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# Testing Cr(II)-BTC for Ammonia Adsorption Capabilities: A Research Proposal

Tyler Hemingway  
*Gardner-Webb University*

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# Testing Cr(II)-BTC for Ammonia Adsorption Capabilities: A Research Proposal

An Honors Thesis

Presented to

The University Honors Program

Gardner-Webb University

9 April 2018

by

Tyler Hemingway

**Accepted by the Honors Faculty**

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Dr. Benjamin Brooks; Thesis Advisor

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Dr. Tom Jones; Associate Dean; Univ. Honors

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Dr. Candice Rome, Honors Committee

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Dr. Lorene Pagcaliwagan Honors Committee

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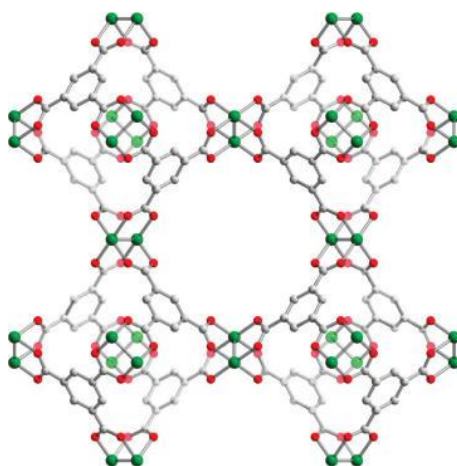
Dr. Don Olive, Honors Committee

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Dr. Anna Sieges Beal, Honors Committee

## 1. Purpose and Hypothesis

The purpose of this thesis is to determine the ability of a particular metal-organic framework (MOF), Cr(II)-BTC, to adsorb ammonia ( $\text{NH}_3$ ) gas. This particular MOF was chosen for this study due to the Cr having open metal sites, which are generally suitable locations for ammonia adsorption as seen in other MOFs.<sup>1,2,3</sup> This study will be done by testing Cr(II)-BTC's ability to adsorb as well as another MOFs ability to adsorb ammonia. From this data, the ability of Cr(II)-BTC to adsorb ammonia repeatedly and under dry or humid conditions will also be determined. Finally, the MOFs practical uses for adsorption will also be examined. My hypothesis is that Cr(II)-BTC (Figure 1.1) may work as an adsorbent for ammonia, but it is unclear if it will work as an adsorbent under all conditions.



**Figure 1.1: “Ball and stick” model of the framework of Cr(II)-BTC. Green, white, and red spheres represent chromium, carbon, and oxygen, respectively.<sup>4</sup>**

Another goal of this work is to discuss the properties of MOFs. Since MOFs were discovered recently, these compounds are unknown to most people. Therefore, this work

will also explore various properties of MOFs that are necessary to understand the MOFs themselves and how their absorption works.

## **2. Background**

### **2.1 Ammonia**

Ammonia is one of the most widely produced chemicals in the world. In fact, about 85% of industrial energy is devoted to making over 100 million tons of ammonia each year.<sup>5</sup> Of the ammonia produced, over 80% is used to make nitrogen-rich fertilizer which provides much of the nitrogen that plants need to grow. Ammonia is also used in many other applications such as fuels, explosives, and for hydrogen storage.<sup>5</sup>

Although ammonia has many important uses, the gas is also a highly toxic substance to humans. This is due to the fact that it readily dissolves in the water present in the body to form a weak basic solution. This base is very good at performing a process called saponification, which refers to the base-promoted hydrolysis of esters. A great portion of the cell membrane is composed of fatty acids and glycerol which form esters when bonded together.<sup>6</sup> Dissolved ammonia in the body will cause a saponification of fatty acids, which destroys the cell membrane. Without the cell membrane, the cell itself will die as well. Additionally, this process also removes water from the body due to the process of forming ammonium hydroxide which can dehydrate cells.<sup>6</sup>

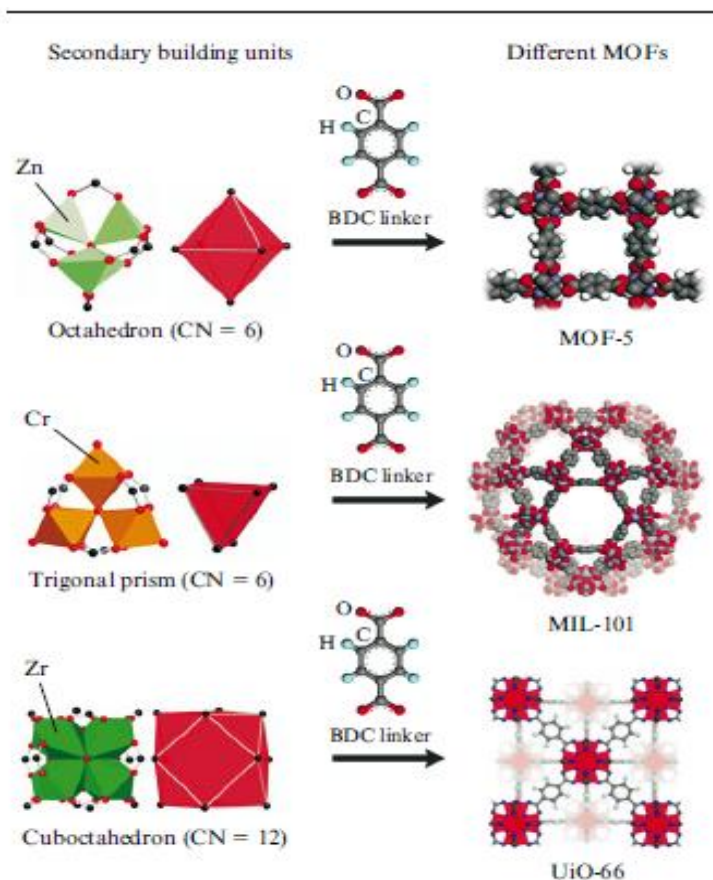
Due to these issues, ammonia can cause a variety of problems to those exposed to it. At low concentrations, exposure to ammonia will cause burns in the mouth, throat, and eyes. Higher concentrations can leave burns on any afflicted area of the body. Very high concentrations of ammonia in the body can even block the passage of air to the lungs. Due to these potential safety issues, ammonia can be a dangerous gas if inhaled, and people that work with it require some level of protection.<sup>6</sup>

Because of aspects such as low cost, ease of use and design, lack of harmful secondary products, and reusability of materials, adsorption, which is the process in which a liquid or gas will adhere to the surface of another substance (specifically one that is porous), has been looked at as a method of protection from ammonia. Recently, compounds called metal-organic frameworks (MOFs) have been examined for their ability to adsorb ammonia. This is due to a variety of reasons, such as the very high surface area and porosity of MOFs, which afford the MOFs much space in which to adsorb molecules of ammonia.<sup>8,9</sup>

## **2.2 Characterization, Synthesis, and Properties of MOFs**

A MOF is a compound with two main components: a secondary building unit (SBU) and an organic linker. The SBU is composed of a metal cation or clusters of metal ions that are coordinated to oxygen, nitrogen, or fluorine atoms.<sup>8,9</sup> These clusters can form into various shapes, such as a cube and an octahedron. The organic linker is an organic compound that has substituents that will bind to these SBUs (carboxylate groups are a notable example of substituents that can bind to the SBUs).<sup>8,9</sup> These SBUs will then be

bound to the organic compound, and then more carboxylate groups on these organic ligands will then bind to more SBUs. Eventually, this process will result in the formation of a complex 1D, 2D, or 3D structure.<sup>8</sup> Butova et. al. describes the formation of MOFs in Figure



2.1.

