns of various crystals synthesized with different amines. These materials exhibited sharp peaks and enough crystallinity for consideration for additional testing.
In Figure 2, various crystals have been generated with different molecules acting as the linker in a MOF. Having the ability to select and choose the appropriate molecule is an extremely useful tool. Different molecules will create different MOFs that have different operating windows in terms of thermal stability.

<table>
<thead>
<tr>
<th></th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylenediamine (ED)</td>
<td>60.10</td>
<td>8.5</td>
<td>117</td>
</tr>
<tr>
<td>1,4-butanediamine (BD)</td>
<td>88.15</td>
<td>27</td>
<td>158</td>
</tr>
<tr>
<td>1,6-hexanediame (HD)</td>
<td>116.20</td>
<td>42</td>
<td>204</td>
</tr>
<tr>
<td>1,12-dodecanediamine (DD)</td>
<td>200.36</td>
<td>67</td>
<td>304</td>
</tr>
<tr>
<td>Triethylenetetramine (TETA)</td>
<td>146.23</td>
<td>12</td>
<td>266</td>
</tr>
<tr>
<td>Tetraethylenepentamine (TEPA)</td>
<td>189.30</td>
<td>-30</td>
<td>340</td>
</tr>
<tr>
<td>Para-phenylenediamine (PPD)</td>
<td>108.14</td>
<td>146</td>
<td>267</td>
</tr>
<tr>
<td>4,4-diaminodiphenylamine (DADPA)</td>
<td>199.25</td>
<td>300</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Boiling points of each of the compounds are listed in Table 1. As the molecules grow larger, the boiling points generally increase. As a result of intermolecular interactions and bonding, a compound within a MOF will not necessarily exhibit the same boiling point as the pure compound, but the values of the pure species’ boiling points can still be used to compare relative stabilities across different molecules. This thermal stability of the compounds affects the temperature at which the MOFs may be
degassed, which is a very important step in creating a permanently porous MOF. Furthermore, in order to activate the framework, the solvent molecules need to be removed at a higher temperature without collapsing the framework.

Ethylenediamine (ED) and 1,6-hexanediamine (HD) are the two amines that were examined closely in this study. The simplicity of the molecules, short molecular length, ease of synthesis, and contrast in boiling points made these two the best candidates for additional testing.

4.2 Ethylenediamine as the Linker (NEU-1)

The initial concentrations of reagents is an extremely important metric in the formulation of a MOF. The concentrations determine what the limiting reagent will be and what the pH of the solution will be. They also may determine the types of metal clusters that form. Ethylenediamine (ED) is a molecule that is utilized very often with MOFs because it can be used for post-synthesis functionalization for enhanced carbon dioxide capture. However, it has not been used as a linker within a MOF. The small molecule size makes ED a perfect candidate for a MOF with a very small pore size to act as a molecular sieve.
As displayed in Figure 3a, when a lower concentration of ED was used, the resulting material was amorphous based on the absence of peaks on the XRD pattern. The broad peak around 23 degrees is the result of background from the glass sample holder. However, when using a higher concentration of ED, there is a dramatic change in the pattern and many peaks appear. From the SEM micrograph in Figure 3b, the materials depicted are amorphous agglomerates. However, in Figure 3c, the crystals of the higher concentration formulation are visible as rectangular pillars. This MOF will be denoted as NEU-1.

The influence of pH on MOF formation was examined. NEU-1 was a very successful synthesis displaying very strong peaks. Before reacting the solution in the
oven, the pH was 12.81. Using this pH as a target, it is possible to use other chemically similar compounds in an analogous fashion. The range of the final resting pH pre-synthesis was desired to be between 12.4-12.8.

Figure 4. SEM micrographs of NEU-1 crystals at various magnifications of a) 1 kx, b) 3 kx, c) 9 kx, and d) 15 kx. a) The rectangular rods of NEU-1 are present, but there is another phase that exists. b) The second phase is very clear and appears everywhere on the sample, even on the rod like crystals. c) and d) The rectangular rod and crystal structure can be seen in these two micrographs.

