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COBALT MOF-5: A NOVEL CATALYST FOR CO₂ CONVERSION TO
CARBONATES

By

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B.S. Ch.E., University of Louisville, May 2011

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MASTER OF ENGINEERING

Department of Chemical Engineering

August 2012

COBALT MOF-5: A NOVEL CATALYST FOR CO₂ CONVERSION TO
CARBONATES

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A Thesis Approved On

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ABSTRACT

As more attention is focused toward carbon dioxide emissions into the environment, conversion of CO₂ to useful chemicals can utilize the extra carbon dioxide captured from power plant stack gas, instead of sequestration. The mainstream method of producing carbonates and carbamates utilizes toxic phosgene. The cycloaddition of carbon dioxide to epichlorohydrin, or other epoxides, can produce carbonates without the use of phosgene. A catalyst with high surface area, Lewis acid sites, and an affinity for carbon dioxide is required to develop carbonates using carbon dioxide.

A cobalt doped metal-organic framework-5 (Co21-MOF-5) was developed to test the cycloaddition reactions with carbon dioxide. The crystalline structure of developed Co21-MOF-5 crystals matched those reported. An average Langmuir surface area of 594 m²/g was developed.

Of the reactions tested, using epichlorohydrin as a precursor at 80 °C and 7 bar over four hours produced the best result with a conversion of 43.3% and 100% selectivity for the carbonate. Using the precursor of styrene oxide under the same conditions produced a conversion of 55% with 35% selectivity to the carbonate. Reactions involving epichlorohydrin at higher temperatures did not show any measureable amounts of the desired product and could not be reproduced. Further investigation into using Co21-MOF-5 to produce a carbamate yielded a conversion of 25% with 100% selectivity, but a collapse of the catalyst crystalline structure.

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NOMENCLATURE

R'OH	=	alcohol group
R'NH ₂	=	amine group
BET	=	Brunauer Emmett Teller
R'NHCOOR	=	carbonate group
CO ₂	=	carbon dioxide
Co21-MOF-5	=	cobalt doped MOF-5
DEF	=	N,N-diethylformamide
DMAP	=	N,N'-dimethylaminopyridine
DMF	=	N,N-dimethylformamide
θ	=	diffraction angle, theta
GC-MS	=	gas chromatograph with mass selective detector
HCl	=	hydrochloric acid
HBr	=	hydrogen bromine
R'NCO	=	isocyanate
MOF	=	metal-organic framework
MOF-5	=	metal-organic framework-5
Zn ₄ O(C ₈ H ₄ O ₄) ₃	=	secondary building unit for MOF-5
N ₂	=	nitrogen
COCl ₂	=	phosgene
SEM	=	scanning electron microscopy
SBU	=	secondary building unit
TGA	=	thermogravimetric analysis
XRD	=	X-ray diffraction
Zn ₄ O(CO ₂) ₆	=	zinc(II) carboxylate clusters

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I. INTRODUCTION

A. Carbon Dioxide Conversion to Chemicals

1. Carbon Dioxide as a Renewable Alternative

The carbon cycle is the process which follows carbon as it circulates through the environment. For thousands of years, this cycle has continued unhindered. Carbon dioxide generates in the cycle through a number of natural processes, such as wildfires, plant and animal decay, and volcanos¹. However, since the dawn of the industrial period, human involvement has been increasingly adding to the amount of carbon dioxide released into the atmosphere². In the past 250 years, the atmospheric level of carbon dioxide has risen by around 31%¹. Carbon dioxide contributes to 60% of the greenhouse gases that cause global warming, with about 82% of the carbon dioxide emissions coming from power plants².

Over the past few decades, industry has greatly reduced the amount of pollutants that escape to the atmosphere, including nitrogen and sulfur oxides. Now the focus is shifting towards reducing the amount of carbon dioxide released into the atmosphere. Specifically, much attention has been aimed towards processes that emit high amounts of carbon dioxide, such as power plants. Power plants generate a large amount of carbon dioxide by burning fossil fuels, like coal and natural gas. Motivated, in part, by the threat of carbon emissions regulation, many power plants have funded research towards capturing the carbon dioxide released during the combustion process of power

generation. After the carbon dioxide is captured, it is usually stored in the ocean by sequestration¹. However, this carbon dioxide could alternatively be utilized or recycled for technical applications or implementation into chemicals.

Some technical applications for carbon dioxide are enhanced oil recovery, extraction, drink additives, antibacterial agents, refrigeration, food packaging, and fire extinguishers³. Carbon dioxide can also be fixated into chemicals. The industrial processes where this fixation currently occurs is limited to the synthesis of urea, salicylic acid, Group 1 and 2-element inorganic carbonates, polycarbonates from epoxides, and methanol³. Preparing polycarbonates from epoxides and synthesizing methanol using carbon dioxide as an additive require a catalyst for the reactions to occur³. Research is being done both to identify more chemical processes which could utilize CO₂ and to improve carbon dioxide activation³⁻⁴. Since carbon dioxide is the most oxidized state of carbon, it has a very low energy level, which makes activation difficult and the largest obstacle moving forward in the utilization of carbon dioxide as a raw material for chemical production⁵.

2. General Routes for the Conversion of Carbon Dioxide to Chemicals

Using carbon dioxide as an alternative approach for chemical production is appealing. The “green” perspective shows advantages to utilizing carbon dioxide. Once carbon dioxide is captured from combustion generated flue gas, it can be recycled as a renewable resource, instead of being sequestered into the ocean. Using this recycled carbon dioxide can help to alleviate some of the stress on the environment by CO₂ emissions. Carbon dioxide is a nontoxic, plentiful, and cost effective alternative in

chemical production when compared to harsh conventional raw materials, such as phosgene¹.

Four methods have been suggested to convert carbon dioxide into chemicals: using hydrogen, unsaturated compounds, small-membered ring compounds, organometallics, or other higher energy starting materials; aiming towards oxidized and lower energy products; shifting the equilibrium of the reaction towards the final product; or adding physical energy to reach completion of the reaction^{4b}. FIGURE 1 shows a visual of the difficulties regarding the transformation of carbon dioxide from a raw material into a useful chemical^{4b}.

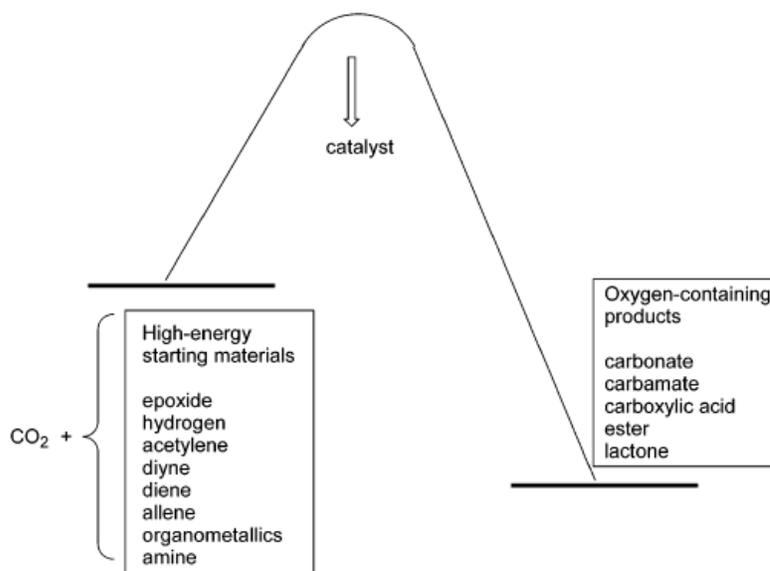


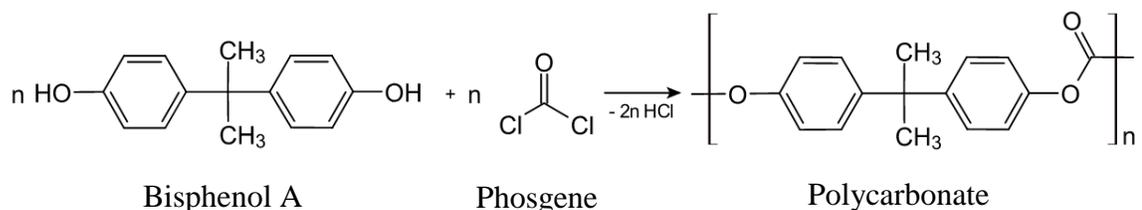
FIGURE 1 - Conversion of Carbon Dioxide into Useful Chemicals^{4b}

3. Methods for Producing Cyclic Carbonates and Carbamates

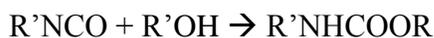
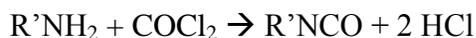
Cyclic carbonates and carbamates are precursors to a variety of polymers⁶. Cyclic carbonates are a raw material that can be converted to polycarbonates. Carbamates are used to manufacture polymers such as polyurethanes; ingredients in herbicides, fungicides, and pesticides; and drug intermediates⁶. The current preferred method of

production for polycarbonates and carbamates is by the use of phosgene as a raw material³. Although phosgene is a commonly used chemical intermediate, it is highly toxic. During World Wars I and II, phosgene was used as a chemical weapon because at room temperature and pressure it is a poisonous gas⁷. The commercial production of carbamates most commonly follows a route that uses both phosgene and an isocyanate⁶. Much research has been done to develop a competitive method of preparing carbonates and carbamates via a reaction pathway that does not utilize phosgene or an isocyanate as raw materials. Carbon dioxide is an attractive replacement if a viable method of reducing the activation barrier could be achieved. The typical commercial phosgene routes and the alternative carbon dioxide route to producing carbonates and carbamates can be seen in Scheme 1.

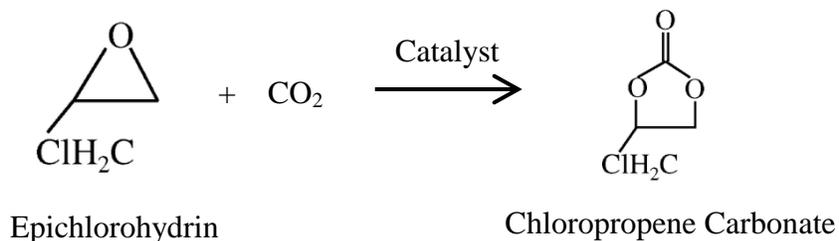
a.) Phosgene Route to Producing Polycarbonates⁸:



b.) Phosgene and Isocyanate Route to Producing Carbamates⁶:



c.) Phosgene-Free Route to Producing Carbonates⁹:



d.) Phosgene/Isocyanate-Free Route to Producing Carbamates¹:



Scheme 1: Reactions for the production of Carbonates and Carbamates

Non-phosgene based cyclic carbonates are produced commercially by BASF and Chimei-Asahi Corporation using quaternary ammonium salts, which are less expensive than alternate catalysts and are homogeneous¹. However, this reaction has to be performed at high temperatures (180-200 °C) and pressures (50-80 bar)¹⁰. Research has been performed to determine a catalyst that improves the process conditions and performance.