Figure 2.1: Explanation of the formation of MOFs. The left-most box shows three different metallic SBUs, and the right-most box shows four different organic compounds that can be used as linkers. The middle photo shows the different MOFs that are made by combining the metal node and organic linker that each arrow originates.<sup>9</sup>

Next, it is important to discuss the nomenclature of MOFs. This is especially relevant since MOFs are named in several ways. Some MOFs are simply named as “MOF” followed by a number (MOF-5 as an example). The number denotes in which order the MOFs were

discovered. For example, MOF-5 was the 5<sup>th</sup> MOF discovered.<sup>9</sup> Secondly, MOFs can be named by abbreviation IRMOF and a number (an example would be IRMOF-5). IRMOF stands for “Isorecticular metal-organic framework.” These MOFs are named this way because they have the same symmetry and overall structure as another MOF.<sup>9</sup> Third, a MOF can be denoted with a variety of other abbreviations such as UiO, MIL, and HKUST along with a number (*e.g.*, HKUST-1) these abbreviations correspond to the university in which they were discovered. Thus, UiO stands for Universitetet i Oslo, MIL stands for Materials of Institut Lavoisier, and HKUST stands for Hong Kong University of Science and Technology.<sup>9</sup> Additionally, some MOFs are named by first naming the metal cation used in the SBU followed by a hyphen and the name of the organic ligand. The overall charge of the metal cation is shown by placing the number in Roman numerals in parentheses after the name of the metal cation Cr(II)-BTC is an example of this naming scheme in which Cr(II) refers to chromium with a +2 charge, and BTC refers to the organic compound 1,3,5-benzenetricarboxalate. Finally, some of the MOF’s names give insight into their structure. For example, some MOFs have a similar structure to other kinds of porous crystalline compounds called zeolites. These types of MOFs have metal ions connected by tetrahedra of nitrogen atoms that are connected by imidazole rings. Thus, these MOFs have been named ZIF along with a number (ZIF-8 for example).<sup>9</sup> ZIF stands for “zeolite imidazolate framework,” denoting that the MOF resembles a zeolite that is also connected by imidazole rings. Overall, MOF nomenclature is very inconsistent and even arbitrary at times since their names can have different meanings and that significance may not even be related to the structure of the MOF itself.

Figure 2.1 helps explain the properties of MOFs that have caused them to be the center of much study. The first such property is their very high porosity. The figure shows that the width of the wall of each crystal is only about the length of a carbon atom, but the distance between two walls is about the length of the whole organic ligand which is significantly longer than a single carbon atom. The space between the two ligands contains a pore in the crystal lattice of the MOF structure. Since each of these outer crystals should have a pore, this leads to the formation of a structure consisting mostly of pores. This high porosity creates many possible sites for gas adsorption to occur. Additionally, high porosity also leads to MOFs having another one of their important properties: a very high surface area.<sup>8,9</sup>

Furukawa et al. show that this description of the MOFs also illustrates one of the main reasons why they have received much attention from chemists recently: their tunability. As shown in Figure 2.2 and 2.3, in principle many different MOFs can be made by changing either the metal salt or the organic compound. By changing either of these, the other properties of the MOF, such as pore size and the shape of the subunit, will also be altered. This means that the properties of the MOF can be potentially tuned to fit a specific reaction.<sup>9</sup> For example, if the pores of the MOF are too small to properly adsorb a given gas, one would need to use a longer organic compound (since a longer distance between two SBUs will yield a larger pore size). This, in turn, will also decrease the surface area of the MOF as well.<sup>9</sup> Due to this property, MOFs can be adapted to many different reactions if the chemist chooses the correct compounds and methods to make them. Figures 2.3 and 2.4 list some of the potential SBUs and organic linkers that can be used to form a MOF. The figures



illustrate just how many can potentially be synthesized with different shapes, pore sizes, etc.

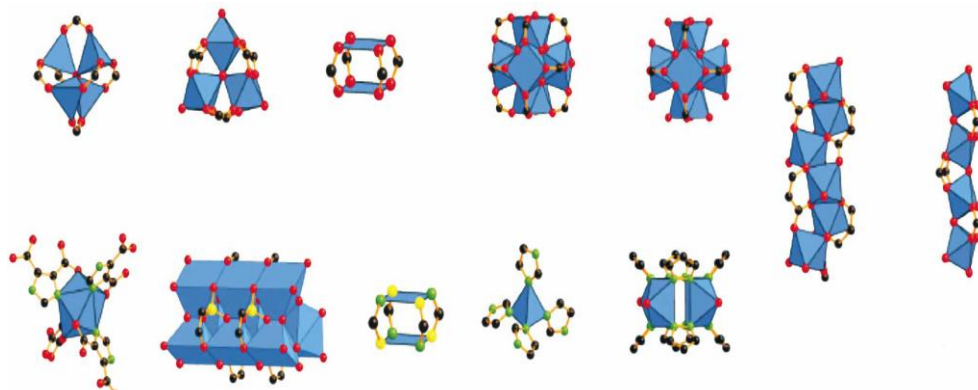


Figure 2.2: SBUs that can be used for MOFs. Most of these SBUs have different shapes, which will change the overall shape of the MOF.<sup>8</sup>

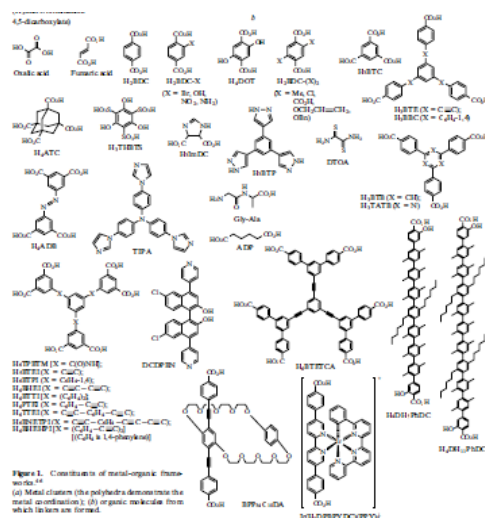
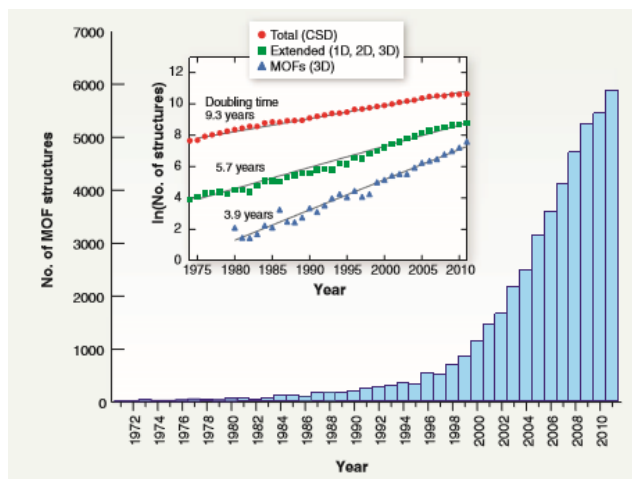


Figure 2.3: organic ligands that can be used to form MOFs. Their size, shape, and substituents are all vastly different, and these will change some of the properties of the resulting MOF<sup>8</sup>

Another property of MOFs discussed is their thermal stability. Since the MOFs are formed using strong covalent bonds (*e.g.*, C-C, C-H, M-O, etc.) these structures will not readily decompose in heat. Reports show that MOFs can survive in temperatures from 250-500 °C without decomposing.<sup>8</sup> Because of this fact MOFs can be used to facilitate reactions that take place at elevated temperatures.

