Structural Modification of Metal Organic Frameworks for Applications in Carbon Dioxide Capture

A Dissertation Presented

By

Dinara Andirova

To

The Department of Chemical Engineering

In Partial fulfillment of the requirements For the degree of

Doctor of Philosophy

In the field of

Chemical Engineering

Northeastern University
Boston, Massachusetts

May 2016
ABSTRACT

Metal organic frameworks (MOFs) belong to a class of crystalline materials where metal constituting building blocks are connected by organic ligands to form well-defined nanoporous structures. These materials exhibit uniform pores, extremely high surface area, and potential for chemical tunability rendering MOFs available for many applications such as gas storage and separations, drug delivery, catalysis, etc.[2]

In the first part of this work structural optimization of MOFs for practical CO$_2$ capture processes have been studied. It has been reported that the adsorption properties of MOFs in practical CO$_2$ capture tend to be harmed by the presence of moisture possibly due to the hydrophilic nature of the coordinatively unsaturated sites (CUSs) present within the frameworks. Here, the CUSs were functionalized with amine-containing molecules to prevent its structural degradation in a humid CO$_2$ capture environment. Specifically, it was demonstrated that amine groups could be grafted on the metal sites of the magnesium dioxybenzenedicarboxylate (Mg/DOBDC) without changing the framework structure of the material. The amine modified framework showed better structural preservation and retained CO$_2$ capture capacity after exposure to strident humid conditions [3, 18].

In the second part of this work, synthesis of layered metal organic frameworks was investigated. Layered materials are solids with strong in-plane chemical bonds and weak out-of-plane bonds, which are stacked to form 3D materials. Currently this field is expanding from layered clays, graphene, silicates to studies of layered MOFs [102]. Here, a layered MOF where each layer is composed of cobalt-carboxylate building units connected via organic ligands of benzene 1,4-dicarboxylic acid was synthesized. The
interlayer space provides the ability for introduction of additional ligands and simple post-synthesis interlayer ligand exchange with larger or smaller molecules. Such ligand introduction was performed using simple amine groups. It was found that crystalline materials could be generated with well-defined layers and addition of amine ligands might be exhibiting a templating role in the crystallization. This type of modification could open up chemistry of MOFs providing structures where both micropores and mesopores could exist and introduce a post-synthesis method of exchanging interlayer ligands therefore manipulating the gallery space between the layers. These layered MOF structures have a promising potential in CO$_2$ selective separation from mixed gas streams.

In the third part of the work, metal oxide nanoparticles were obtained utilizing structures of MOFs as precursor materials. It was found that crystalline cobalt oxide nanoparticles could be generated where particle size could be controlled with different calcination temperatures. The obtained nanoparticles also retained the original morphology of starting MOF crystals.
ACKNOWLEDGEMENTS

This has been a long, challenging, yet truly rewarding journey and I cannot believe I am nearly at the end of it. Many people have helped me throughout my graduate school at Northeastern University and I would like to take this special moment to say with all of my heart: THANK YOU!

- Thank you to my advisor, Professor Sunho Choi for believing in me and for giving me an opportunity in assisting in such an important task of setting up the research laboratory in the very beginning. It has been a truly rewarding experience. Thank you for guidance and support, for the constant words of encouragement even at the hardest of the times. I have learnt so much from you and I truly believe your guidance has made me a stronger and more confident researcher. Thank you for everything.

- Thank you to my committee: Professor Elizabeth Podlaha-Murphy, Professor Hicham Fenniri, and Professor Sanjeev Mukerjee. Thank you for taking time from your busy schedules to serve on my committee. I really appreciate it! Thank you!

- Thank you to my amazing labmates! Thank you, Christopher Cogswell, for your support, advice, and words of encouragement. Chris is one of the most positive people I know and I am so happy we got to become close friends doing research side by side for the last four years. Thank you, Zelong Xie, for all your help and support. Thanks to Yu Lei, Duy Le, Xiaodan Zhao who now have successfully graduated with Masters degrees and who I had an honour of working with very closely. Thanks to our undergraduate students for their help and for being careful and responsible with our experiments and instruments. There are too many to list but I will try…Rachel Vozikis, David Urick, Madeleine Finkenaur, Daniel Accetta, Lisa Chan, Becky Chinn, Justin Ramberger, Tom Nigl, and Liah Dukaye. It was a pleasure mentoring you! Thanks to all other students I got to collaborate with. Thanks to students from Professor Mukerjee’s lab for teaching me X-ray diffraction and FTIR operation and techniques.