Some of the effective attempts for the cycloaddition reaction using homogeneous catalysts include quaternary ammonium salts^{4b}, metal halides, metal complexes⁶, and ionic liquids¹⁰. Metal complexes propose a problem as a catalyst because they are toxic and sensitive to air and water¹¹. Because of these issues, care needs to be taken when handling them. High temperatures and pressures are also required to gain a high conversion and selectivity¹¹. Some successful attempts at homogeneous catalysts that lower the reaction temperature are CH_3SnBr_3 , Ph_4SbBr , and $n\text{-Bu}_3\text{SnI}$ ¹¹. However, due to the required high catalyst concentration, another problem is created regarding separation and purification of the product¹¹. Research has been completed regarding non-toxic catalysts, such as Schiff bases, porphyrines, and phthalocyanines¹. Although these types of catalysts allow for lower reaction temperatures and pressures, a cocatalyst, such as *N,N'*-dimethylaminopyridine (DMAP) or tetralkyl ammonium halide, is also required to obtain higher yields¹.

Heterogeneous catalysts have also been widely studied for the carbonate forming reaction¹². Heterogeneous catalysts are intriguing compared to homogenous catalysts, because separating the catalyst from the products becomes a much simpler process: filtration. Although metal oxides catalyze the reaction between CO₂ and epoxides, a polar organic solvent, such as N,N-dimethylformamide (DMF), is required to obtain higher carbonate yields¹⁰. Other problems that arise when researching heterogeneous catalysis of the carbonation reaction are low stability, a need for a cocatalyst, recyclability, and high temperatures and pressures¹⁰.

There are several phosgene-free alternative routes to making carbamates. The reductive carbonylation of nitro aromatics using carbon monoxide is one route⁶. It is cost prohibitive to produce carbamates through reductive carbonylation because of these three following disadvantages. It can effectively utilize only about one-third of the carbon monoxide⁶. After the reaction, the excess carbon monoxide would need to be separated from carbon dioxide. Finally, catalyst recovery is problematic because of the corrosion problems associated with the ferrous chloride co-catalysts⁶. Another route studied is the oxidative carbonylation of amines. This route involves high temperature and pressures and also requires the hazardous mixing of carbon monoxide and oxygen⁶. One route researched is the methoxycarbonylation of amines, but separation of an azeotrope formed during the reaction magnifies the costs⁶. Other routes that have been studied are the Hoffmann rearrangement of amides and reactions involving chloroformates and amines⁶.

A phosgene- and isocyanate intermediate-free path to producing carbamates that has received much attention involves primary amines, carbon dioxide, and alkyl halides¹. As with the non-phosgene carbonate route, homogeneous and heterogeneous catalysts

have been researched to reduce the temperature and pressure needed to obtain high yields when following the phosgene-free path to make carbamates. Homogeneous catalysts that have been studied are organic and inorganic bases, crown ethers, and cryptands¹². Heterogeneous catalysts that have been used are zeolite-encapsulated metal complexes, titanosilicates, zeolites, and adenine-modified Ti-SBA-15¹². Except for adenine-modified Ti-SBA-15, all the other catalysts require a solvent, like DMF, to obtain high yields¹². However, the adenine-modified Ti-SBA-15 catalyst requires a cocatalyst to create high product yields¹².

B. Catalysis

1. Why Catalysts for CO₂ Conversion?

The phosgene-free routes for the cycloaddition reactions to produce cyclic carbonates and carbamates require a catalyst to activate the carbon dioxide under lower temperatures and pressures. A catalyst increases the reaction rate of a process while remaining unchanged, usually by making another reaction pathway more appealing¹³. In heterogeneous catalysts, the catalytic reaction occurs at the solid-liquid/gas interface¹³. Therefore, typical catalysts have a large surface area with an inner porous structure that promotes the reaction¹³. These porous structures not only add to the surface area of the catalyst, but can also be used to increase selectivity by having pore sizes that promote the reaction between specific molecules¹³.

Another important property for a catalyst is recyclability, or the ability to reuse the catalyst over several reactions. This helps to increase the economic feasibility of catalysts that are expensive to produce. Another advantage of catalyst recyclability is ease of implementation when scaling to commercial production; operation time can be

decreased if the catalyst is replaced less often. Catalyst deactivation can occur by three processes: aging, poisoning, and fouling/coking¹³. Aging is a process that occurs in all catalysts over time, where the crystal structure of the catalyst changes into a structure that no longer promotes the desired reaction¹³. Poisoning occurs with the catalyst when an irreversible reaction occurs between one of the chemicals or side products in the reaction and the active site (the location where the reaction occurs) of the catalyst¹³. The final method of deactivation, fouling/coking, occurs when carbonaceous species or other materials build up on the surface of the catalyst and close off the pores¹³.

2. Metal-Organic Frameworks as Novel Catalysts for CO₂ Conversion

Among the catalysts that have been discovered to catalyze cycloaddition reactions are metal-organic frameworks (MOFs). Metal-organic frameworks, discovered in the 1990s, were developed because of the need for superior catalytic materials that had desirable fundamental properties compared to conventional catalysts¹⁴. Since discovery, research of metal-organic frameworks has revolved around gas storage, gas separation, carbon dioxide capture, sensor techniques, and, more recently, catalysis¹⁵. Metal-organic frameworks are microporous materials having a pore diameter of less than two nanometers, and are crystalline structures with polar walls. MOFs are formed by the copolymerization of organic ligands with transition metals¹⁶. Interest in these crystalline, porous materials spiked after the discovery of many desirable properties associated with MOFs. A typical metal-organic framework has a high surface area, 270-4500 m²/g, and a tunable pore size¹⁷.

Although a variety of metal-organic frameworks have been created with differing bi-functional organic linker molecules and transition metal building blocks, special care

needs to be taken when designing a MOF to be used for catalysis. Many of the originally discovered metal-organic frameworks have a low thermal stability or are chemically sensitive towards air, acids, bases, water, or common organic solvents used in reactions. These issues are lessened by choosing framework backbones and linkers to produce a more robust metal-organic framework for catalytic purposes, while maintaining all the other ideal properties originally associated with MOFs. Other methods to improve the chemical and thermal stability of a MOF are to introduce metallic nanoparticles into the pore structure or to introduce active centers into the MOF using linker molecules with functional side groups¹⁵. Some reactions studied using metal-organic frameworks as a catalyst are: the Knoevenagel condensation reaction, Friedel-Crafts type reaction, aldol reaction, oxidation, asymmetric olefin epoxidation, asymmetric hydrogenation, transesterification, and photochemical reaction. However, these reactions, along with others that have used MOFs as a catalyst, hold little commercial interest when compared to the production of carbonates and carbamates¹⁸.

3. Background and Research on MOF-5

Of the metal-organic frameworks developed, one that draws much attention for research is MOF-5, appearing in publications starting in 1999¹⁹. This metal-organic framework is produced by linking octahedral $Zn_4O(CO_2)_6$ clusters with phenylene rings. The final chemical structure of a MOF-5 secondary building unit (SBU) is $Zn_4O(C_8H_4O_4)_3$, which forms an open pore, cubic topology¹⁹. FIGURE 2 shows the secondary building unit for MOF-5. In the figure, the yellow sphere represents the largest van der Waals sphere that would fit into the open pore while blue, gray, and red represent zinc, carbon, and oxygen molecules, respectively. MOF-5 has thermal stability

up to 400°C, measured by thermogravimetric analysis (TGA)²⁰. After this point, the catalyst starts to lose weight, which likely represents the decomposition of the organic linker. This thermal stability is higher than many metal-organic frameworks. The higher thermal stability arises because of the specific arrangement of the secondary building units, with a shortened tetrahedral envelope of the cationic clusters and rigid, planer linker molecules²⁰. It is also a porous, crystalline structure with a high surface area of 2,900 m²/g and a pore size of 0.7-0.8 nm²¹. Research in carbonation reactions¹⁵, hydrogen adsorption²², and gas separation and storage² has been performed on this microporous material.

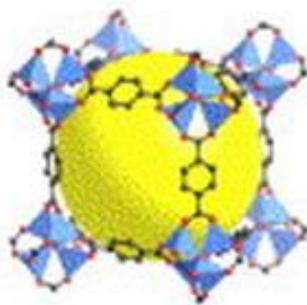


FIGURE 2 - Cubic Topology of MOF-5¹⁷

4. Chemical Modifications to Improve MOF-5 Properties

Gas adsorption properties have been the main source of research for this material; several strategies have been attempted to further increase the gas adsorption capacity in MOF-5¹⁵. These attempts include synthesizing new materials which have the cubic SBU of MOF-5, but with larger organic linkers, incorporating metallic species into the synthesized MOF-5 framework; incorporating lithium or chromium into the aromatic rings in the linker; and substituting other divalent cations in place of the zinc molecules²⁰.

In 2010, Botas, Calleja, Sánchez-Sánchez, and Orcajo described differing percentages of cobalt doped MOF-5 materials for improved gas-adsorption properties. When the zinc molecule was substituted with cobalt by 21%, Co21-MOF-5, the carbon dioxide uptake per weight percentages performed better as the pressure increased²⁰. The thermal stability decreased slightly from 471°C to 440°C for MOF-5 to Co21-MOF-5²⁰. Carbon dioxide adsorption isotherms were measured for the cobalt doped MOF-5 crystals. As the pressure increased, the cobalt substitution of 21% had the most desirable carbon dioxide uptake values when compared to the original MOF-5 and a sample with 8% substitution, shown in FIGURE 3.

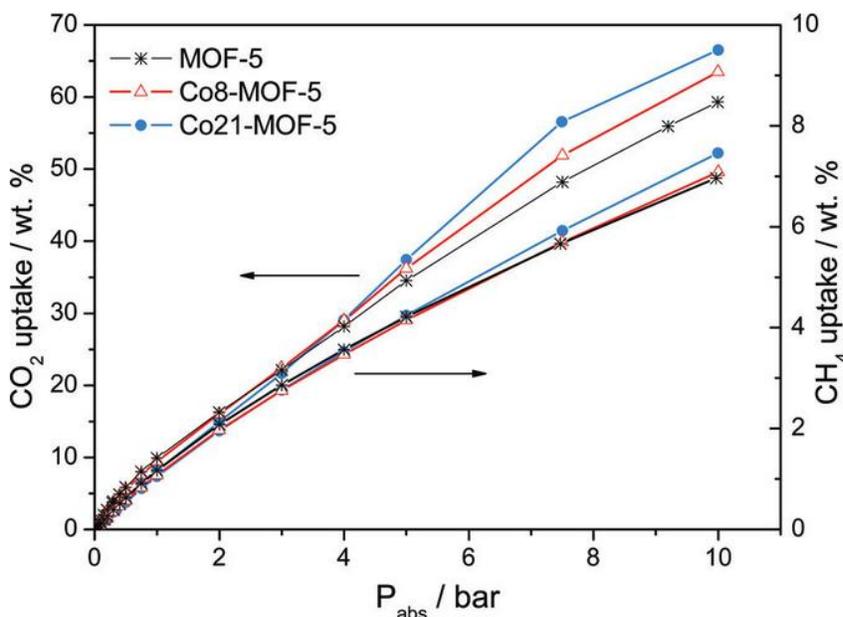


FIGURE 3 - Carbon Dioxide and Methane Adsorption Properties for Various Cobalt Doped Percentages of MOF-5²⁰

The powder X-ray diffraction patterns, FIGURE 4, matched very closely between the cobalt doped MOF-5 and the MOF-5 without doping²⁰. X-ray diffraction measures

the angles where scattering occurs, which associates with a specific crystalline structure, or a theoretical “fingerprint” for a material.