One final important element to MOFs is their history: namely the fact that they were only recently discovered and studied. Specifically, interest in the MOFs did not start until the 1990s, and it was not until 1995 that Omar Yaghi, coined the term “metal-organic framework.”<sup>10</sup> In 1999 two papers were published that reported the synthesis of the MOFs HKUST-1 and MOF-5. These papers showed that these MOFs had a significantly high porosity and pore volume that could contest zeolites (another set of compounds with similar properties to MOFs). Since this time, the study of MOFs has increased tremendously with over 20,000 different MOF structures having been found since then (Figure 2.1)



**Figure 2.1: Number of MOF structures discovered for a given year and the doubling time of the discovery of MOFs.<sup>8</sup>**

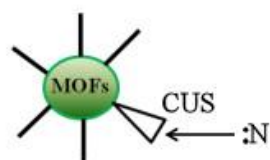
### **2.3 General MOF Adsorption**

Khan et. al. discusses the mechanisms by which the absorption of gases and liquids onto MOFs occurs. When the gaseous substance enters one of the pores of the MOF, the substance will interact with the walls of the pores. At this point, two possible methods of adsorption can occur: physical adsorption or chemical adsorption. Physical adsorption occurs when the MOF traps the substance using weak intermolecular forces (*e.g.*, Van der Waals forces) and chemical adsorption occurs when a covalent chemical bond is formed between the MOF and the substance.<sup>11</sup> The main difference between these forms of adsorption is the method of removal of the adsorbed substance from the MOF. The forces between the substance and the MOF are weak enough in physical adsorption that washing the MOF in a solvent that will dissolve the adsorbed compound is sufficient to remove the substance from the MOF. Since the covalent chemical bonds of chemical adsorption are much stronger than intermolecular forces, chemical treatments are required to remove the substance from the MOF.<sup>11</sup>

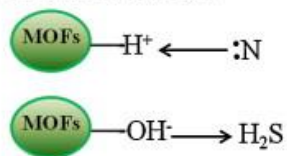
MOFs can create a chemical bond with substances in many ways. First, as previously shown, MOFs have a metal cation in the center of each of their SBUs. These SBUs have areas in which a substance can interact and form a bond with the metal cation. These spaces are referred to as open metal sites. Second, functional groups present on the ligand of the MOF can act as a Lewis acid (electron acceptor) or Lewis base (electron donor) to

form bonds with adsorbates that will readily give an electron or receive an electron. Third, an open metal present on the ligand of a MOF can form  $\pi$ -complexes with substances that can have  $\pi$ -bonds. Fourth, if the MOF itself exhibits a positive or negative charge in the SBUs, then electrostatic forces can allow a compound with the opposite charge to bond to the MOF. Fifth, If the compound has any hydrogens on it that are able perform hydrogen bonding, then they will form a hydrogen bond with the oxygens that are bonded to the SBU. Finally, some MOFs were shown to be able to expand and contract their pores in order to have more space for adsorption. This “breathing effect” that is present in some MOFs allow these MOFs to adsorb polar molecules.<sup>11</sup> From this list, MOFs are shown to have diverse methods to adsorb substances onto them. Figure 2.5 below summarizes the mechanisms of the methods of adsorption of the MOFs.

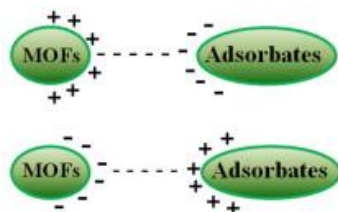
1) Adsorption on CUS



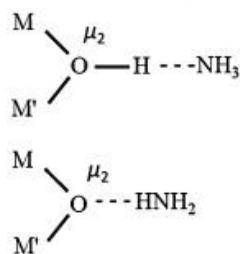
2) Acid base interaction



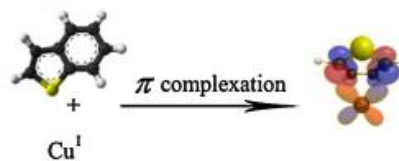
3) Electrostatic interaction



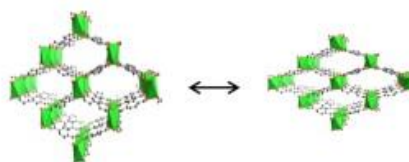
4) Hydrogen bonding



5)  $\pi$ -complex formation



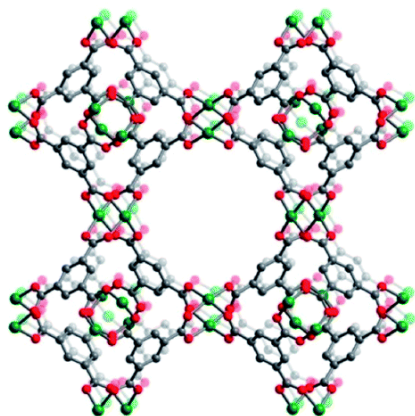
6) Breathing effect



**Figure 2.5: Variety of methods that MOFs use to adsorb substances<sup>11</sup>**

## **2.4 Plan to Quantify the Adsorptive Ability of Cr(II)-BTC**

To determine the adsorptive abilities of Cr(II)-BTC, literature that details this adsorptive ability of Cr(II)-BTC was examined. Additionally, literature that discusses the ability of other MOFs to adsorb ammonia will be examined. In particular, the ability of the MOF HKUST-1 to adsorb ammonia will be examined since these MOFs have the same crystalline structure (*i.e.*, they use the same organic ligand to connect the SBUs, and the SBUs produce the same shape). The only difference between these frameworks is the metal in the SBU. HKUST-1 has Cu(II) metal nodes, but Cr(II)-BTC has Cr(II) nodes. While this does create differences between the adsorption ability, many similarities in the adsorptive ability should also be present. After these sources are examined, conclusions of Cr(II)-BTCs ability to adsorb ammonia will be drawn. Figure 2.6 shows the structure of HKUST-1.



**Figure 2.6: “Ball and stick” model of the framework of HKUST-1. Green, white, and red spheres represent copper, carbon, and oxygen, respectively.<sup>12</sup>**

## 2.5 Properties and Mechanism of Adsorption for Cr(II)-BTC:

To determine the adsorptive ability of ammonia for Cr(II)-BTC, Sumida et. al. examined the properties of the MOF by performing several characterization tests. The MOF has a surface area of  $1,810 \text{ m}^2/\text{g}$ , which is relatively high for MOFs, so the MOF has much space on which to adsorb ammonia. Additionally, the MOF has open metal sites, which were shown previously to be suitable sites of adsorption.<sup>4</sup>

Additionally, the mechanism for adsorption in Cr(II)-BTC was also discovered by performing a hydrogen adsorption test. This was done by allowing the MOF to adsorb deuterium (an isotope of hydrogen) at the following volumes: 0.5, 1.0, 1.5, 2.0, and 3.0 moles of deuterium gas for every chromium ion present in the MOF.<sup>4</sup> The MOF was then examined after each of these volumes were allowed to pass through the MOF for areas on the MOF in which deuterium is present. The adsorption sites for the MOF and their adsorption strength were then determined.

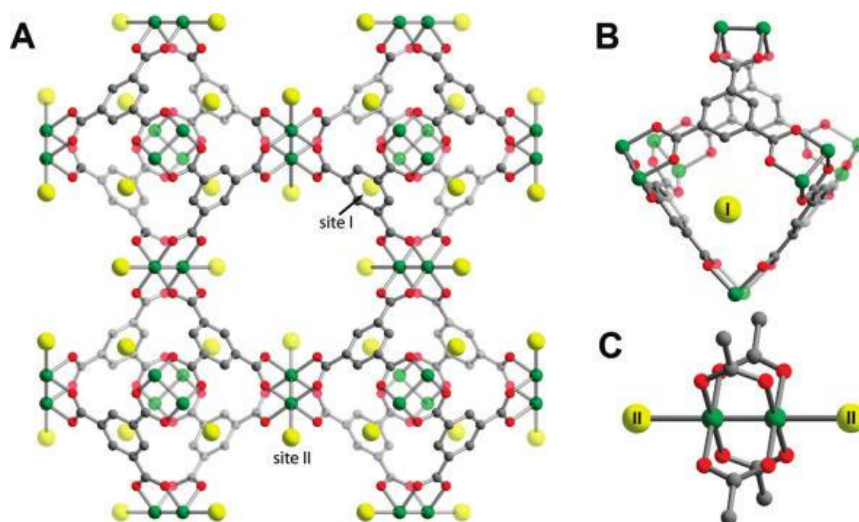
After 0.5 moles of deuterium gas passed through the MOF, only one adsorption site was observed. This site is in the middle of the octahedral portion of the MOF formed in the middle of several of the organic ligands. No adsorption was seen on the open metal sites of the MOF at this level, however, which is unusual since these sites are generally the preferred site of adsorption for other MOFs including HKUST-1. In fact, this may be the first MOF discovered with open metal sites in which the metal site is not the most preferred adsorption site.<sup>4</sup>