- Special thanks for Rob Eagan, who was always there to help in any kind of situation, whether it was a safety question, instrumentation question, or just pure advice on setting up specific experiment. Thanks to William Fowle and Wentao Liang for teaching me the theory and operation of SEM, TEM, and HRTEM, for being patient, and for helping me to learn how take the best images I possibly can.

- Thanks to my parents for their constant unconditional support and love. Thanks for inspiring me to become an engineer, and for encouraging me to pursue my dreams! Thanks for being so brave and for deciding to send me to the United States to receive the best education I can. I would not be here if it weren’t for my parents in many ways. Thanks to my beautiful, inside and out, sister for her support and love! Thanks to my awesome friends, who stuck with me for the last few years and to new friends I made here at Northeastern! I highly cherish these friendships. Thanks to my boyfriend, Jonathan, for his constant support and love.
# Table of Contents

LIST OF FIGURES ..................................................................................................................... VIII

LIST OF TABLES ......................................................................................................................... XVI

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

2.0 CRITICAL LITERATURE REVIEW .......................................................................................... 6

2.1 Nanoporous materials and metal organic frameworks .......................................................... 6
   2.1.1 History of metal organic frameworks ............................................................................ 6
   2.1.2 Synthesis of metal organic frameworks ....................................................................... 12

2.2 Metal organic frameworks for carbon dioxide capture ......................................................... 14
   2.2.1 Structural modifications of MOFs for improved CO₂ capture .................................... 18
   2.2.2 Effect of the presence of water and corrosive gases on the performance of metal organic frameworks .............................................................................................................. 23

2.3 Layered metal organic frameworks ....................................................................................... 28
   2.3.1 Current examples of layered metal organic frameworks ............................................. 29
   2.3.2 Applications of layered metal organic frameworks ...................................................... 30

2.4 Metal oxides and applications ................................................................................................. 34

3.0 EXPERIMENTAL .................................................................................................................... 37

3.1 Materials synthesis and characterization ................................................................................. 37
   3.1.1 Hydrothermal synthesis of Mg/DOBDC MOF ................................................................. 37
   3.1.1.2 Experimental procedure for hydrothermal synthesis of Mg/DOBDC ......................... 38
   3.1.2 Modification of the Mg/DOBDC framework with functional groups for enhanced CO₂ capture ................................................................................................................................. 39
      3.1.2.1 Choice of functional groups .................................................................................... 39
      3.1.2.2 Experimental procedure for amine functionalization ............................................. 40

3.2 Synthesis of layered metal organic frameworks ..................................................................... 41
   3.2.2 Synthesis of CoBDC-HD MOF ....................................................................................... 41
      3.2.2.1 Experimental procedure for hydrothermal synthesis of CoBDC-HD ....................... 41
      3.2.2.2 Modified experimental procedure for hydrothermal synthesis of CoBDC-HD ......... 43
   3.2.3 Synthesis of CoBDC-ED MOF ........................................................................................ 43
### 3.2.4 Synthesis of CoBDC complexes in dimethylformamide