From various SEM micrographs in Figure 4, the different aggregates suggest the formation of multiple phases. The largest crystals most likely represent the desired phase of the MOF. The other phases are the outcomes of impurities and processing techniques.
4.3 Hexanediamine as the Linker (NEU-3)

Another candidate for a linker within the solution is 1,6-hexanediamine (HD), which is very similar to ED but contains four more carbons in the chain, making it slightly longer. Whereas ED is a liquid at room temperature with a melting point of 8.5 °C, HD is a solid at room temperature with a melting point of 42 °C. HD required an additional lengthened dissolving step before the reaction could take place. Various concentrations of HD were tested to accommodate for the correct pH and environment for crystal growth. At first, an HD solution with the same molar concentration of 210 mM as ED was prepared.

<table>
<thead>
<tr>
<th>Concentration of HD (mM)</th>
<th>Final pH of Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>11.77</td>
</tr>
<tr>
<td>315</td>
<td>12.18</td>
</tr>
<tr>
<td>420</td>
<td>12.41</td>
</tr>
</tbody>
</table>

From Table 2, it is clear that HD at 210 mM does not result in the same final pH of the solution as ED at 210 mM, 11.77 as opposed to 12.81. This difference may result from the varying levels of solubility and stability in solution between HD and ED. Various higher concentrations were used to attain a final pH very close to the ED solution. Once the correct pH solution had stabilized, it was allowed to react in the oven under the same conditions. The MOF synthesized with HD will be denoted as NEU-3.
Figure 5. XRD patterns of crystal made with HD (NEU-3) with the standard one-pot procedure (in black) and the pre-mixed procedure (in gray).

In Figure 5a, the XRD pattern of NEU-3 synthesized using the one-pot and pre-mixing methods is displayed to have a number of characteristic peaks. When it was found that the one-pot method of synthesis was not as easily reproducible, a different approach was examined. Two solutions, one with the amine and one with TPA, were created. After both solutions reached full dissolution, the TPA solution was added to the amine solution. This allowed for greater control over the dissolution of the reagents. Both patterns have been normalized to the maximum intensity for each crystal. Both the one-pot and the pre-mix crystals maintain the same characteristic peaks, so the same crystal is being synthesized. The sharper peaks from the pre-mix crystal indicates that the bulk powder
contains a higher amount of crystalline material. The SEM micrographs in Figure 5 also present some insight on the process of the crystallization and growth of the MOF, which will be discussed further in the next section.

![Graph showing XRD patterns](image)

**Figure 6. XRD patterns of the crystals created when varying the main components of the MOF, hexanediamine (HD) and terephthalic acid (TPA)**

In Figure 6, the absence of HD or TPA result in a completely different crystal. While it still creates a crystalline material, the XRD pattern describes a completely different structure. It is possible that as the layer material with TPA is being formed, the linker material HD can then be used as pillars. Therefore, the role of the amine in the synthesis of the MOF is paramount.
Figure 7. Varying terephthalic acid (TPA) amounts in the synthesis of NEU-3

In all of the previously described syntheses, terephthalic acid (TPA) has been the limiting reactant. Increasing the amount of the linker (ED or HD) increases the yield and purity of the MOF, as indicated with NEU-1 from Figure 3. The MOF requires a very basic solution in order to self-assemble. The effect of increasing the concentration of the limiting reactant, TPA, was examined and the results are displayed in Figure 7. The characteristic peaks in the XRD patterns of the synthesized crystals do not change as TPA concentration increases. The sharpness of the peaks increase with increasing concentration of TPA. Therefore, the percentage of crystalline material that is synthesized increases with increasing TPA concentration. This amount of TPA is reaching the upper limit of solubility in the precursor solution. When increased to 50 mM of TPA, the TPA did not fully dissolve even with extended mixing times of over 24 hours. The first three peaks between 5 and 10 degrees change in intensity as the concentration of TPA increases, whereas the peaks in the middle range between 15-25 degrees stay relatively the same in intensity. This result could be due to the layer
structure with TPA being formed in the absence of the secondary phase within the material.