After 1.0 moles of deuterium gas passed through the MOF, a larger density of deuterium was seen on the first adsorption site, and a second adsorption site was examined. This second site was the open metal site, but the distance between the bond of the metal site and the deuterium was longer than the distances seen for HKUST-1. As a nonpolar molecule, such as deuterium gas, moves closer to a cation, a partial charge will be formed in the molecule, and a weak intermolecular bond called an induced dipole will be created. If the nonpolar molecule moves closer to the cation, the induced dipole will get stronger. Due to the increased distance between the cation and the gas, the induced dipole between them is weaker. This property explains why the open metal site was not an adsorption site until the second test: a much weaker bond is formed when compared to other metals.<sup>4</sup>

Upon further investigation into why the distance is greater for chromium, the bond length between two chromium cations was found to be shorter than the bond length between the two copper cations seen in HKUST-1. This is due chromium possessing a larger ionic radius than copper. Because of the decreased bond length, chromium does not project out of the MOF as far as copper does and remains closer to the walls of the pore. Although an attractive force does allow the MOF to adsorb the deuterium, molecules will begin to repel each other if they are too close to each other.<sup>4</sup> This repelling force is known as steric hindrance. Because of this steric hindrance, the deuterium molecules cannot move as close to the chromium cations as they could the copper cations. In general, this means that the open metal sites present in Cr(II)-BTC are not nearly as effective at adsorption as the open metal sites of other known MOFs.

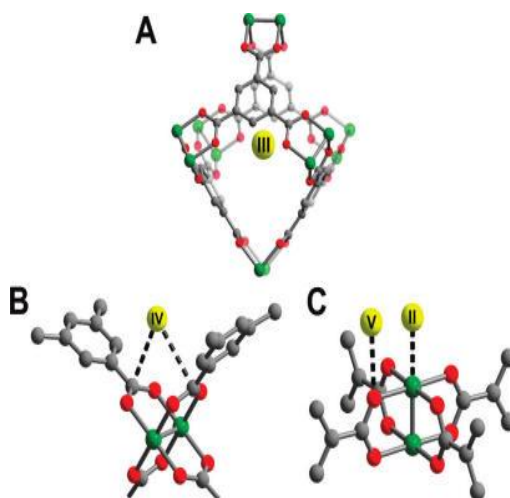
Something interesting happens when 1.5 molecules of deuterium gas pass through the MOF, however. The extra deuterium causes the bonds between the chromium cations to weaken and the bond length to increase. This increase in bond length allows the deuterium to more readily access the chromium cations, and the second adsorption sites are filled. Additionally, a third adsorption site found in the middle of the octahedral cages of the MOF are also filled.

Finally, when 2.0 and 3.0 molecules of deuterium gas passed through the MOF, two more adsorption sites were found. The fourth site was present in between two benzene rings and next to the SBU, and the fifth site was adjacent to the oxygen atoms of the carboxylate groups (although very little deuterium adsorbed onto the fifth site even at the highest volume of gas). The interactions found on sites 3-5 were also found on HKUST-1 due to both having the same structure. Figures 2.7 and 2.8 further depicts the exact locations of the adsorption sites.





**Figure 2.7: Locations of adsorption sites 1 and 2 for Cr(II)-BTC.<sup>4</sup>**



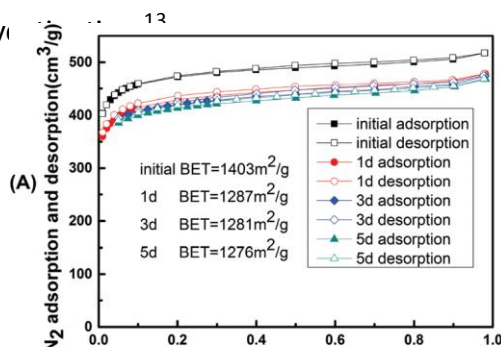
**Figure 2.8: Locations of adsorption sites 3-5 for Cr(II)-BTC.<sup>4</sup>**

## **2.6 Potential Practical hinderance with the Cr(II)-BTC**

Zhang et. al. discuss a notable potential issue of the adsorption ability of Cr(II)-BTC. This issue involves the stability of the MOF in an environment with both oxygen and water. This is a problem because the natural outside environment has oxygen and generally has some degree of water vapor in the form of humidity. As a result, if the MOF could not survive under these conditions, then the people that hope to use this MOF for practical applications will need to work around this issue. For this experiment, Cr(II)-BTC was tested under an environment of oxygen without water, water without oxygen, and both water and oxygen. The stability was determined by a powder X-ray diffraction test. In this test, X-ray radiation is passed through the MOF at specific angles and then refracts off of the MOF onto a

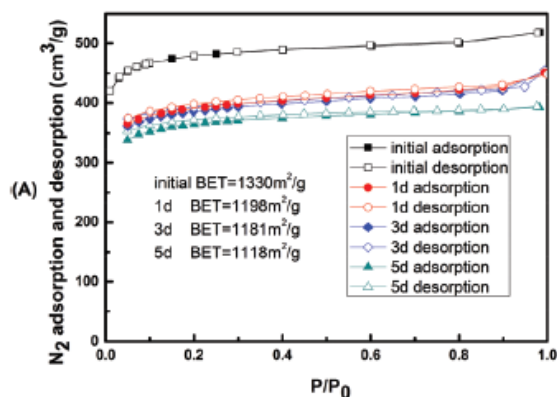
detector on the opposite side. This test will then create a graph of the refractions which provides information about the structure of the sample. This graph can then be compared to the known graph of a particular compound to determine if the compounds have the same structure. Additionally, the MOF was also tested for its surface area before and after exposure to the oxygen environment by performing an adsorption/desorption test. In this test, nitrogen gas was allowed to adsorb onto the MOF at low temperatures, and then the temperature was raised to allow the gas to desorb off the MOF. A change in surface area will determine a change in the structure of the MOF (*e.g.*, the decomposition of the MOF).

First, the MOFs were tested in a pure oxygen environment. This was done by placing the MOF in an oxygen environment for a period of time, and then the adsorption/desorption test was performed on it. This was then repeated several times. The surface areas found for this MOF at the end of each interval of this test are shown on Figure 2.9. After each day, the adsorption/desorption curves move down slightly, which indicates that the amount of oxygen adsorbed, as well as surface area, has decreased.<sup>13</sup> A decrease in surface area indicates that the MOF has deteriorated slightly. The total surface area of the MOF decreased by 8.3% after one day of this oxygen exposure and by 9.0% after five days of this exposure.<sup>13</sup> These data show that in a pure oxygen environment, the MOF does deteriorate slightly, and most of the deterioration occurs after the first day. After the first day, little further deterioration is observed. This decrease in surface area was not significant enough to change the overall crystallinity of the MOF. Also, the exact way that oxygen deteriorates the MOF is still under inv



**Figure 2.9: adsorption/desorption shown for Cr(II)-BTC and the corresponding surface areas found in a pure oxygen environment<sup>13</sup>**

Next, the MOF was tested in an environment that contained water vapor. The method of testing the MOF was similar to the method for the pure oxygen environment. The MOF was exposed to a 90% relative humidity (RH) environment.<sup>13</sup> This means that the air was almost saturated with water. Additionally, argon was chosen as the other gas used for this environment since it is a very stable gas and will not react with the MOF. This exposure lasted for different durations of time each day for 1 to 5 days. After 5 days, the MOF had lost about 15.9% of its total surface area.<sup>13</sup> Again, this loss of surface area was not significant enough to cause the MOF to lose its overall crystallinity. After the method of deterioration was examined, the researchers found that the water was breaking the bond between the metal node and the ligand. This would form a bond between the metal and water and leave the ligand free, destroying the structure in that area.<sup>13</sup> Figure 2.10 shows the surface area change over time for the water vapor environment.