44

### 3.2.5 Ligand introduction to CoBDC complexes and further recrystallization

44

### 3.2.6 Calcination trials for conversion of MOFs to metal oxide nanoparticles

45

### 3.3 Characterization Techniques

45

#### 3.3.1 Structural characterization using X-ray diffraction (XRD)

45

#### 3.3.2 Transmission Electron Microscopy (TEM)

48

#### 3.3.3 Scanning Electron Microscopy (SEM)

50

#### 3.3.4 Surface area and pore size analysis

51

#### 3.3.5 Fourier Transform Infrared Spectroscopy

55

#### 3.3.6 Thermo-gravimetric analysis (TGA)

56

#### 3.3.7 Accelerated Steam Treatment Tests

56

#### 3.3.8 Carbon dioxide capture tests

57

#### 3.3.9 Energy Dispersive X-ray Spectroscopy (EDS) on the SEM

57

### 4.0 Results and Discussion

59

#### 4.1 Aim 1: Pore surface modification of metal organic frameworks for CO₂ capture in the humid conditions

60

##### 4.1.2 Structural and physical analysis of Mg/DOBDC metal organic framework

62

##### 4.1.3 Effect of amine functionalization on the crystallinity of Mg/DOBDC

67

##### 4.1.4 Effect of the amine functionalization on the porosity of the Mg/DOBDC

69

##### 4.1.5 FT-IR analysis of the amine functionalized Mg/DOBDC framework

70

##### 4.1.6 Effect of steam exposure on the crystallinity and porosity of bare and functionalized Mg/DOBDC samples

71

##### 4.1.7 Effect of steam exposure on the carbon dioxide capture in bare and functionalized Mg/DOBDC samples

78

##### 4.1.8 Conclusions and significance

83

#### 4.2 Aim 2: Design, synthesis, and characterization of layered metal organic frameworks

85

##### 4.2.1 Synthesis and characterization of CoBDC-HD framework

85

##### 4.2.1.1 Synthesis trials of CoBDC-HD framework

87

##### 4.2.1.2 Structural characterization of CoBDC-HD framework

92

##### 4.2.1.3 Attempts of activation of CoBDC-HD framework

122

##### 4.2.1.4 Decomposition profile of CoBDC-HD framework

131

##### 4.2.1.5 Chemical identification of CoBDC-HD

133

##### 4.2.1.6 Fourier Transform Infrared Spectroscopy (FT-IR) analysis of CoBDC-HD

133

##### 4.2.1.7 Carbon dioxide capture by CoBDC-HD framework

136

##### 4.2.1.8 Summary on the structure of the synthesized layered MOFs

137
4.2.2 Synthesis of other layered MOF materials based on different linkers .......... 139
  4.2.2.1 Structural characterization of the CoBDC-ED framework ...................... 139
  4.2.2.2 Structural characterization of the CoBDC-DD framework ...................... 146
4.2.3 Ligand Exchange in CoBDC-ED/HD MOFs ........................................ 148
  4.2.3.1 Synthesis conditions and characterization of linker exchanged CoBDC-ED
          (NEU-1) .......................................................................................... 148
  4.2.3.2 Synthesis conditions and characterization of linker exchanged CoBDC-HD
          (NEU-3) .......................................................................................... 150
  4.2.4 Conclusions and significance ................................................................ 153
4.3 AIM 3: CONVERSION OF METAL ORGANIC FRAMEWORKS INTO METAL OXIDE
          NANOPARTICLES ............................................................................. 155
  4.3.1. Conversion of CoBDC-HD MOF into cobalt oxide nanoparticles ................ 155
  4.3.2 Conclusion and significance .................................................................. 165
4.4 ONGOING STUDY: PRELIMINARY TRIALS OF FABRICATION OF THE GRAPHENE/MOF
          COMPOSITES .................................................................................... 167
5.0 CONCLUSION .......................................................................................... 172
6.0 RECOMMENDATIONS ............................................................................... 177
7.0 NOMENCLATURE .................................................................................... 181
8.0 REFERENCES .......................................................................................... 182
LIST OF FIGURES

Figure 1: The main constituents of metal organic frameworks [52]................................. 9

Figure 2: Summary of various interactions that could exist between connectors and linkers within metal organic frameworks [52]. .......................................................... 9

Figure 3: A crystal structure of MOF-5 where metal sites of Zn are shown in blue tetrahedral units and C and O atoms are in gray and red, respectively, and H atoms were omitted for clarity [78]. ........................................................................ 11

Figure 4: Experimental CO\textsubscript{2} uptake by various MOF frameworks at 0.1 bar and 293-298 K [117]. ........................................................................................................ 17

Figure 5: Reactions between molecules of carbon dioxide and monoethanolamine (MEA) and triethanolamine (TEA) molecules, the benchmark materials for current CO\textsubscript{2} technology. .................................................................................. 20

Figure 6: CO\textsubscript{2} isotherm at 25 °C for HKUST-1 with different pre-loaded amounts of H\textsubscript{2}O[71]. .................................................................................................................. 24

Figure 7: CO\textsubscript{2} isotherms at 25 °C for Ni/DOBDC samples with different pre-loaded H\textsubscript{2}O loadings [71]. ........................................................................................................ 25

Figure 8: CO\textsubscript{2} capacities of the dry Mg/DOBDC framework and regenerated samples after hydration of different levels [55]. ................................................................. 26

Figure 9: Schematics of the mixed matrix membranes with dispersed nanoporous solid particles (a) and layered nanoporous solid particles (b).[51] ......................... 32