4.4 Crystal Growth and Effect of Time

The mechanism of crystal growth was deduced from SEM micrographs coupled with the XRD patterns. Different time trials were tested and XRD and SEM were both performed on the resulting MOFs. The MOF crystals grow in stages. The first stage is nucleation, the second stage is continued crystal growth, and the last stage is termination due to depletion of resources. These MOFs grow out radially as demonstrated in the SEM images in Figure 8 and Figure 9. In these images, it is clear that there is an initial site that is generated in a spherical fashion. Afterwards, the crystals are able to grow out radially in rectangular pillars. Concentrations and time play a role in the particle size and particle size distribution. Longer reaction times may facilitate large particles and a broad particle size distribution with many agglomerates of smaller particles forming. Shorter reaction times facilitate smaller particles but a narrower particle size distribution.
Figure 8. SEM micrographs of NEU-1 at various time points during the synthesis. a) 0 hours, b) 3 hours, c) 6 hours, and d) 8 hours.
Figure 9. SEM micrographs of NEU-1 at various time points during the synthesis. a) 17 hours, b) 24 hours, c) 48 hours, and d) 120 hours.

Figure 10. XRD patterns of NEU-1 at various times during the reaction.
A SEM image was taken of the initial precipitate of the solution without any time to react in an oven at higher temperature, denoted by 0 hours. In the SEM in Figure 8, there are no clear crystal structures, and from the XRD in Figure 10, there are no peaks so the precipitate formed initially is amorphous. The intensities of the individual peaks are not a great indication of how pure a phase is. However, the relationships between the various peaks can tell how much of one phase may exist relative to another, i.e. the purity of the phase. The subsequent XRD patterns indicate that certain phases in the solution could be depleting while others are forming as the time of reaction increases.

A peak at around 12 degrees 2θ forms initially but disappears by 24 hours. The peaks at 23.3 and 24 degrees 2θ begin to form at 17 hours and are very prominent by 24 hours. However, the peak at 27.9 degrees 2θ forms initially, but disappears. This peak may be a secondary unwanted phase of the crystal. Another possible explanation for disappearance of peaks is that it represents a phase that is formed only initially, so after time, the other phases begin to self-assemble which decreases the percentage of the initial phase, which decreases its relative intensity.

5.0 CONCLUSION

In this study, a new series of layered metal organic framework with very simple amine groups were utilized as pillaring ligands. Specifically, MOFs with ethylenediamine and 1,6-hexanedianine (NEU-1 and NEU-3, respectively) were closely examined for their crystal structure and growth at varying concentrations of linker and layer molecules to test their potential as a new class of simple MOFs. Other simple amines and amine containing molecules can also be used to generate metal organic framework, each with
their own crystalline fingerprint. Scanning electron microscopy and x-ray diffraction were both used to visualize and understand the growth of the MOFs.

A synthesis method was formulated that generated crystals of much higher purity and allowed for much more control over the chemistry. The MOF growth is extremely sensitive to many factors. In this case, for both NEU-1 and NEU-3, a high pH was necessary to form crystals. Increasing the other acidic ligand, terephthalic acid, did not lower the pH significantly, but increased the quality of the crystals.

**6.0 RECOMMENDATIONS**

Further steps to assess both NEU-1’s and NEU-3’s ability to capture and store carbon dioxide need to be taken. Additional drying steps and possibly solvent exchange are necessary to fully take advantage of the pore size of the MOFs. In addition, surface areas and pore volumes need to be fully characterized for the validation of the practicality of these MOFs.

The amines are currently used in a large excess to increase the pH. Another economical method to increase the pH without using as much amine would decrease waste and increase yield. The impurities of other phases that exist with the MOFs as synthesized need to be addressed. Possible cleaning and purifications steps including centrifugation and decanting need to be examined.

Implementation of the MOFs in a practical manner such as mixed matrix membranes would be a step towards scaling up from the laboratory scale.
REFERENCES