**Figure 2.10: adsorption/desorption shown for CR(II)-BTC and the corresponding surface areas found in a water vapor environment<sup>13</sup>**

To examine the change in crystallinity for the MOF under the water vapor environment, powder X-ray diffraction (PXRD) was used. PXRD tests a MOF for its crystalline structure by blasting the MOF with X-rays at a specific angle. The MOF will then refract these X-rays onto the detector. The instrument then records the angles at which the X-rays were detected. This process will produce a graph of each angle with peaks at the angles in which the X-rays were detected. This graph can then be compared to other PXRD graphs and if two structures share the same peaks, those structures have the same crystallinity. PXRD can be used in two ways. First, PXRD is used to determine if two MOFs are the same structure. Since each MOF has its own PXRD graph, two graphs with the same exact peaks will be the same structure. The other way PXRD is used is to determine if there are any changes in the crystalline structure. Since the peaks in the graph correspond to the crystalline structure, a loss of peaks will also mean a loss of a crystalline structure. In the case of the water vapor test of the MOF, Figure 2.11 shows the PXRD graphs for the MOF before exposure to the water vapor and after the exposure over the 5 days. No change in the location of the peaks is observed for any of the graphs, which indicates that no loss of crystalline structure is observed for the MOF.<sup>13</sup>

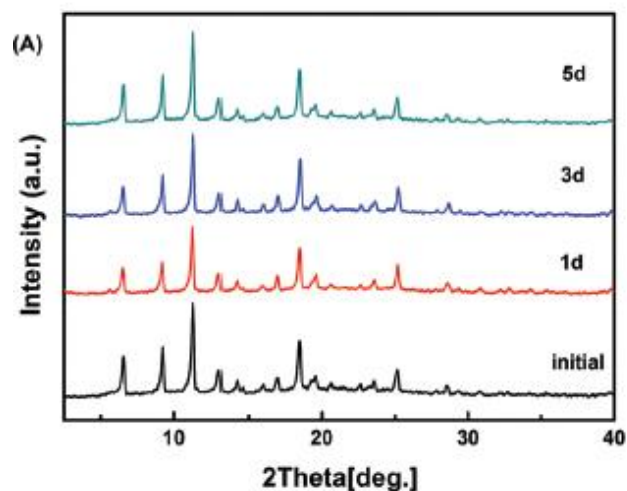


Figure 2.11: PXRD data for the Cr(II)-BTC MOF exposure to water vapor over time.<sup>13</sup>

A significant change is observed, however, when the MOF is placed in an environment consisting of oxygen and water vapor. The MOF was placed in another 90% RH environment, but the argon was replaced with oxygen. After one day of exposure to this environment, the MOF's surface area was reduced by 96.2%, which is much worse what was observed for the MOF under the oxygen or water vapor environments.<sup>13</sup> The surface area differences are shown in Figure 2.12. This shows that water vapor and oxygen will work together to cause a much larger degradation of the MOF than either could cause on its own. Also, The MOF crystallinity was completely lost after this one-day exposure. PXRD graphs of the MOF shown in Figure 2.13 before and after the exposure to this environment also show a complete loss of the peaks after exposure which means that the crystallinity of the MOF was completely lost as well. Although this MOF is different than the one examined in this study, the similarities between the MOFs mean that this synergy could affect the Cr(II)-BTC MOF as well, and the MOF should not be stored under a normal environment.

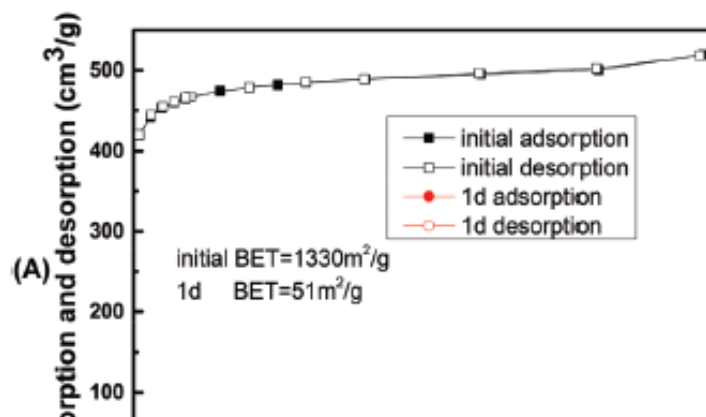


Figure 2.12: adsorption/desorption shown for CR(II)-BTC and the corresponding surface areas found in a water vapor and oxygen environment<sup>13</sup>

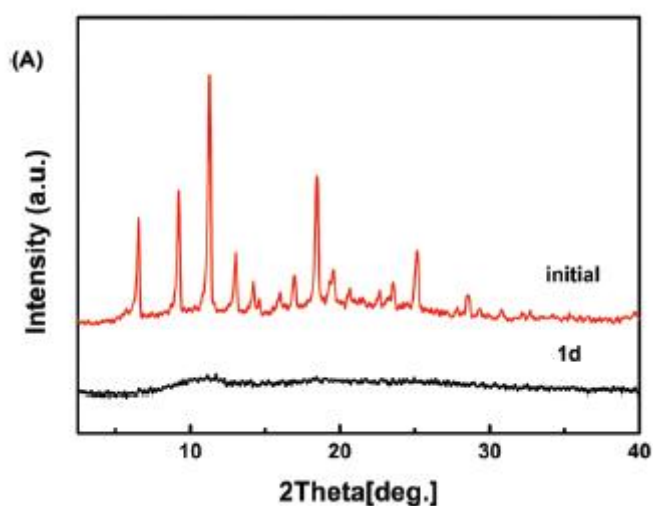


Figure 2.13: PXRD found for the Cr(II)-BTC MOF before and after exposure to the water vapor and oxygen environment.<sup>13</sup>

## 2.5 Mechanisms of Ammonia Adsorption by Other MOFs

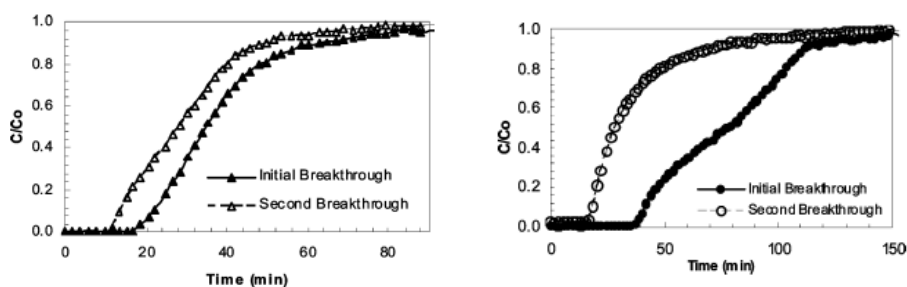
Although the Cr(II)-BTC MOF has not been used for ammonia adsorption up to this point, other MOFs, namely the aforementioned HKUST-1, has been examined for its ability to adsorb ammonia. This MOF will be examined for the mechanisms by which they

adsorbed ammonia to help elucidate the mechanism for ammonia adsorption on the Cr(II)-BTC. Additionally, any factors that would affect the MOFs ability to adsorb ammonia will also be discussed.