Figure 10: Schematics of the potential structure of graphene-metal organic frameworks composite (MOF-5-GO).[90] ......................................................................................... 33

Figure 11: SEM micrographs of different shapes possible cobalt oxide nanoparticles [95, 113].......................................................................................................................... 35

Figure 12: Organic linker source, 2,5-dihydroxyterephthalic acid (H\textsubscript{4}DOBDC) .......... 39

Figure 13: Molecular structure of ethylenediamine (ED) molecule used as functional group for pore modification of the Mg/DOBDC MOF ........................................... 41
Figure 14: Molecular structure of organic ligands of terephthalic acid (a) and 1,6-hexanediame
Figure 15: Graphical representation of Braggs' law where atoms of the crystals serve as re
Figure 16: A representation of the Miller indices assignments based on the intercepts of th
Figure 17: Transmission electron microscope (TEM) JEOL JEM-1010.
Figure 18: Six classes of adsorption/desorption isotherms characteristic to solid materials (l
Figure 19: Quantachrome NOVA 2200e pore size and surface area analyzer.
Figure 20: Simple schematics of the setup for the accelerated steam treatment experiments.
Figure 21: Representation of processes occurring during the EDS analysis to the atom and its electrons [38].
Figure 22: Crystal structure of the Mg/DOBDC MOF. The metal sites of Mg are bonded to fiv
Figure 23: Representation of the unit cell of Mg/DOBDC and the plane of (2,-1,0) slicing the cell in h
Figure 24: Representation of the unit cell of Mg/DOBDC and the plane of (3,0,0) slicing the unit cell in three equal distances represent the distance of the half of the pore opening. (Image generated in Mercury software).
Figure 25: Reference XRD pattern of Mg/DOBDC MOF obtained by Kong et al.[56] (a) and XRD pattern of the material synthesized in this work (b).
Figure 26: Nitrogen adsorption and desorption isotherms of as-synthesized Mg/DOBDC framework.
Figure 27: Fourier Transform Infrared Spectroscopy (FT-IR) pattern of the as-synthesized Mg/DOBDC.

Figure 28: Schematics of the unit cell of Mg/DOBDC occupied with ED molecules with various loadings: a) 0 ED, b) 1ED, c) 3 ED, d) 6 ED, and e) 18 ED.

Figure 29: XRD profiles of the bare Mg/DOBDC (bottom) and ED-Mg/DOBDC (top).

Figure 30: Nitrogen adsorption-desorption isotherm for ED-Mg/DOBDC MOF.

Figure 31: FT-IR spectra of the Mg/DOBDC, ED-Mg/DOBDC, and ED-Mg/DOBDC after carbon dioxide and nitrogen adsorption. The dashed lines mark the peaks indicating presence of amines across all four samples.

Figure 32: XRD patterns of the original Mg/DOBDC and ED/Mg-DOBDC before and after steam treatment. The full XRD pattern of Mg/DOBDC is also provided.

Figure 33: BET surface area (a) and total pore volume (b) values of the original Mg/DOBDC and two ED-Mg/DOBDC samples with different amine loadings before and after steam treatment.

Figure 34: Nitrogen adsorption and desorption isotherms of steam treated Mg/DOBDC MOF (a) and steam treated ED-Mg/DOBDC samples (b).

Figure 35: CO$_2$ adsorption capture capacity (a) and initial CO$_2$ adsorption rate (b) of the original Mg/DOBDC and two ED-Mg/DOBDC samples before and after steam treatment.

Figure 36: Initial CO$_2$ adsorption capture curves of Mg/DOBDC and ED-Mg/DOBDC before and after steam treatment.

Figure 37: XRD patterns of the initial synthesis run (2), the synthesis run with pre-dissolved components (1), and synthesis without amine completely (3).

Figure 38: SEM micrographs of CoBDC-HD crystals at different magnifications.