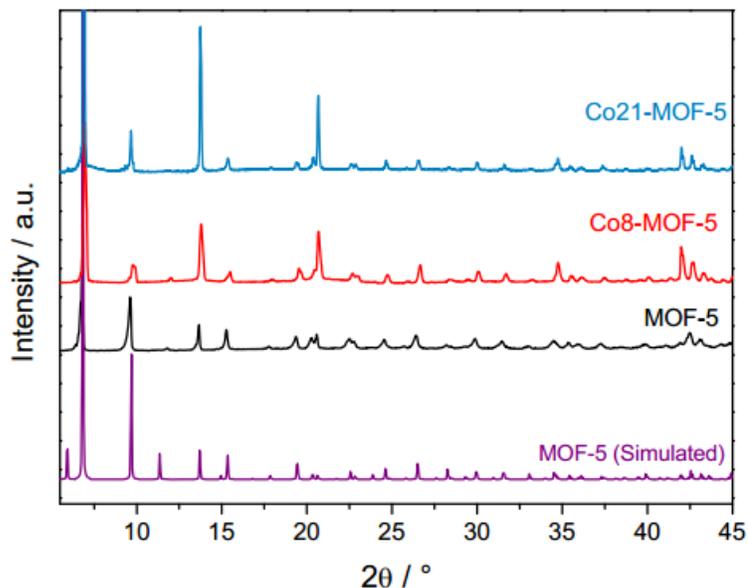


FIGURE 4 - X-ray Diffraction Patterns for Regular and Cobalt-Doped MOF-5²⁰

C. Justification

Cobalt doped MOF-5 possesses highly desirable properties that are necessary to catalyze the cycloaddition reactions to produce carbonates and carbamates. Metal-organic frameworks are dual type materials because of the bifunctional structure associated between the linker and metal building blocks¹⁵. The organic linker has high carbon dioxide adsorption properties¹⁸. The cobalt and zinc in the backbone act as Lewis acid sites which catalyze the reaction¹⁸. This bifunctional structure should increase the activity of the reaction. This process can be seen in FIGURE 5. Other promising properties of cobalt doped MOF-5 are the high surface area, the porous, crystalline structure, and high chemical and thermal stability.

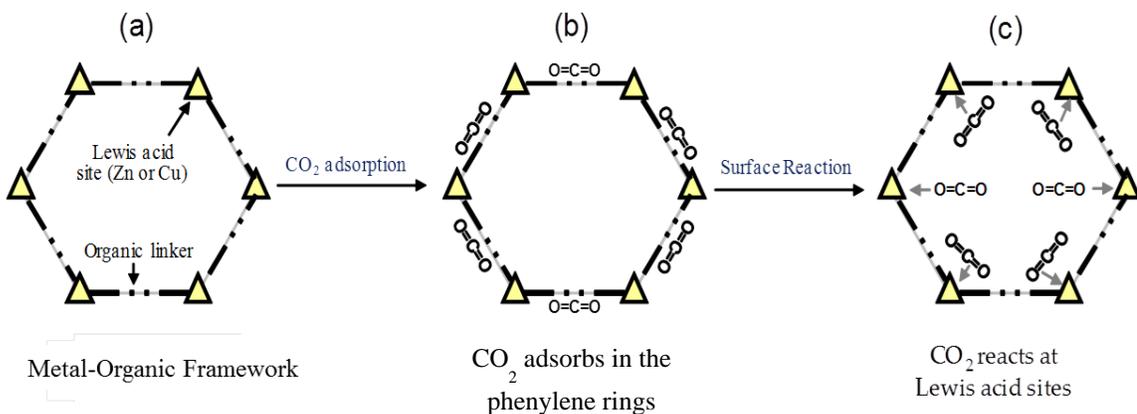


FIGURE 5 - Process of MOF Catalyst Reacting with CO_2 : (a) Main Components of a MOF, (b) CO_2 Adsorbing at the Organic Unit Sites, (c) Adsorbed CO_2 Reacts at the Lewis Acid Sites.

D. Objectives

- 1) Develop cobalt doped metal-organic framework-5 with 21% of the zinc backbone replaced with cobalt.
- 2) Study the textural and morphological properties of Co21-MOF-5 using comprehensive characterization by BET, XRD, and SEM.
- 3) Evaluate the catalytic ability of Co21-MOF-5 in cycloaddition reactions to produce carbonates and carbamates.

II. EXPERIMENTATION

A. Synthesis of Co21-Mof-5

The cobalt doped metal-organic framework was synthesized similarly to the method described by Botas et al. for Co21-MOF-5²⁰. Under this method, cobalt was substituted for 21% of the zinc molecules. In a typical synthesis, shown in FIGURE 6, 1.683g (6.44mmol) of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma Aldrich Inc., $\geq 99.0\%$), 0.438g (1.47mmol) of cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fluka, $\geq 98\%$), and 0.392g (2.36mmol) of terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$, Acros Organics, $>99\%$) were dissolved in 60 mL of diethylformamide ($\text{HCON}(\text{C}_2\text{H}_5)_2$, Acros Organics, 99%). To dissolve, the solution was vigorously stirred for about one hour. The dissolved solution was halved and poured into a 50 mL Teflon vessel. Each vessel was placed into the autoclave, FIGURE 7, to allow the solution to reach an autogenous pressure as heated. The autoclave was placed into an oven, FIGURE 8, at 105°C for 20 hours.

The pink crystals obtained after heating were separated from the effluent by centrifugation, FIGURE 9, and washed thrice with N,N-dimethylformamide ($\text{C}_3\text{H}_7\text{NO}$, Acros Organics, extra pure). The resulting crystals were then placed in a Precision vacuum oven, FIGURE 10, with a small vacuum of $>10^{-7}$ bar and a temperature of 100 °C for 18 hours. Then the crystals were placed in a calcining oven, FIGURE 8, to remove the solvent. The program for calcination was a 1 °C/min ramp up from room temperature to 350 °C. This temperature was held for six hours then there was a 5 °C/min ramp down to room temperature. The resulting crystals were blue in color.

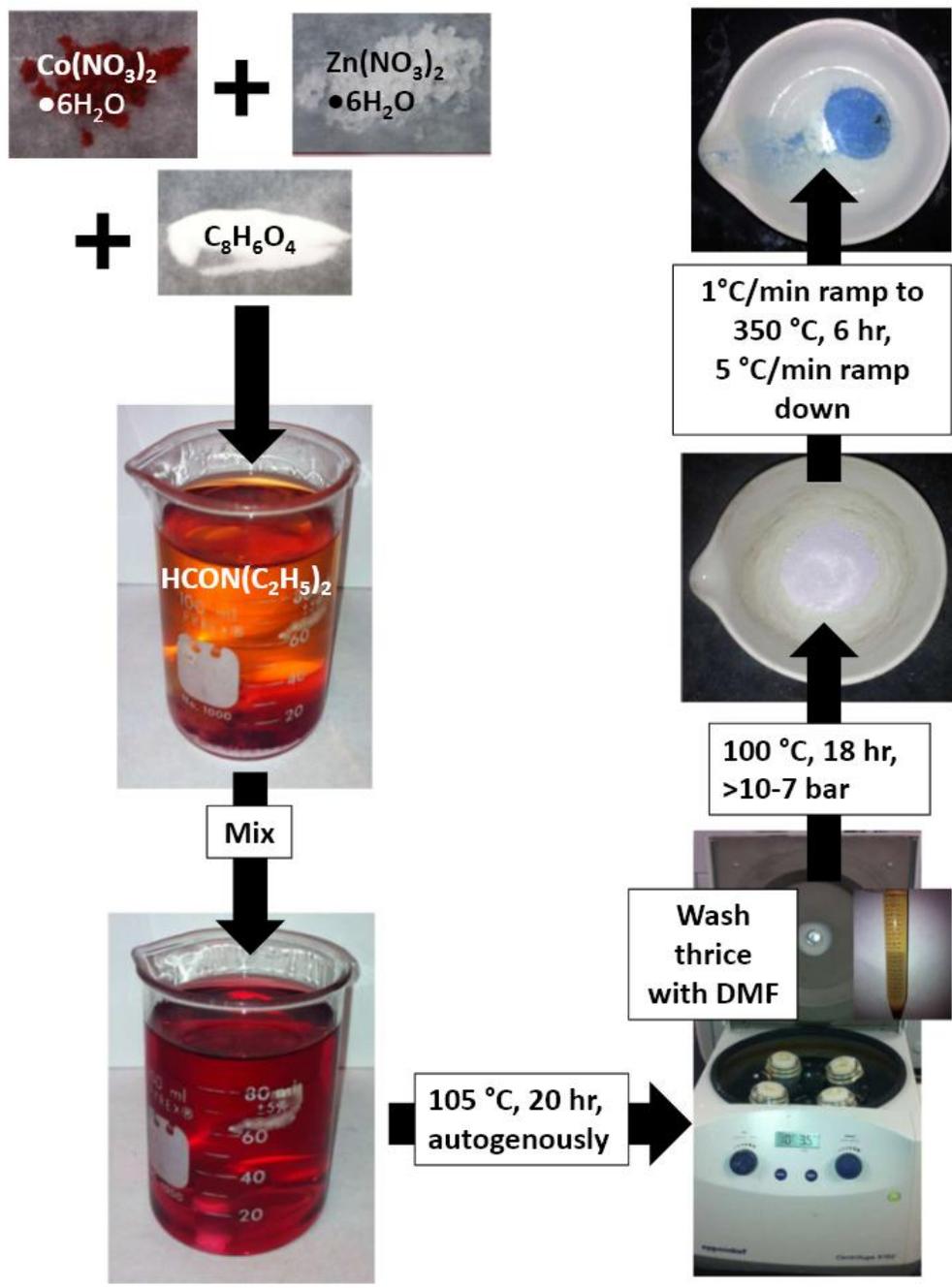


FIGURE 6 - Catalyst Preparation Process

B. Catalyst Characterization

The resulting crystals were then characterized using X-ray diffraction, scanning electron microscopy, surface area, and adsorption-desorption isotherm measurements. The powder X-ray diffraction patterns were gathered by use of the Bruker D8-Discover diffractometer, FIGURE 11, at 40 kV, 40 mA with Cu K α radiation. The surface area and adsorption-desorption isotherm measurements were taken on a Micromeritics Tristar 3000 porosimeter,

FIGURE 12. The conditions on the porosimeter were a temperature of -196 °C using liquid nitrogen as a coolant. The samples were degassed at 150 °C for two hours directly before being placed in the porosimeter. The scanning electron microscopy was performed on a FE-SEM (FEI Nova 600), FIGURE 13, with an acceleration voltage of 6 kV.

C. Catalyst Testing

Four different reactions involving the cycloaddition of carbon dioxide were performed to test the catalytic ability of the synthesized Co21-MOF-5 crystals. Chloropropene carbonate was generated using epichlorohydrin (C₃H₅ClO, Fluka, $\geq 98.0\%$) and CO₂ using reaction pressure of 7 bar and temperatures of 80, 100, and 115 °C. Similarly, CO₂ and styrene oxide (C₈H₈O, SAFC, $\geq 97\%$) were converted to styrene carbonate at 7 bar and 100 °C. The cobalt doped metal-organic framework was also catalytically tested to convert aniline, N-butyl bromide, and carbon dioxide into butyl N-phenyl carbamate at 40 °C and 3.4 bar.