Peterson et. al. performed one experiment to test HKUST-1's ability to adsorb ammonia. For these tests, the main focus was on two properties: how the MOF performed under dry versus humid conditions, and how the MOF performed after it had already adsorbed ammonia once before. For the second aspect of the experiment, all of the ammonia was removed from the MOF before more ammonia was adsorbed. Figure 2.13 shows the breakthrough curves of the MOF under dry and humid conditions. For the dry condition, this graph shows that ammonia broke through the MOF quicker when the MOF had already adsorbed ammonia previously, and the MOFs ability to adsorb ammonia was hindered. The overall shape of the curve is shown to be similar, however. The reason that the MOF was hindered on the second adsorption is that ammonia can react with both the carboxylate groups on the ligand and the copper cations of the node. The carboxylate group on the ligand forms the bond between the nodes and the ligands of the MOF.<sup>2</sup> If these bonds are broken, either by ammonia reacting with the node or the carboxylate group, then the structural integrity of the framework will weaken. When too many of these bonds are broken in a particular area of the MOF, that portion of the framework will collapse completely, and most of the surface area in that region will be lost.<sup>2</sup> Since the MOF will have less surface area, then there will be less area for the ammonia of the second test on which to adsorb, and less ammonia will be adsorbed by the MOF. Since the curves of the

graph have a similar shape, however, the MOF should still be able to regain a similar structure after the adsorption of ammonia.<sup>2</sup>

The curve of the humid MOF is different. With the first adsorption test the curve is similar to the dry tests. Once the MOF was tested again, however, the curve completely changed its shape, and the capacity for ammonia adsorption decreased even more than with the dry test. Under the dry test, the MOF would form a bond with the ammonia that would form a complex with the ammonia and the ligand. This complex will then slowly break apart by reacting with the little water still present in the air to form copper hydroxide and a  $\text{BTC}(\text{NH}_4)_3$  group. Under humid conditions, this process occurs much faster and will skip forming the complex, which means that the MOF breaks down quicker.<sup>2</sup> This extra speed allows the ammonia to also react with the copper hydroxide to form copper amines. When ammonia is being removed from the MOF, any ammonia on the ligands (under dry conditions) will be readily released and reform the MOF bonds. Any ammonia that has already bonded to the copper (under humid conditions), however, will only reform the copper hydroxide instead.<sup>2</sup> Figure 2.13 shows the equations for these mechanisms. Because of this fact, the MOF under humid conditions will retain some of the adsorbed ammonia, further hindering its ability to adsorb ammonia on a second adsorption. Overall, this research has shown that the MOF cannot perform multiple adsorptions efficiently, especially under humid conditions, which would only make it useful for a single-use.<sup>2</sup>

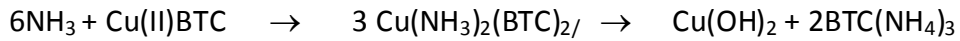




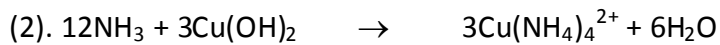
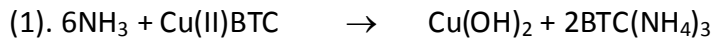
**Figure 2.12: breakthrough curves for copper (II) BTC under dry conditions (left) and humid conditions (right)**

Dry condition:

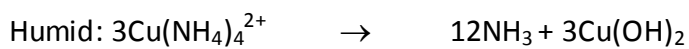
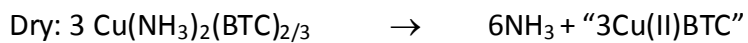
**slow**



Humid condition:



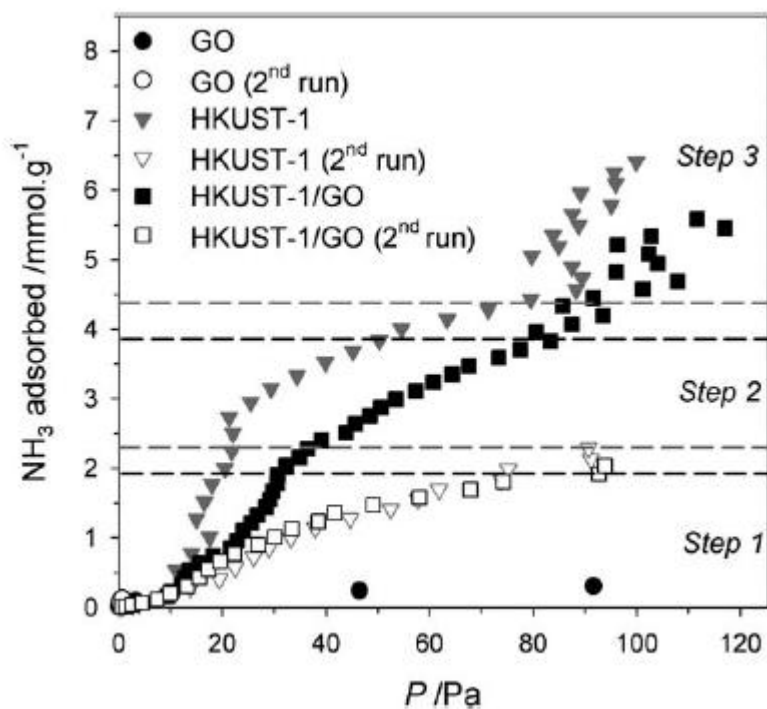
Removal of nitrogen:



**Figure 2.13 Mechanism of ammonia adsorption under dry and humid conditions. The quotations mean that a structure like the MOF is formed, but the true MOF is not reformed. Notice that when the ammonia is removed, the MOF like structure is formed under dry conditions but not under humid conditions.<sup>2</sup>**

Petit et. al. performed another test on HKUST-1's ability to adsorb ammonia. This test had two points of focus: the volume of ammonia adsorbed over multiple runs and the heat of adsorption for the MOF. The heat of adsorption is the strength of the bond between the ammonia and the MOF. A higher heat of adsorption indicates a stronger bond.

Figure 2.14 shows the volume of ammonia adsorbed by the MOF over multiple runs. This test of HKUST-1 also showed that this MOF adsorbs less ammonia on a second run versus the first run. Although this source does not go into as much detail, the most likely cause of the MOF losing its ability to adsorb ammonia is that some of the main sites of adsorption on the MOF are lost during the first run through.<sup>1</sup>



**Figure 2.14: Volume of gas adsorbed by ammonia. For the purposes of this proposal, only the triangles are to be considered. The other shapes represent part of the research conducted that will not be considered by this proposal.<sup>1</sup>**

The second point of focus was on the heat of adsorption of ammonia to find the mechanisms of adsorption. Figure 2.15 shows how ammonia was adsorbed in different sections. In the first section, a downward trend in the volume of ammonia adsorbed over time is shown. This first section was linked to the acid-base interactions between the copper nodes and the ammonia. At this point, only half of the copper nodes had adsorbed ammonia. This is because, as the ammonia is adsorbed onto the nodes, the ability of the neighboring nodes to adsorb ammonia is decreased. This is the main cause of the loss of the heat of adsorption over time.<sup>1</sup> In the second section, however, the heat of adsorption does not change very much at all. In this step, the ammonia is adsorbed by the neighboring

copper nodes. The heat of adsorption does not change since no more nodes are losing their adsorption capabilities.<sup>1</sup> In the final section, the heat behaves erratically, and no trend is seen as a result. This is due to other reactions that occur due to the destruction of the framework of the MOF. As ammonia adsorbs onto the MOF, it will create distortions within the MOF that will eventually break the bond between the metallic node and the ligand. The ammonia will then form bonds with the ligand as well.<sup>1</sup> Overall, the heat of adsorption revealed the mechanisms for the adsorption of ammonia onto the MOF.