Figure 39: XRD patterns of the synthesis runs of CoBDC-HD with higher amounts of terephthalic acid.
Figure 40: SEM micrographs of CoBDC-HD synthesis runs with 0.74:1 molar ratio (A and B) and 0.5:1 molar ratio of Co (NO₃) 6H₂O: H₂BDC.......................... 92

Figure 41: Schematics of the structure of CoBDC-HD framework.................................. 93

Figure 42: XRD pattern of the as-synthesized CoBDC-HD framework with interlayer peaks assignments................................................................. 95

Figure 43: Comparison of the XRD patterns between MOF-71 and CoBDC-HD frameworks. The red arrows indicate the matching peaks and CoBDC-HD characteristic peaks are in black. ................................................................. 98

Figure 44: The structure of MOF-71 composed of infinite rods of metal-oxygen-metal complexes which are further connected to each other by a benzene ring of the terephthalic acid generating a 3D structure shown on the right.[93].................. 98

Figure 45: XRD patterns of brown and purple solids of Co-BDC complex formed after 48 hours in the oven at 80 °C......................................................... 99

Figure 46: Transmission electron micrographs (TEM) of CoBDC complex. Layered structures with 3-4 nm interlayer distances are observed on the micrographs. ............................................................................................................. 99

Figure 47: High-resolution TEM (HRTEM) images of the layers observed in CoBDC-1 complex...................................................................................... 100

Figure 48: XRD patterns of CoBDC-1, MgBDC-1, and CuBDC MOFs after 1 day of hydrothermal synthesis in the solvent solution of dimethylformamide at 110 °C. .................................................................................................................. 103

Figure 49: Structural representation of the Mg₃(bdc)₃ layers parallel to the [1,0,1] plane (a) and the views of stacked layers along the b-axis (b). Orange polyhedral represent octahedral coordination of the magnesium metal sites. DMA molecules are not included. [24]................................................................. 103

Figure 50: XRD patterns of the MgBDC complexes after 1 day (b), 2 days (c), and 3 days (d) of synthesis. The XRD profile of Mg₃(bdc)₃(DMA)₄ is also presented for comparison (a). Similar characteristic peaks with the reference profile are indicated with a star. ...................................................................................... 106
Figure 51: A representation of one layer with shown DMF molecules coordinated to
terminal cobalt centers (a), and a view in the (1 0 1) plane where cobalt
clusters shown as polyhedrons connected via benzene rings og 1,4-
benzenedicarboxylate ligands (terephthalic acid ligands).[6]......................... 106

Figure 52: XRD profiles of the reported in the literature $\text{Co}_3(\text{BDC})_3(\text{DMF})_2(\text{H}_2\text{O})_2$ (a)
and CoBDC-3 complex synthesized in this work........................................... 107

Figure 53: XRD patterns of the CoBDC synthesized for 1 day (b), 2 days (c), 3 days (d),
and 4 days (e). XRD profile of the $\text{Mg}_3(\text{bdc})_3(\text{DMA})_4$ complex is also shown
for comparison................................................................. 108

Figure 54: SEM micrographs of the CoBDC-3 complex at high and low magnifications.
............................................................................................................ 108

Figure 55: XRD profiles of the $\text{Mg}_3(\text{bdc})(\text{H}_2\text{O})_2$ complexes obtained via vacuum drying
of the $\text{MgBDC-2}$ complex (b) and via resolvation of $\text{MgBDC-2}$ complex in
ethanol and air drying (c). The reference XRD profile is also presented (a).110

Figure 56: XRD patterns of the CoBDC-HD sample (a) and resolvated CoBDC-HD
sample in ethanol and then dried in ambient conditions (b)...................... 111

Figure 57: XRD patterns of the CoBDC-HD (a), heated at 200 °C CoBDC-HD (b) and
further resolvated in DMF CoBDC-HD (c).................................................. 112

Figure 58: XRD profiles of CoBDC-3 complex before (a) and after (b) resolvation in
ethanol and drying in air.............................................................. 113

Figure 59: Comparison of XRD profiles of the calcined at 350 °C $\text{Mg}_3(\text{bdc})(\text{H}_2\text{O})_2$
complexes and CoBDC-HD MOF. Stars indicate similar peaks.................. 116

Figure 60: XRD profiles of CoBDC-3 complex before (b) and after (c) addition of 1,6-
hexanediamine and reheating. Profiles of CoBDC-HD (denoted as NEU-3 in
the figure) and $\text{Mg}_3(\text{bdc})_3(\text{DMF})_4$ are also shown for comparison......... 118

Figure 61: XRD profiles of CoBDC-3 (a), CoBDC-3 to which 1,6-hexanediamine was
added in the solution of DMF (b) and in the solution of acetonitrile (c), and of
CoBDC-HD (denoted as NEU-3 in the figure)........................................... 119
Figure 62: Comparison of the XRD profiles of NEU-3 and ZnBDC with peaks indicated for ZnBDC as they are and recalculated Miller indices for NEU-3 if terephthalic acid is in between the layers.