All reactions followed the same general procedure using the stainless steel high pressure Parr reactor, FIGURE 14. Ingredients were placed into the 250 mL reaction

vessel. The reaction vessel was attached to the reactor by tightening down the eight bolts on the clamp, alternating to bolts opposite one another to ensure proper clamping. The heating jacket was pulled up to cover the reaction vessel. Then the stirrer, heater, and cooling water were turned on. The vessel was heated stepwise to avoid overshooting the temperature. All air in the vessel was evacuated while the reaction vessel was heating. This was accomplished by pressurizing the reactor to 10 bar of carbon dioxide and then venting the vessel, repeated four times. After the air was removed, the reactor was pressurized with carbon dioxide to the experimental pressure. Once the reactor reached the experimental temperature, timing started for reaction. After four hours, the stirrer, heater, and cooling water were turned off. The excess CO₂ was vented from the reactor. Then the heating jacket was removed from the reactor. The reactor was allowed to cool to room temperature. The effluent was separated from the catalyst by centrifugation and tested for conversion and selectivity.

The products were analyzed by GC-MS (HP 5890 Gas Chromatograph equipped with 5970 Mass Selective Detector, 30 m x 0.32 mm HP-5 column coated with 5% phenyl poly siloxane stationary phase). The temperature ramp rate and conditions were 15 °C/min from 70 °C to 220 °C during the gas chromatographic analysis. The GC-MS used for analysis can be viewed in FIGURE 15. The catalyst was then washed with acetone (C₃H₆O, Alfa Aesar, 99+%), dried, and characterized again to determine degradation.

D. Equipment

1. Synthesis of Co21-Mof-5



FIGURE 7 - Hydrothermal Autoclave with 50mL Teflon Vessel²³



FIGURE 8 - Ney® Vulcan 3-550 Furnace
Dentsupply Ceramco International
Serial No.: 9493308
York, PA 17404²⁴



FIGURE 9 - Eppendorf Centrifuge
Model No: 5702
Serial No: 5702YN320989



FIGURE 10 - Precision Vacuum Oven
Model No.: 29
Serial No.: 69902505
Winchester, VA 22602

2. Catalyst Characterization



FIGURE 11 - X-Ray Diffraction,
Bruker AXS – Diffraktometer D8
Serial No.: 203407
Karlsruhe, Germany D76181²⁴

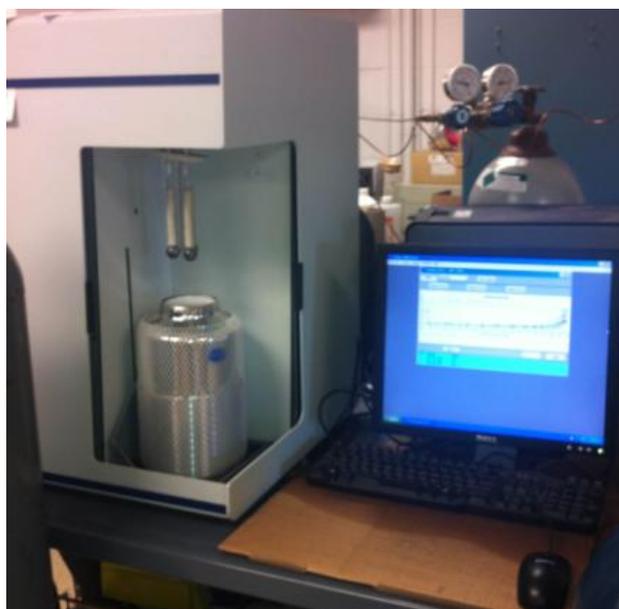


FIGURE 12 - Micromeritics Tristar 3000 Porosimeter



FIGURE 13 - Nova NanoSEM 600
FEI²⁵

3. Catalyst Testing



FIGURE 14 - Stainless Steel High Pressure Parr Reactor
Model No: 4576A



FIGURE 15 - GC-MS
HP 5890 Gas Chromatograph equipped with 5970 Mass Selective Detector

III. RESULTS AND DISCUSSION

A. Characterization of Co21-MOF-5

The method provided by Botas et al. was followed closely to create Co21-MOF-5²⁰. These samples were produced using a diethylformamide solvent purchased from Alfa Aesar. Five samples were created using this method, generating approximately 0.5 g of product per sample. This yielded the correct crystalline structure, with the powder X-ray diffraction patterns matching closely to those shown in FIGURE 4. The primary peaks at the 2-theta angles of 10, 12, 15, and 19 appeared in nearly all the samples.

The specific surface area according to the research performed by Botas et al. was 2900 (± 200) m²/g following the Langmuir model²⁰. However, when the Langmuir surface area was measured on the porosimeter for the samples produced for this study, the surface area fell short of the published values. The Langmuir specific surface area values for the sets of generated Co21-MOF-5 crystals ranged from a low of 48.3 m²/g to a high of 527.8 m²/g. The mean measured surface area was 216 (± 160) m²/g, less than 20% of the reported specific surface area. The low surface area can be attributed to local structural disorder or incomplete removal of the solvent guest species.

In an effort to decrease the gap between the published specific surface area and those obtained experimentally, the generation technique was scrutinized. It was determined that the proper preparation, heating, and washing techniques were being applied. Then other methods were investigated to develop a higher surface area in the

experimentally generated crystals by removing potential solvent occluding the pores of the crystals.

First, a higher vacuum oven temperature and pressure setting, along with a shorter vacuum drying time were considered. The crystals that had previously dried at a vacuum of $>10^{-7}$ bar and 100 °C for 18 hours were then exposed to a vacuum of 0.2 bar and temperature of 120 °C for two hours. This did not disturb the powder X-ray diffraction patterns, but also had negligible effects on the porosity measurements of the crystals. Therefore, changing the vacuum oven settings and times did not improve the surface area of experimental Co21-MOF-5.

Next the same crystals were placed in a calcining oven in attempts to remove the solvent blocking the pores of the crystals by thermal treatment. The Co21-MOF-5 crystals reported by Botas et al. were exposed to thermogravimetric analysis (TGA). In the reported sample, weight loss occurred starting at 400 °C, representing the decomposition of the organic linker²⁰. To prevent any thermal degradation during thermal treatment of the Co21-MOF-5 crystals produced for this study, 350 °C was chosen as the maximum calcining temperature. The crystals were placed in the calcining oven at room temperature. Then the oven heated at a rate of 1 °C/min until reaching a temperature of 350 °C. This temperature was held for six hours. Then the temperature was decreased at a rate of 5 °C/min until room temperature was reached again.

The calcination process did not alter the crystalline morphology, maintaining a similar X-ray diffraction pattern. A representative X-ray diffraction pattern for the Co21-MOF-5 crystals before and after the thermal treatment can be seen in FIGURE 16. Calcining the cobalt doped metal-organic framework caused changes in intensity peak

values, representing shifts in the crystal lattice. Although the crystal lattice structure might change slightly, which affects intensity at certain angles, almost all peaks still appear after calcination. This means that the identity of the crystalline structure is maintained during thermal treatment. The splitting of the peak at a 2 theta of around 10° does not appear in the reported literature. The split in the peak may suggest irregularities in the lattice orientation throughout the structure, and not necessarily a different crystal arrangement.

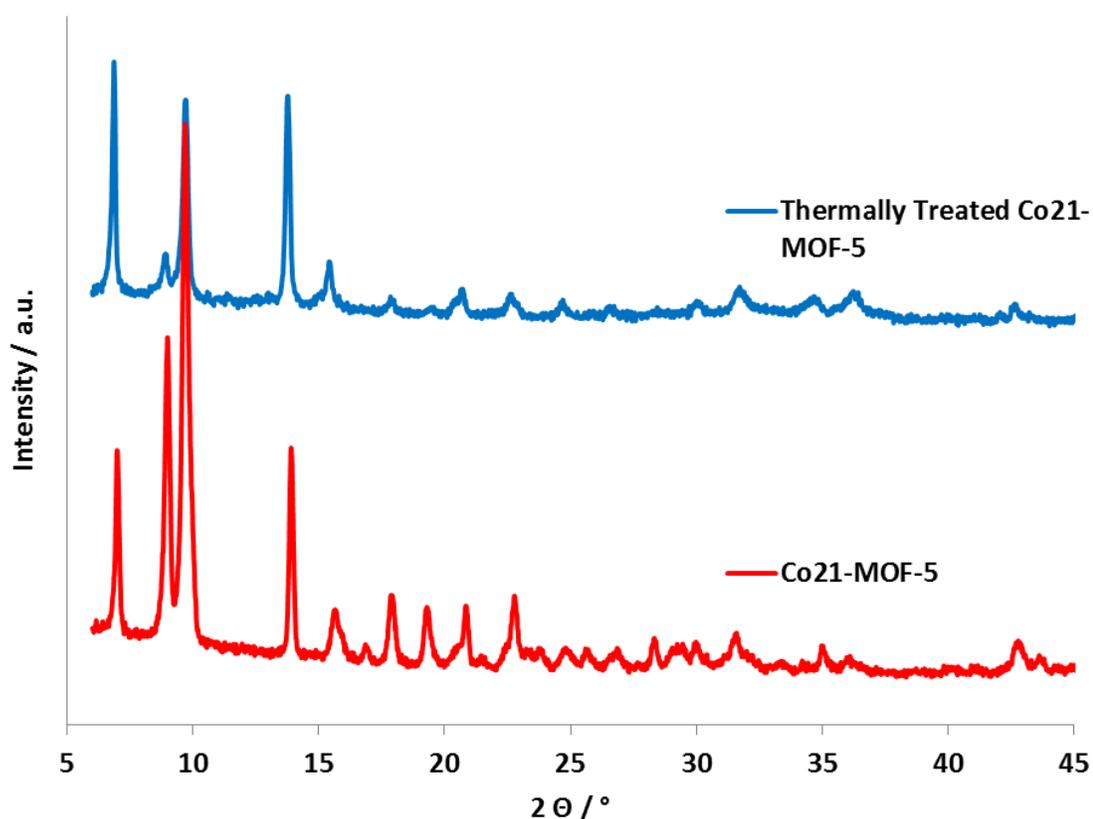


FIGURE 16 - Comparison of the Co21-MOF-5 Powder XRD Patterns Before and After Thermal Treatment

After calcination, the specific surface area of the experimental crystals based on the Langmuir model increased to 594 (± 130) m²/g, over twice that obtained using the synthesis method presented by Botas et al. Although this value falls short of the 2900

(± 200) m^2/g reported in literature, it bridged the gap sufficiently to consider catalytic testing. A representative N_2 adsorption-desorption isotherm of the generated Co21-MOF-5 crystals can be seen in FIGURE 17. This is a Type I isotherm, typical for a microporous type material, and was expected for the synthesized Co21-MOF-5 crystals.

Due to the general sensitive nature of synthesis of metal-organic frameworks, the lower surface area shown by the crystals developed for this study and the published values could be a result of several different factors. This lower surface area can be caused by a lower structural order or occluded solvent in the pores of the crystals. The synthesized Co21-MOF-5 crystals appeared to have a lower structural order. This is apparent when viewing the X-ray diffraction patterns. Most of the XRD reflections reported by Botas et al. appear, but not all. Also, despite the attempts to remove pore blocking substances, like the DEF solvent, occlusions still could occur. Synthesis times, crystal washing, vacuum oven settings, and small differences in the synthesis reactant values could also cause the difference in surface area.