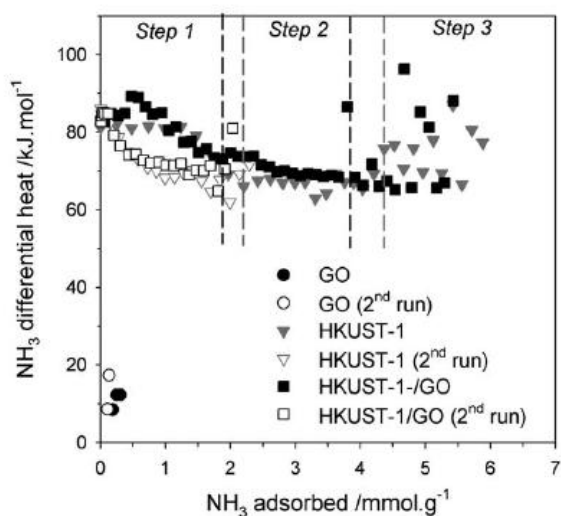


Figure 2.15 Heat of adsorptions for the adsorption of ammonia onto HKUST-1.<sup>1</sup>

### 3. Experimental Plan

#### 3.1 Synthesis Procedure

Prices for each compound necessary for synthesis<sup>14</sup>:

- Chromium hexacarbonyl: \$83:40 for 10g

- benzene-1,3,5-tricarboxylic acid: \$79.50 for 100g
- oxygen-free dimethylformamide: \$56.50 for 100mL

For this study, the MOF will be synthesized according to the procedure provided in the literature.<sup>15</sup> The procedure for the synthesis of Cr(II)-BTC is the same as the synthesis of the MOF Mo(III)-BTC that was discussed by Kramer et. al., so although the literature describes the synthesis of Mo(III)-BTC, this procedure can also be used to synthesize Cr(II)-BTC.<sup>16</sup> To synthesize Cr(II)-BTC, 1.5 g of benzene-1,3,5-tricarboxylic acid (H3BTC) will be added to 100 mL of oxygen-free dimethylformamide (DMF). Then, 2.26 g of chromium hexacarbonyl ( $\text{Cr}(\text{CO})_6$ ) will be added to this solution. In the presence of heat and H3BTC, the  $\text{Cr}(\text{CO})_6$  will be oxidized and form into Cr(II)-BTC. The resulting mixture will be placed in an atmosphere of argon, heated to reflux at 425°C and stirred for 5 days. The resulting precipitate will then be filtered out, washed with fresh oxygen-free *N,N*-dimethylformamide (DMF), and dried *in vacuo* for one day at 400°C, and then for several days at 425°C. Upon finishing these steps, the MOF should be fully made and clear of impurities.

This process works mainly due to an equilibrium between an acid formed in this reaction and a base (namely DMF in this reaction).<sup>6</sup> The reaction (shown in Figure 3.1) will occur without the addition of a base, but the reaction poses two problems. First, another product of the normal reaction is nitric acid ( $\text{HNO}_3$ ), which is a strong acid that could be hazardous to work with. Secondly, all the reactions without base are reversible since the strong acid will destroy some of the MOF formed, which will lead to a lower yield of the desired product. When the reaction is performed in a solution of a base, the base will neutralize the acid formed by the reaction. This process eliminates the potentially

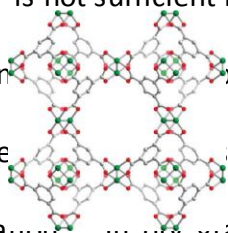
hazardous byproduct and forces the reaction to irreversibly form the MOF and increase the yield of the reaction.



**Figure 3.1. Formula to make Cr(II)-BTC MOF<sup>4</sup>**

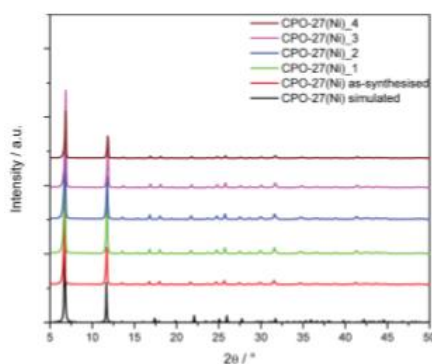
### 3.2 Forming the MOF into Granules

Formation of the MOF is not sufficient for this proposal because MOFs are formed as powders, and powders will not absorb the ammonia. Instead, the MOF must be formed into granules. There are two methods that can be used to form the MOF: dry granulation and wet granulation. In dry granulation, a small press is used to force an immense pressure onto the MOF and cause it to form into a large pellet. This pellet would then be compressed over sieves of particular sizes to form granules in the desired size range. In wet granulation, liquids, such as water, are used to form the MOF into the granule shape followed by the use of sieves of particular sizes to form the granules into the desired size range.<sup>18</sup>



In order to determine the optimal process for the granulation of the Cr(II)-BTC MOF, the results of the two types of granulation were examined by Hindocha et. al. for other MOFs tested (CPO-27, Cu-BTC, and MIL-100). The first method to compare the MOFs is powder X-ray diffraction. This technique is used to determine the structure of the product and compare it to the simulated structure spectra for each MOF. While the CPO-27 and

MIL-100 kept their structure through both forms of granulation, Cu-BTC was only able to retain its structure through dry granulation and decomposed somewhat during wet granulation.<sup>18</sup> Another way to examine the different types of granulation is to examine the ammonia capacity of each type of granule and the breakthrough time (*i.e.*, the time at which the ammonia will start to penetrate the MOF and escape). In this test, although the ammonia capacity found for the wet and dry granulation was close to Mil-100, the breakthrough time was higher for dry granulation. Additionally, dry granulation was found to have superior ammonia capacity and breakthrough times for both CPO-27 and Cu(II)-BTC (Table 3.1).<sup>18</sup> This is especially true for Cu(II)-BTC since this MOF decomposed somewhat during wet granulation. This decomposition is concerning considering that Cr(II)-BTC has the same ligand structure and overall crystal structure as Cu(II)-BTC, so the structure of Cr(II)-BTC is susceptible to this type of decomposition. After examining this data, dry granulation would be used for this experiment.



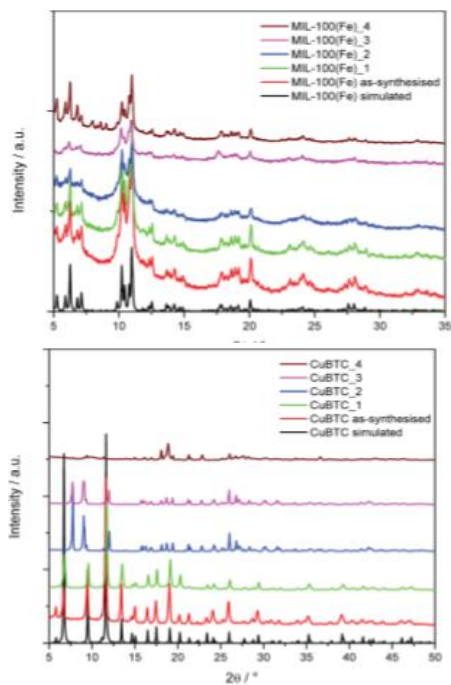


Figure 3.2: Powder X-ray diffraction data for each MOF tested for granulation. MOF\_1 and MOF\_3 refer to dry and wet granulation respectively.<sup>18</sup>

Table 3.1 ammonia capacity and breakthrough times found for each MOF using both types of granulation<sup>18</sup>

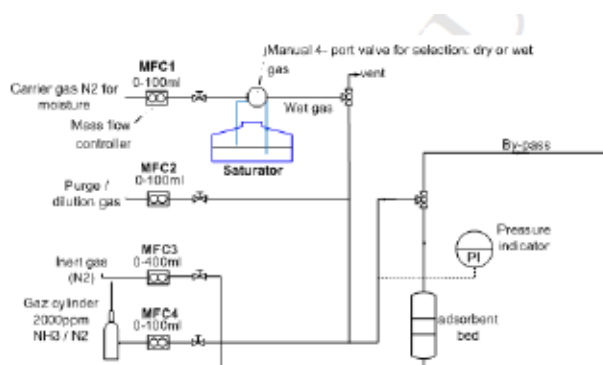
MOF	Ammonia capacity (dry) mg/g	Ammonia capacity (wet) mg/g	Breakthrough time (dry) sec	Breakthrough time (wet) sec
MIL-100	47	50	135	100