Figure 63: Structural configuration of Zn(bdc) complex where 2D layers are pillared with organic ligands of terephthalic acid.

Figure 64: XRD patterns of the as-synthesized CoBDC-HD before activation and after activation at four different temperatures. All temperatures were kept constant for 24 hours under vacuum.

Figure 65: Nitrogen adsorption and desorption isotherms of CoBDC-HD samples activated at six different temperatures under vacuum. Adsorption isotherms are presented in solid lines and desorption in dashed lines.

Figure 66: XRD patterns of the as-synthesized CoBDC-HD (denoted as NEU-3) and after methanol exchange and activation by heating at 100 °C and 180 °C.

Figure 67: XRD patterns of the materials synthesized in ethanol/acetonitrile, methanol/acetonitrile, and the original DMF/acetonitrile solutions.

Figure 68: Nitrogen adsorption and desorption isotherms of CoBDC-HD samples activated at four different temperatures. All temperatures were kept constant for 24 hours under vacuum.

Figure 69: EDS analysis of the CoBDC-HD crystals. The following elements were detected: cobalt, nitrogen, and oxygen. Platinum was also detected because of the platinum sputter coating used prior to the analysis.

Figure 70: Fourier Transform Infrared Spectroscopy (FTIR) spectra of the as-synthesized CoBDC-HD, Co-BDC complex, each of the organic linkers used, and metal source.

Figure 71: FTIR spectra of the CoBDC-HD synthesized using original recipe, 0.1 and 0.15 g of terephthalic acid.

Figure 72: FTIR spectra of CoBDC-HD samples activated at various temperatures.

Figure 73: XRD patterns of the as-synthesized CoBDC-HD with Miller indices assignments.
Figure 74: Simple schematics of the potential structure of CoBDC-ED framework. .... 142

Figure 75: SEM micrographs of CoBDC-ED crystals at various magnifications. ........ 142

Figure 76: TEM micrograph of CoBDC-ED crystal clearly showing layers within the structure of the framework. ................................................................. 144

Figure 77: Decomposition profile of CoBDC-ED framework. .............................. 144

Figure 78: EDS analysis of CoBDC-ED. Cobalt, nitrogen, carbon, oxygen were detected. Platinum is also detected due to the platinum coating using prior to the analysis ................................................................. 145

Figure 79: XRD patterns of as-synthesized CoBDC-DD framework, the sample after evacuation at 200 °C in the Schlenk line, and the sample additionally washed in the solution of dimethylformamide ............................................... 147

Figure 80: SEM micrographs of synthesized CoBDC-DD .................................... 148

Figure 81: XRD patterns of linker exchange trials with NEU-1 (CoBDC-ED) showing evidence of structural change from the original material of NEU-1 (CoBDC-ED). XRD patterns of NEU-1(CoBDC-ED) and NEU-3 (CoBDC-HD) are also provided for comparison .................................................. 150

Figure 82: XRD patterns of the white and brown solids resulted from the exchange trials of NEU-3 to NEU-1 along with patterns of NEU-3 and NEU-1 for comparison ...................................................................................... 152

Figure 83: XRD profile of the NEU-3 linker exchange trial with ethylenediamine. NEU-3 XRD profile is also provided for comparison .................................................. 152

Figure 84: XRD patterns of the CoBDC-HD (NEU-3) crystals used as a template for generation of cobalt oxides and calcination trials at six different temperatures. Peaks marked with a star belong to the cubic phase of CO$_3$O$_4$ nanoparticles. .................................................................................................................................. 157

Figure 85: SEM micrographs of the CoBDC-HD samples after calcination at four different temperatures for 24 hours under nitrogen flow .................................. 159
Figure 86: Comparison between SEM micrographs of the CoBDC-HD MOF before calcination (A) and after calcination at 250 °C under nitrogen flow (B). .... 160

Figure 87: Compositional analysis by EDS spectroscopy of CoBDC-HD sample treated at 250 °C. ..................................................... 160

Figure 88: TEM micrographs of the CoBDC-HD samples after calcination at 250 °C (A), 300 °C (B), 450 °C (C), and 500 °C (D). ........................................ 162

Figure 89: Nitrogen adsorption-desorption isotherm for a Co₃O₄ metal oxide sample calcined at 270 °C. The Barrett-Joyner-Halenda (BJH) pore size distribution is also presented........................................ 164