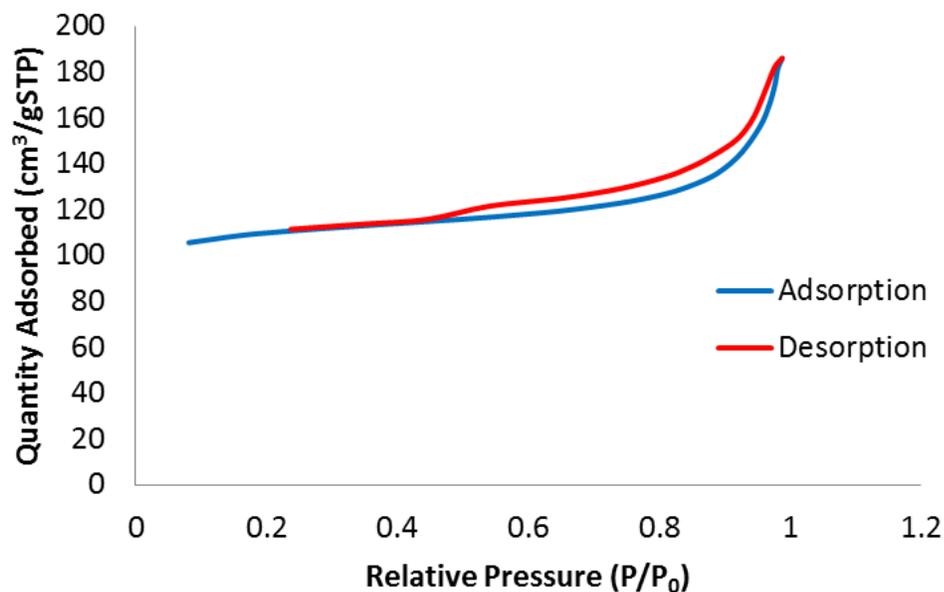


FIGURE 17 - N₂ Adsorption-Desorption Isotherms of Co21-MOF-5

The generated cobalt doped MOF-5 crystals were also analyzed using scanning electron microscopy. Botas et al. did not publish SEM images of the cobalt doped MOF-5 crystals, so there were no previous images for comparison. Scanning electron microscopy helps to determine surface morphology and crystal size. Images obtained from the SEM analysis of the experimentally produced Co21-MOF-5 crystals can be viewed in FIGURE 18. By viewing FIGURE 18a, one notices that the entire particle is covered with mainly interwoven rod-like structures, approximately 0.2 μm in diameter. This indicates a highly-ordered crystalline structure. FIGURE 18b zooms closer into the particle to give a better representation of the layered crisscross pattern in the crystalline structure.

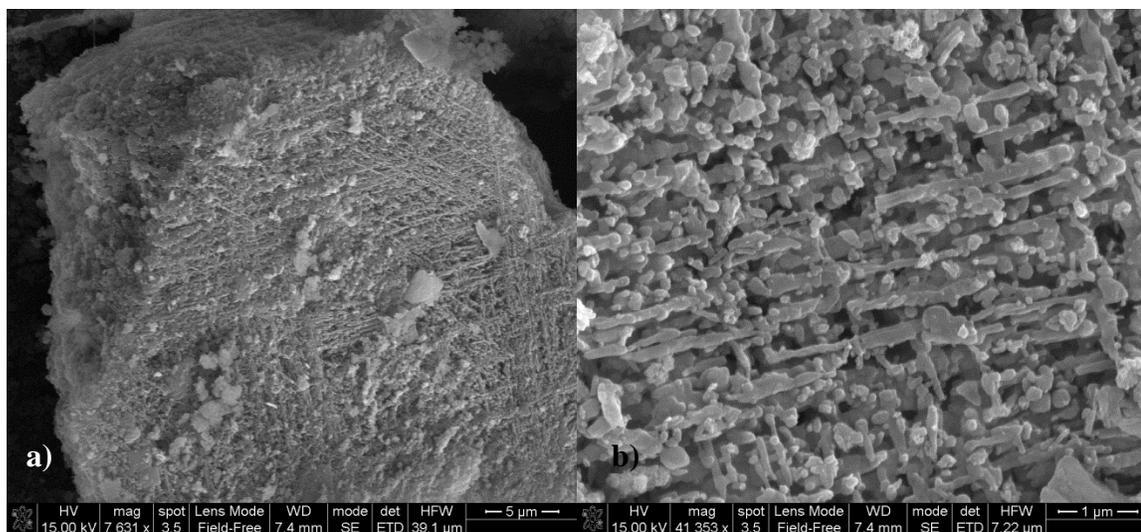


FIGURE 18 - Scanning Electron Microscopy Images of Co₂₁-MOF-5

Diethylformamide is an expensive solvent, costing \$256 per 100 mL from Acros Organics. After the first three crystalline samples were produced, the previous DEF solvent from Alfa Aesar was close to being exhausted. Because of the high cost of the solvent to produce Co₂₁-MOF-5, attempts at solvent recyclability were also investigated. The last two syntheses of Co₂₁-MOF-5 using the solvent from Alfa Aesar investigated solvent recyclability. For each synthesis, the solvent poured off the crystals after hydrothermal treatment was then used as the main DEF solvent for a new Co₂₁-MOF-5 synthesis. A very small amount of fresh solvent, less than 2.5 mL, was used to make up for solvent lost during hydrothermal treatment and solvent recovery.

The cobalt doped MOF-5 crystals obtained by utilizing recycled DEF were then characterized. Powder X-ray diffraction was performed to determine the effectiveness of using a recycled solvent. Although the first three primary peaks appeared, the next few peaks disappeared, indicating that the proper crystalline structure could not be achieved using a recycled diethylformamide solution. Also, the specific Langmuir surface area

was an insufficient 12.9 m²/g. Likely, the recycled diethylformamide contained trace elements of products and various side products which limited the solvent functionality.

After the initial five batches of cobalt doped MOF-5 catalyst were made, a new batch of N,N diethylformamide was obtained in order to develop enough material for the catalytic testing. However, five attempts to thermally treat the developed catalyst using the new container of DEF all resulted in collapse of the porous structure. The synthesis methods were copied in an identical fashion and even altered to try and discover the cause of this structural collapse. The vacuum oven times and temperatures were altered in ways similar to those previously discussed. After these five unsuccessful attempts to calcine the catalyst, the previous method of Co21-MOF-5 synthesis without the thermal treatment was revisited. Therefore, only three out of the five experiments used to test catalytic ability utilized the thermally treated Co21-MOF-5, with the other two experiments used a Co21-MOF-5 without calcination. It is hypothesized that the diethylformamide bought during the second half of Co21-MOF-5 developmental studies, being from a different company, may have differed materially, and thus have been the cause of the issues relating to the thermal treatment of the catalyst. However, this theory was not tested for this study.

B. Catalytic Activity

After the Co21-MOF-5 catalyst was developed and characterized, five different experiments were performed to test the catalytic ability. The main catalytic testing revolved around testing the metal-organic framework on the cycloaddition of carbon dioxide to create carbonates. A summary of the catalyst identity along with the reactions parameters tested can be viewed in TABLE I. By viewing this table it can be seen that

three reactions were performed testing the cycloaddition of carbon dioxide to epichlorohydrin, Reactions 1, 2, and 3. One reaction tested the cycloaddition of carbon dioxide to styrene oxide, Reaction 4. The final reaction tested was to investigate Co21-MOF-5 as a catalyst to produce carbamates, Reaction 5. It should be noted that, as a result of a previous research topic investigated, one of the produced Co21-MOF-5 samples developed with a high surface area was tested on an epoxidation reaction. The reaction was not catalyzed by the Co21-MOF-5 crystals.

TABLE I
SUMMARY OF CO21-MOF-5 CATALYST PROPERTIES WITH REACTION
PARAMETERS

Reaction Label	Calcined?	Langmuir Surface Area (m ² /g)	Reaction Precursor	Temperature (°C)	Pressure (bar)
1*	yes	574.4	epichlorohydrin	80	7
2	yes	796.8	epichlorohydrin	100	7
3	no	137.2	epichlorohydrin	115	7
4	no	60.6	styrene oxide	80	7
5	yes	432.1	aniline/ <i>n</i> -butyl bromide	40	3.4

* Combined two batches of Co21-MOF-5 synthesis, averaged the surface area

For the first reaction, two batches of the Co21-MOF-5 catalyst were combined to create 0.9145 g catalyst with 16.52 g of epichlorohydrin. All the following reactions used only one batch of Co21-MOF-5 catalyst, ranging from 0.23 – 0.30 g catalyst per reaction. In order to insure some comparability for the four carbonate reactions, the same molar ratio between chemical precursor and catalyst was used: 0.18 moles precursor per gram catalyst. The results for these four reactions based on the data collected by the GC-MS can be viewed in TABLE II.

TABLE II

CONVERSION AND SELECTIVITY RESULTS FOR THE CO₂ CYCLOADDITION
REACTIONS TO PRODUCE CHLOROPROPENE CARBONATE AND
STYRENE CARBONATE

Reaction Label	Reaction Precursor / Temperature (°C)	Reactant Conversion (%)	Selectivity (%)		
			Carbonate	Diol	Dimer
1	epichlorohydrin (80)	43.3	100	0	0
2	epichlorohydrin (100)	100	0	100	0
3	epichlorohydrin (115)	100	0	100	0
4	styrene oxide (80)	55	34.9	57.5	0

Reaction 1 produced a conversion of epichlorohydrin of 43.3%. However, although it appears that the selectivity is 100% in the table, it should be noted that both diols and dimers of epichlorohydrin appeared in the graphical output from the GC injection. The amounts were not large enough to be included in the tabular data, and therefore, could not be included in the calculations of the selectivity. The graphical output of the GC-MS injection from Reaction 1 can be viewed in FIGURE 19. Notice that there are three large peaks associated with the diols of epichlorohydrin and one significant peak for the dimers of epichlorohydrin that do not appear in the tabular data. The first large peak represents the unreacted epichlorohydrin at a retention time of 3.5 minutes. At 12.3 minutes, the peak representing the chloropropene carbonate appears. The other GC-MS tabular and graphical results can be viewed in Appendix I.