CPO-27	64	51	189	106
Cu-BTC	105	19	210	43

### 3.3 Procedure for Ammonia Adsorption Test

Next, the procedure for the ammonia adsorption test of the Cr(II)-BTC MOF will be described by Khabzina et. al. The MOF in its granulated form will be placed in a 7 mm i.d. fritted glass tube (0.15 cm<sup>3</sup>) until the height of the granules reaches 4 mm of the tube (this will be called the bed height), and this tube will then be attached to a gas flow apparatus.<sup>19</sup> An infrared (IR) spectrometer will then be attached to the end of this apparatus. During the set-up process, N<sub>2</sub> gas will be allowed to flow through the system to prevent the MOF from reacting with the air. N<sub>2</sub> will be used for this task because the gas is very stable and will not react with the MOF. Then, water vapor will be allowed to flow through the pipes along with the nitrogen gas. A mixture of the nitrogen gas and water vapor will then be made for any tests done under humid conditions. Then, the flow of nitrogen will be ended. The ammonia in the gas phase will be allowed to flow through the 7 mm i.d. fritted glass tube (0.15 cm<sup>3</sup>) containing the MOF at a rate of 100 mL/min. If the test is performed under humid conditions, the ammonia will be allowed to mix with the water vapor before it is passed through the MOF. This condition will continue until the MOF is no longer adsorbing the ammonia.<sup>19</sup> Figure 3.3 shows the schematic diagram of the MOF.



**Figure 3.3: Schematic diagram of the gas flow apparatus. The multiple starting point (MFCs) allow for different gases to flow through at the same time. The valves throughout the apparatus allow gas to only flow through the sample when the sample is ready for the test.<sup>19</sup>**

As the ammonia is allowed to pass through the MOF, the IR spectrometer would detect how much ammonia is passing through the MOF over time. The essential information that would be obtained from the IR spectrophotometer would be the breakthrough time and the time that the full volume of ammonia is starting to pass through the MOF. The breakthrough point is the time that ammonia starts to move past the MOF and be detected by the IR spectrometer. This point is important to know since the time up to the breakthrough point is when the MOF can completely adsorb ammonia. When the full volume of ammonia gets through the MOF, then the MOF is saturated and no longer adsorbing any more ammonia. These two times can also be used to determine the total volume that the MOF adsorbed.<sup>19</sup> Figure 3.4 shows an example of a breakthrough curve.

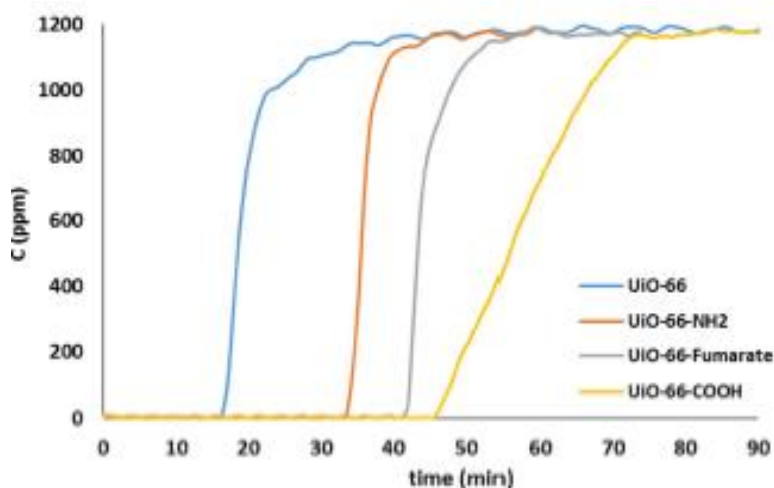


Figure 3.4: example of a breakthrough curve. The point that the graph begins to go up is the breakthrough point, and the point that the full volume of ammonia is getting through is shown when the line plateaus.<sup>19</sup>

### 3.4 Proposed Results

The information gained about how Cr(II)-BTC adsorbs and about how the other MOFs adsorb ammonia will be discussed. From the information gathered the following points will be examined: how effective will Cr(II)-BTC adsorb ammonia compared to the others examined, how will Cr(II)-BTC adsorb ammonia over multiple runs, how will Cr(II)-BTC perform in humid versus dry conditions, and how practical is Cr(II)-BTC as an adsorptive material in a real-world setting.

First, how effective is Cr(II)-BTC as an adsorptive material for ammonia in comparison to the other MOFs? As shown in the examination of the adsorption mechanism of HKUST-1, the main point of adsorption seems to be on the metal node, as metal node adsorption was attributed to both the first stage and the second stage of the mechanism, which was most

of the adsorption. This could potentially be a problem for Cr(II)-BTC since, as stated in the section on the adsorption mechanism for Cr(II)-BTC, the metal nodes are not very effective adsorption sites. In fact, this MOF seems to be the only MOF that has metal nodes as adsorption sites in which the node is not the primary point of adsorption in the MOF. This characteristic is a result of the nodes being farther inside the pores of the MOF and therefore not as accessible. The additional adsorption sites seen on the Cr(II)-MOF will probably not be very useful for this adsorption. This is due to the fact that these sites were not mentioned in the sources detailing the adsorption of ammonia onto HKUST-1, even though HKUST-1, being a MOF of the same shape, should have these sites. Overall, I hypothesize that Cr(II)-BTC will have less adsorptive capabilities than HKUST-1.

Secondly, how will Cr(II)-BTC adsorb ammonia over multiple runs? All three of the MOFs examined share the same ligand, BTC, which has three carboxylate groups. As shown with the adsorption of ammonia HKUST-1, the ammonia will readily react with the carboxylate groups by severing the bond between the metal node and the carboxylate group. The ammonia seems to do this mainly by bonding with the metal first and placing a strain on this bond. Since the Cr nodes will not as readily bond to the ammonia as the Cu nodes, the ammonia will not be able to place the strain on the MOF. Therefore, I hypothesize that under dry conditions Cr(II)-BTC will be more stable in ammonia adsorption and will not lose as much of its adsorptive ability over multiple runs.

Third, how will the MOF adsorb under humid conditions? Cr(II)-BTC was shown to decompose slightly under humid conditions, but it retained its overall shape. As such, humidity alone will most likely not be an issue. Since ammonia in humid conditions causes

HKUST-1 to fall apart more quickly, however, Cr(II)-BTC will probably follow a similar trend, though this effect will probably still be lessened in Cr(II)-BTC when compared to the Cu MOFs.

Finally, can the MOF be used in practical applications such as a filter for a gas mask? Cr(II)-BTC was shown to completely degrade after an exposure to an atmosphere of oxygen and water vapor after one day. Therefore, Cr(II)-BTC would need to be tested to see if it will also deteriorate under these conditions. Since the atmosphere contains water and oxygen, a MOF that decomposes in this atmosphere would need to be kept in a more stable atmosphere in order to be useful. As a result, a device that needs to be used in our environment will need to be designed around this flaw.

#### **4. Conclusion:**

Overall, Cr(II)-BTC may be a challenging MOF to use for adsorption. Since the open metal sites seem to be the major site for adsorption, Cr(II)-BTCs ability to adsorb ammonia may be greatly hindered by its open metal sites if they are less effective. Also, Cr(II)-BTC may not be able to survive under normal atmospheric conditions and would thus be impractical to use in settings that could use its adsorptive abilities such as in gas masks.

Although the MOF may be challenging to use, it still has potential as an adsorbent. As shown from the other MOF tested, open metal sites are a great adsorption point for ammonia. As a result, the MOF should still have a decent adsorptive ability. Additionally, the MOFs open metal sites could make it more stable over multiple runs of adsorption, so it could be better as a long-term adsorbent. The main issue is the practicality under normal

atmospheric conditions. As a result, gas masks using Cr(II)-BTC would have to take this flaw into consideration. Overall, the MOF has potential as an adsorbent if these flaws can be overcome.

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