Figure 90: XRD patterns of two graphene/CoBDC-ED (NEU-1 in the figure) composites compared with XRD profile of CoBDC-ED only............................................. 168

Figure 91: Low angle XRD pattern of graphene/CoBDC-ED (NEU-1 in the figure) trials compared to the XRD profile of only CoBDC-ED and of synthesis run without amine completely.......................................................... 169

Figure 92: SEM micrographs of ammonia functionalized graphene (A,B), graphene/CoBDC-ED trial 1 without ED (C,D), and graphene/CoBDC-ED trial 2 with ED (E,F)........................................................................ 171
LIST OF TABLES

Table 1: Summary of the synthesis conditions used to obtain CoBDC-HD frameworks. 90

Table 2: Summary of porous properties of CoBDC-HD samples activated at various temperatures. ........................................................................................................................................ 123

Table 3: Summary of solvents used with their polarity values and boiling points for the solvent exchange experiments. ........................................................................................................... 127

Table 4: Summary of the pore characteristics after solvent exchange with various solvents. ........................................................................................................................................ 128

Table 5: CO₂ adsorption capacity values for CoBDC-HD materials activated at three different temperatures. ........................................................................................................................................ 137

Table 6: Summary of weight loss after calcination of CoBDC-HD at different temperatures. ........................................................................................................................................ 161

Table 7: Summary of chemical compositions of Co₃O₄ oxide nanoparticles after calcination of CoBDC-HD at two different temperatures. ............................................................. 163

Table 8: Porosity characteristics of the cobalt oxide nanoparticles. ......................... 165
1.0. Introduction

Metal organic frameworks (MOFs) are a new class of hybrid materials where inorganic and organic counterparts form single-phase crystalline materials. These frameworks are also sometimes called porous coordination polymers or coordination networks. The material is composed of metal nodes, which could be represented by metal ions, metal centers, or metal clusters; and organic ligands, which play the role of linkers between those metal nodes. The interest in these materials was sparked in the 1990s with hundreds of these frameworks now known. Such interest in MOFs is related to their unique properties. MOFs are crystalline and highly porous materials with accessible pore surfaces. With a high variety of metals and organic ligands counterparts, the possible combinations of MOFs are seemingly infinite. These are self-assembled crystals, so controlled synthetic procedures are required to obtain high quality crystals and permanent porosity of the frameworks is not always guaranteed. As for known MOFs, exceptionally high permanent porosity (up to 5000-6000 m$^2$/g in surface area), low density, and simplicity of methods to introduce various functional groups have been observed [61, 82, 94].

Because of the unique properties of MOFs, such as high porosity and tunable chemical and physical properties, these materials have been widely studied for gas separation and storage and could be promising in the fields of electrically active materials and biomedicine. Rising CO$_2$ concentrations in the atmosphere are thought to be a main contributor to average global climate change and systems to capture and store carbon dioxide are needed [17]. One of the largest classes of point sources of CO$_2$ emissions are
coal burning power plants, leading researchers to focus on capture from these facilities. Decarbonization of flue gas from the post-combustion process via adsorption onto porous solid media such as metal organic frameworks (MOFs) has shown their effectiveness among a variety of carbon mitigation technologies [17, 104]. Some other porous solid materials include zeolites, activated carbon, and mesoporous silica materials. Compared to other porous solids, metal organic frameworks exhibit one of the highest CO₂ capacities at atmospheric pressures. The unique structural characteristics of MOFs discussed previously coupled with the presence of nanopores has led to the screening of MOFs for CO₂ capture. MOFs demonstrated competitive CO₂ adsorption capacity under conditions that simulate the CO₂ concentration in flue gases (10-15% partial pressure) however tend to degrade when exposed to humidity. There are few different hypotheses exist about why MOFs undergo loss in capture capacity after exposure to steam [67, 68, 71]. One of the hypotheses states that MOF undergo structural degradation due to the adsorption of water molecules, which weakens metal ion-linker bonding leading to collapse of the structure. Another hypothesis suggests during adsorption from simulated flue gas, water molecules are preferentially adsorbed onto open metal sites, decreasing uptake of CO₂. While highly promising, MOF structures still need to be modified to withstand practical conditions for CO₂ capture. In order to utilize unique properties of these materials and high adsorption capacity values for CO₂, structural modification was performed on the known MOF structures to demonstrate these materials are highly versatile and their structures could be tailored for targeted applications. The first part of this dissertation investigates how known structures of MOFs could be modified for improved stability in the humid conditions. Specifically, a well-known framework of
Mg/DOBDC was chosen as a porous platform and modified at the metal sites with amine groups [115]. Liquid amines are currently the benchmark materials for carbon dioxide capture, however these materials require high energy input for regeneration and cause corrosion of the instrumentation. To this end, this work investigates how high capture properties of liquid amines could be coupled with porous solid adsorbents, which capture gases primarily via physical adsorption and require less energy to regenerate and utilize in multiple cycles of adsorption [2, 3, 17].