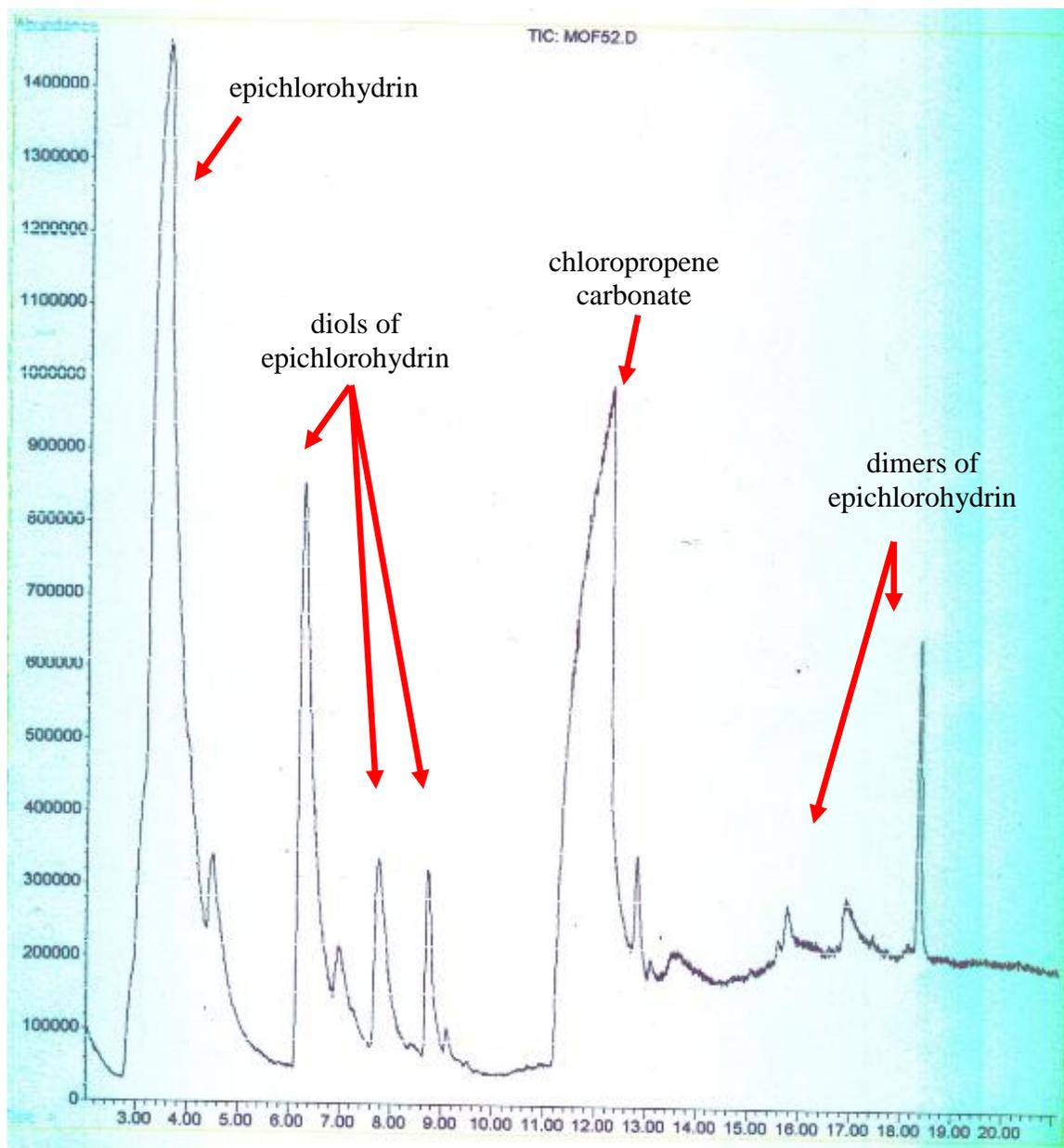


FIGURE 19 - GC-MS Graphical Results for Reaction 1

For both Reaction 2 and 3, the resulting product was dark brown in color and extremely viscous (virtually solid, but slightly elastic). In order to inject the products the reaction into the GC-MS, approximately 5 mL of acetone had to be utilized to retrieve the catalyst and effluent from the reaction vessel, before centrifugation. Acetone was used because it is not detected by the GC-MS, but would enable the effluent to be tested. As

the reaction temperature was increased, and based on the results from the GC-MS, it is apparent that the carbonate was formed and then further reacted to produce the diols of epichlorohydrin. Diols are also precursors to polycarbonates. Based on the extremely viscous nature of the resultant product, the reaction may have continued to form some polycarbonate material, as well. The equipment to test polycarbonates was not available for this study.

Reaction 4 showed that the Co21-MOF-5 catalyst can also catalyze carbonate reactions for other precursor materials. Although conversion of the precursor was highest for this reaction, most of the product was also the diol of styrene oxide. Only 34.9% of the converted styrene oxide resulted in styrene carbonate. The overall yield of styrene carbonate for this reaction was only 19%. If the temperature for this reaction were decreased, one might find a higher carbonate yield. Also, it must be noted that this reaction used the Co21-MOF-5 catalyst with the lowest specific surface area, 60.6 m²/g. This decreased surface area negatively affects the catalytic ability of the material.

To test the functionality of the cobalt doped MOF-5 catalysts, catalytic ability was also investigated for the production of carbamates. The molar ratio used for the reaction followed that described by Srivastava et al. of 10 mmol aniline, 10 mmol n-butyl bromide, and 1.5 g catalyst. The amount of calcined Co21-MOF-5 used for this reaction was 0.43 g. Reaction 5 resulted in a 25.4% conversion of aniline and n-butyl bromide with 100% selectivity for butyl n-phenyl carbamate. Although these appear to be promising results, the crystalline identity of the Co21-MOF-5 catalyst was not maintained. This means that the catalyst could not be recycled and used in successive reactions, a very important parameter when investigating industrial applications.

C. Characterization of Spent Co21-MOF-5

All but approximately 0.1 g of catalyst was lost during the drying process for the spent Co21-MOF-5 catalyst used for Reaction 1. Less than 0.5 g of catalyst was used in Reactions 2-5. Retrieving the spent catalyst from the reaction vessel, successive washing of the catalyst with acetone, and powder X-ray diffraction resulted in the amount of spent catalyst remaining to be an unusable amount for both porosity measurements and catalyst recyclability tests. Still, powder X-ray diffraction was obtained for the spent Co21-MOF-5 catalyst from all five reactions.

The X-ray diffraction patterns provide a good representation of the crystalline structure, and therefore the identity of the catalyst. For Reaction 1 and 4, the X-ray diffraction patterns showed that the crystals were preserved. All of the main peaks still appeared in the patterns. The crystals for Reaction 2 and 3 did not maintain the crystalline structure, producing an XRD pattern without significant peaks. The crystals changed to a black color. This could be a coating of the product from the reactions, which could possibly be removed by either washing or heat treatment. The Co21-MOF-5 crystals from Reaction 5 lost all original color, turning white. When tested with powder X-ray diffraction, it was discovered that the crystalline structure was not maintained throughout the reaction. FIGURE 20 shows the X-ray diffraction patterns for the reactions 1, 4, and 5. Reactions 2 and 3 are shown in FIGURE 21, because the details of the XRD patterns did not show up when all five reactions were placed on the same graph.

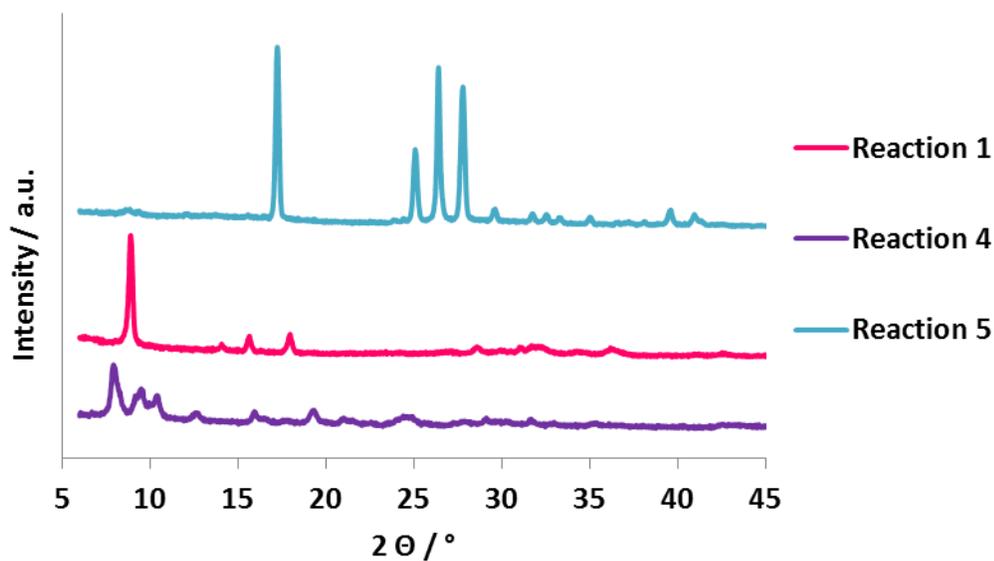


FIGURE 20 - Powder X-ray Diffraction Patterns for Spent Co21-MOF-5 Catalysts – Reactions 1, 4, and 5

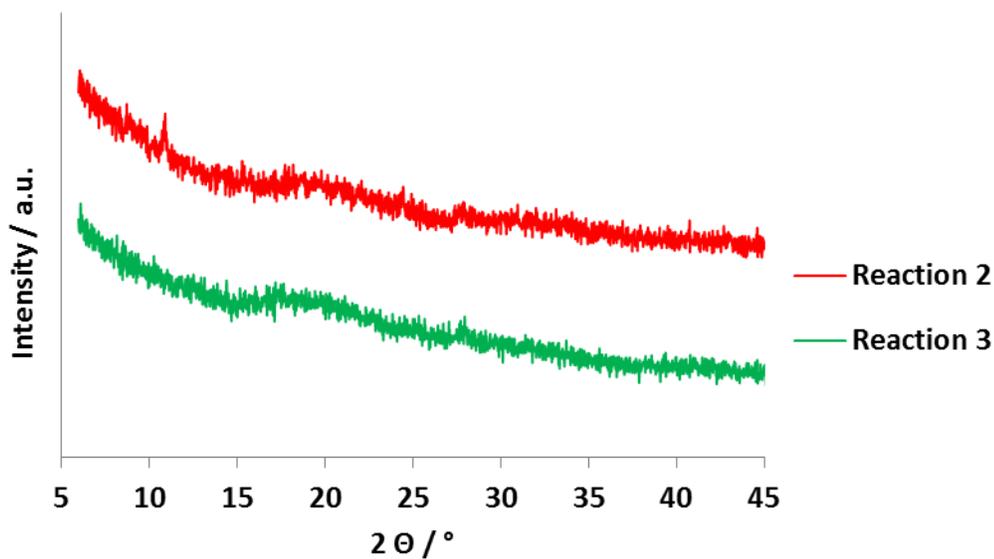


FIGURE 21 - Powder X-ray Diffraction Patterns for Spent Co21-MOF-5 Catalysts – Reactions 2 and 3

Another important characterization method to determine the stability of the catalyst throughout the reaction is porosity measurements. During the reaction, the porous structure could become blocked with material. This would be indicated by testing

the specific surface area of the spent catalyst. However, there was not enough material left in any reaction to perform this characterization technique.

IV. CONCLUSIONS

Cobalt doped metal-organic framework-5 catalysts were developed following a method similar to those presented by Botas et al. with 21% of the zinc backbone replaced with cobalt. Like zinc, cobalt is also a Lewis acid that attracts carbon dioxide molecules. Comprehensive characterization techniques were used to study the textural and morphological properties of the generated Co21-MOF-5, including BET, XRD, and SEM. The Botas et al. method was altered slightly to accommodate the low Langmuir surface areas (less than 20% of reported values) that appeared experimentally. The developed crystals were subjected to a thermal treatment at 350 °C for six hours to help remove the DEF solvent that blocked the pores of the material and decreased the surface area. The catalyst calcination resulted in a powder XRD pattern which closely matched those published by Botas et al. The average Langmuir surface areas of the crystals increased from an average of 216 m²/g to 594 m²/g. Although the treatment was originally successful, it could not be reproduced once a new supply of the DEF solvent was ordered. Scanning electron microscopy was also performed on the Co21-MOF-5 crystals, previously unreported. The SEM images reveal rod-like shaped particles, approximately 0.2 μm in diameter, that are interwoven in a crisscross pattern.

In the second half of the research, a catalytic evaluation of Co21-MOF-5 took place in the study of cycloaddition reactions to produce carbonates. The best catalytic activity took place in the cycloaddition of carbon dioxide to epichlorohydrin at 80 °C and 7 bar over 4 hours. This reaction produced 43.3% conversion of the epichlorohydrin at

100% selectivity to chloropropene carbonate. Powder X-ray diffraction of the spent catalyst revealed that the crystalline structure of Co21-MOF-5 was preserved, and that a catalyst recycle is probable. The same reaction studied at temperatures of 100 °C and 115 °C resulted in complete conversion of the epichlorohydrin to the corresponding diols. The catalyst could not be recycled under these circumstances. In a comparative study, the conversion of styrene oxide to styrene carbonate was also attempted at 80 °C and 7 bar over 4 hours. This reaction produced a 55% conversion of styrene oxide with 34.9% selectivity for the carbonate product. The powder XRD pattern suggested that this reaction also allows for a recyclable Co21-MOF-5 catalyst.

To investigate the multifunctional nature of CO21-MOF-5, a final reaction was performed converting aniline and n-butyl bromide to butyl n-phenyl carbamate. The reaction conditions considered 40 °C and 3.4 bar over 4 hours. This reaction produced the carbamate product at 100% selectivity with a precursor conversion of 25.4%. However, the crystalline structure of the cobalt doped MOF-5 catalyst could not withstand this reaction, shown by the powder XRD results. The catalyst did not show characteristics for recyclability.

V. RECOMMENDATIONS

A. Synthesis of Co21-MOF-5

Difficulties were encountered with repeatability in thermally treating the Co21-MOF-5 catalyst to improve specific surface area. When the brand of DEF solvent switched from Alfa Aesar to Acros organics, the Co21-MOF-5 crystals could no longer handle calcination without the collapse of the crystalline structure. It was hypothesized that the change of the diethylformamide provider may be the root cause to this problem. Therefore, it is recommended to return to the old solvent brand to test this hypothesis.

Other, less expensive solvents, such as DMF substitution, could also be investigated to see if the cost of the synthesis could be reduced. Botas et al. researched varying amounts of cobalt substitution and the effects on several characteristics of the structure, such as thermal degradation and carbon dioxide and methane adsorption. It would also be beneficial to further investigate the catalytic effectiveness of differing percentages of cobalt doping to replace the zinc clusters in the backbone of the MOF-5 structure.

B. Characterization of Co21-MOF-5

Valuable information could be obtained if additional characterization techniques were investigated regarding the cobalt doped metal-organic framework. Transmission electron microscopy would be beneficial to better understand the morphology of the crystalline structure and the distribution of cobalt and zinc molecules throughout the

structure. It would also be helpful to run a comparative thermogravimetric analysis on the crystals with respect to the published literature. Considering that the Co₂₁-MOF-5 crystals could not withstand the thermal treatment of 350 °C, the thermal stability of the crystals may have decreased along with the specific surface area when compared to the reported values. This would help to better understand if the experimental crystals matched the properties of those reported.

C. Catalytic Activity of Co₂₁-MOF-5

Further investigation should be performed regarding the catalytic activity of the cobalt doped MOF-5. Most importantly, recyclability of the catalyst should be investigated to determine better effectiveness and possible future implementations into industry. More complete catalyst characterization should also be performed after the reactions. To do these two recommendations, a larger amount of catalyst needs to initially be used in the reactions. After the preliminary catalyst characterization, the amount of catalyst produced per batch diminished to less than 0.4 grams. This is an unavoidable occurrence, since catalyst is inevitably lost when transferring from the storage bottle to the testing container and back again. Also, catalyst is lost during washing after the reaction. After washing, drying, and powder X-ray diffraction measurements on the spent catalyst, many times there would be less than 0.1 grams of catalyst. This amount is not adequate for porosity measurements or further reaction experiments.

In addition to characterization and recyclability, further variety in the reaction parameters should be explored. Both carbon dioxide cycloaddition to epichlorohydrin and to styrene oxide reactions should be investigated at a lower temperature, such as 60

°C. Any time the temperature can be reduced, a cost is saved in heating. Considering that polymerization started once a temperature of 100 °C was reached, it would be advantageous to examine reactions with lower pressures, as well. If a lower pressure could be utilized with a higher temperature, money could be saved in a manufacturing process, because the heat generated could be utilized for another process through a heat exchanger.

Although the crystalline structure of Co21-MOF-5 collapsed during catalysis to produce butyl N-phenyl carbamate, high conversion occurred. Therefore, other precursors to carbamates could be investigated. This would help determine whether the cobalt doped MOF-5 could successfully convert chemicals to carbamates without loss of crystalline identity.

Finally, an in-depth study of reaction kinetics should be performed on the reactions with the best results. Changing temperatures and reaction times will allow for a reaction rate to be determined for the cobalt doped MOF-5 catalyst on the carbonate and carbamate forming reactions. Altering the ratio between reaction precursor and catalyst will also provide useful information regarding kinetics.

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APPENDIX

TABLE III

GC-MS TABULAR RESULTS FOR REACTION 1

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	peak area	peak % max.	% of total
1	3.530	123	257	396	BB 6	1321753	484793939	100.00%	56.673%
2	12.274	1555	1748	1788	BB 6	749638	370626826	76.45%	43.327%
Sum of corrected areas:							855420765		

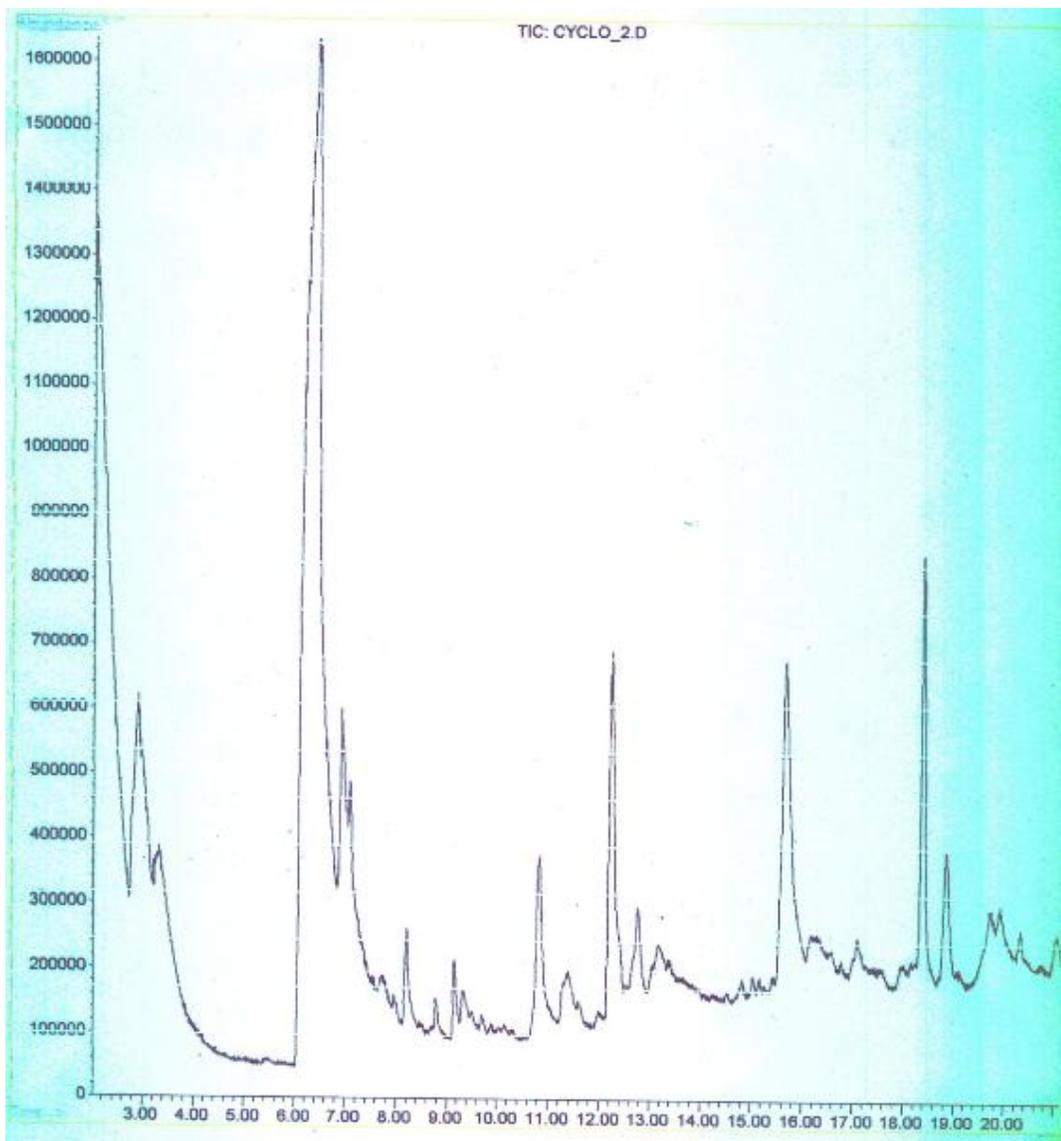


FIGURE 22 - GC-MS Graphical Results for Reaction 2

TABLE IV

GC-MS TABULAR RESULTS FOR REACTION 2

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	peak area	peak % max.	% of total
1	6.435	663	752	821	BV 4	1420764	320208347	100.00%	100.000%
Sum of corrected areas:							320208347		

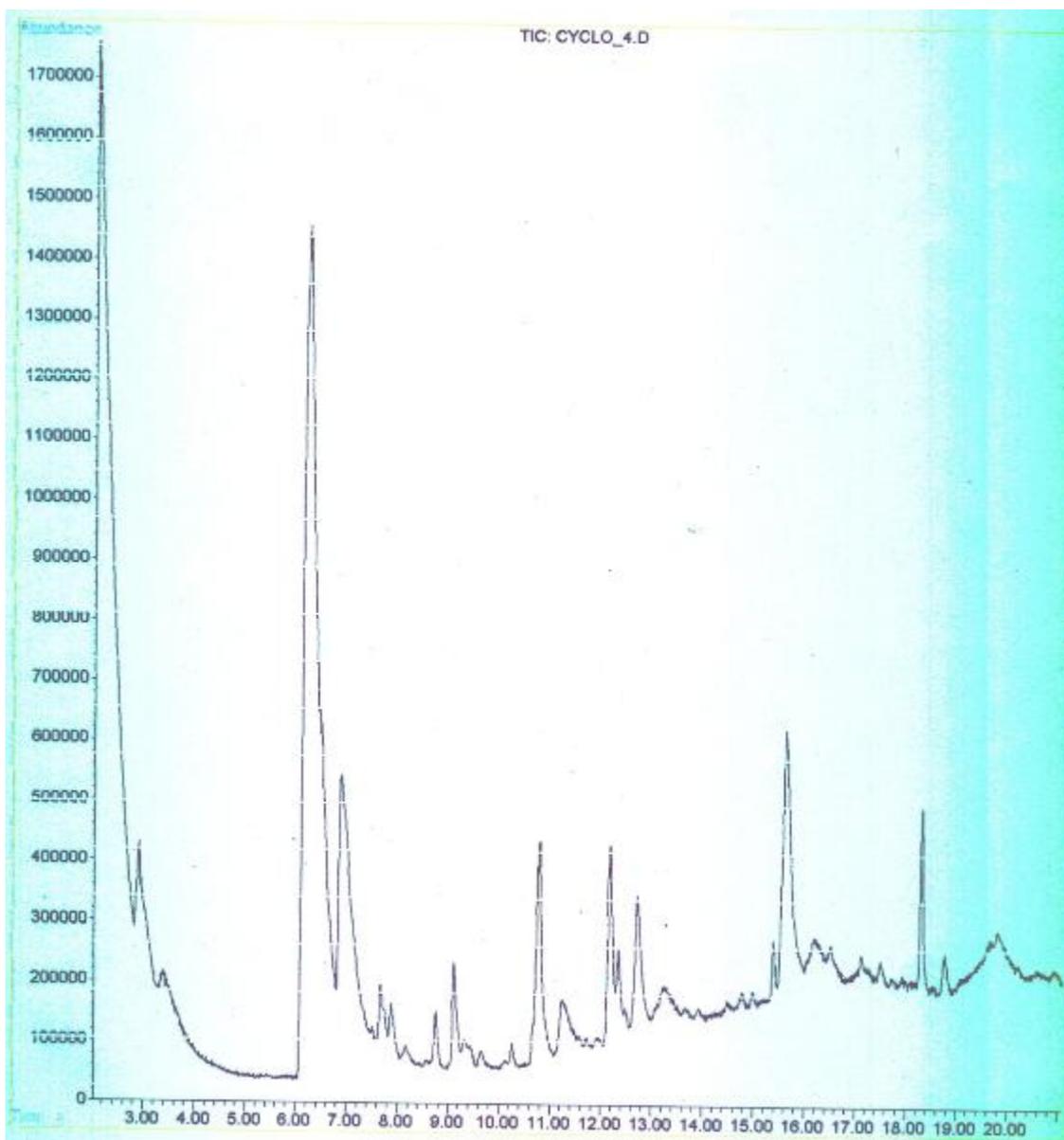


FIGURE 23 - GC-MS Graphical Results for Reaction 3

TABLE V

GC-MS TABULAR RESULTS FOR REACTION 3

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	peak area	peak % max.	% of total
1	6.224	673	717	816	BV 3	1365098	254573054	100.00%	100.000%
Sum of corrected areas:							254573054		

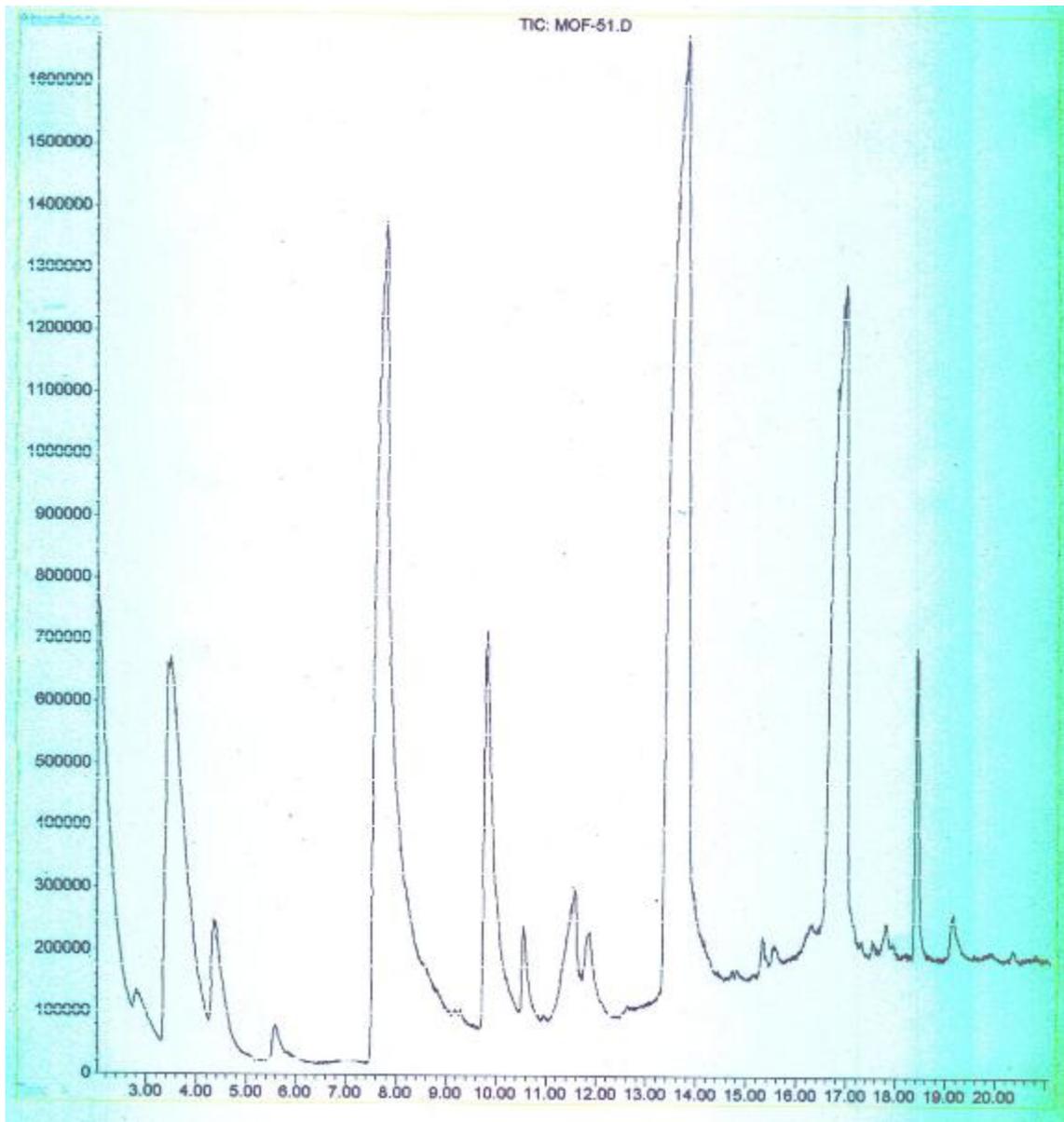


FIGURE 24 - GC-MS Graphical Results for Reaction 4

TABLE VI

GC-MS TABULAR RESULTS FOR REACTION 4

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	peak area	peak % max.	% of total
1	6.255	639	722	778	BB 9	489363	87581757	10.25%	4.174%
2	9.633	1104	1298	1309	BV 4	2080344	854673002	100.00%	40.735%
3	9.791	1309	1325	1362	VB 3	1460934	90240442	10.56%	4.301%
4	13.040	1816	1879	1942	VB 3	1548037	289698090	33.90%	13.807%
5	14.312	2007	2096	2213	BB 4	1154414	372863050	43.63%	17.771%
6	17.819	2510	2694	2728	BB 8	1131776	403075129	47.16%	19.211%

Sum of corrected areas: 2098131470

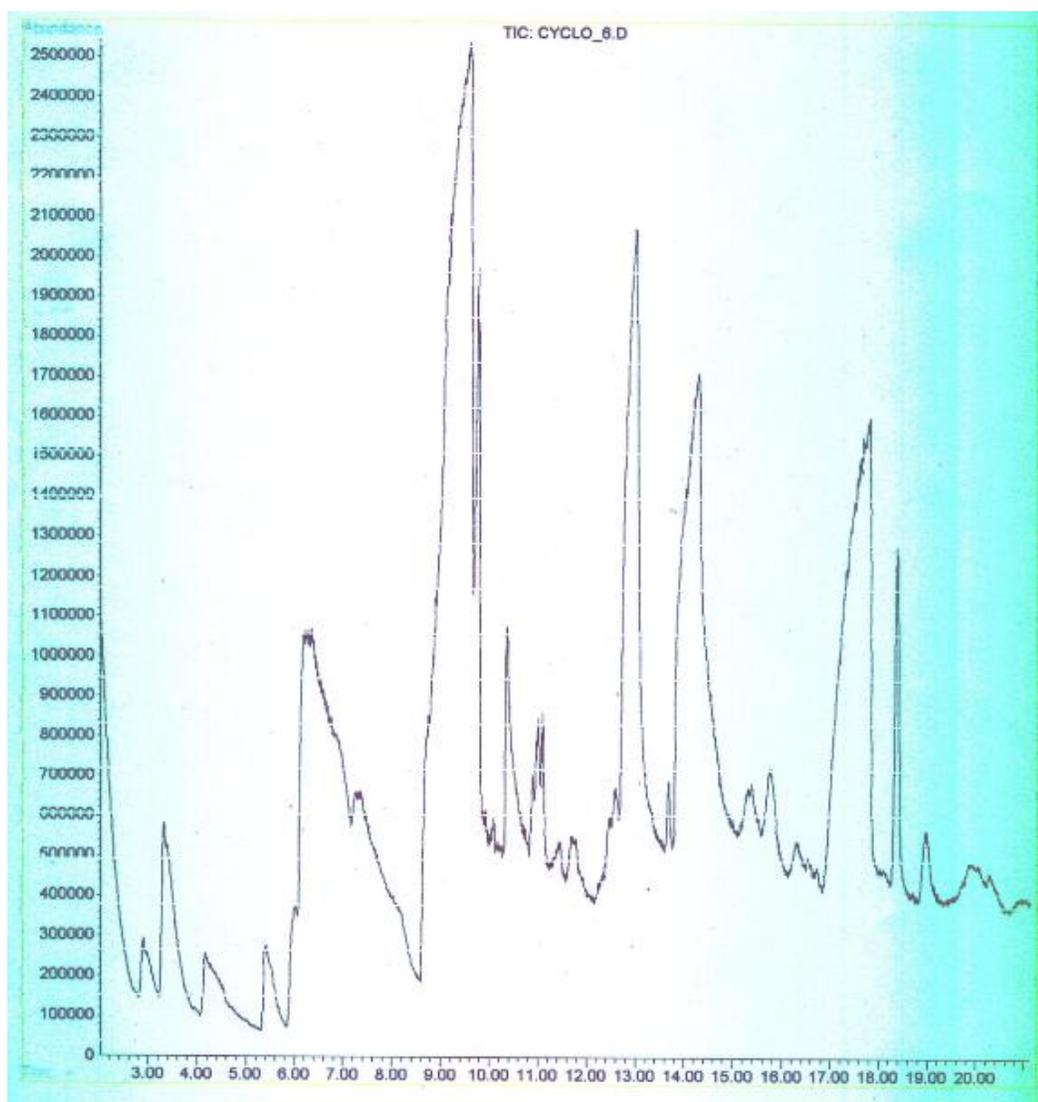


FIGURE 25 - GC-MS Graphical Results for Reaction 5

TABLE VII

GC-MS TABULAR RESULTS FOR REACTION 5

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	peak area	peak % max.	% of total
1	7.815	914	988	1071	BB 3	1235828	246040466	71.06%	31.004%
2	13.838	1908	2015	2063	BB 3	1486029	346225977	100.00%	43.629%
3	17.010	2465	2556	2591	BB 6	1045209	201297552	58.14%	25.366%
Sum of corrected areas:							793563995		

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