While known structures of metal organic frameworks show very high surface areas (up to 7100 m²/g), low density (0.13 g/cm³), interconnected pores in all three dimensions, there still is not any strategies on synthesis or design of these materials [87, 100]. Researchers start from metal sites and organic ligands with at least two coordination sites, however often times, undesired products or amorphous phase materials are formed as a result. The formation of highly crystalline porous materials is very dependent on synthesis conditions, reactants concentrations, pH of the solutions, and many other small details. In this part of the dissertation, synthesis of layered metal organic frameworks is investigated as a potential strategy for predictable structures of MOFs. Ultra thin layered materials are generally highly desirable for separation and catalysis of large molecules. These materials could potentially be used in polymer composites for creation of efficient membranes where size selective CO₂ separation from mixed gas streams could be possible. Layered materials offer an ability for modification of their interlayer spaces which was performed for layered solids such as AMH-3 and MCM-22P. The interlayer spaces in these materials were increased by introduction of longer organic molecules in the process called swelling by Kim et al [50]. In such way,
the pore dimensions within these materials were changed. Such structural modification could also be applied in layered metal organic frameworks. If synthesized properly, the interlayer distance could be changed by introduction of molecules of different lengths and properties. This could potentially provide control over pore size of MOFs. Also, synthesis of new frameworks *de novo* would not be required to achieve desired pore dimensions. Inspired by mesoporous silicate materials like MCM-22P and AMH-3, in this work it was attempted to generate layered MOFs with an interlayer spacing that could be controlled via ligand exchange. Control over MOF structure would be beneficial to this area of research as new structures could be formed and desirable molecules could be introduced for any targeted application. It would be highly helpful to build a structure with interchangeable constituents. This would potentially provide easier control over the pore dimensions available in the frameworks and open up opportunities to build new structures. In this work, cobalt and magnesium based MOF structures were synthesized. Simple amine organic molecules were used as potential pillaring linkers in one-pot synthesis as well as in two-step synthesis. It was found that pillaring or templating the structure molecules could be introduced after the synthesis of layers. The structures of the obtained frameworks were characterized and hypotheses made on the possible roles of the amine linkers in the structures.

Based on the cobalt-based frameworks synthesized here, further fabrication of metal oxides was studied. Currently, cobalt oxides are receiving a lot of attention due to their properties such as high surface area to volume ratio, high theoretical capacitance values, working as magnetic p-type semiconductors. These properties makes these materials useful as heterogeneous catalysts, electrochromic devices, solid state sensors,
etc [66, 75, 95]. It is also known that fundamental properties of cobalt oxides are
dependent on their phase, crystallite size, size distribution, and specific surface areas. To
this end, there are many different shapes that have been achieved for cobalt oxides
including polyhedrons, nanosheets, and microspheres. Based on the different shapes of
these nanoparticles different surface areas and electric properties were observed. Some of
the challenges with these materials are unpredictable shape and non-uniform size
distribution. In this part of the dissertation, a “top-down” approach for synthesis of these
materials was investigated where fabrication from superstructures of metal organic
frameworks via one-step process with controlled heating was performed. Such strategy
has been previously applied to other MOFs but not to layered materials. Therefore, it was
interesting to investigate what type of structures of cobalt oxides could be obtained. It
was hypothesized that such approach of generating metal oxides from periodic structures
of metal organic frameworks would provide controlled evaporation of species and
formation of uniform particles. Also, it was interesting to look at how the overall
morphology of the original MOF structures changes or stays preserved.

This dissertation work as a whole provides an investigation onto how the
structures of metal organic frameworks could be modified for targeted applications. A
simple modification at the metal sites provides better stability of the materials for
practical CO₂ capture. A strategy for generation of multiple MOF structures based on the
layered geometry is proposed which could open up a new chemistry for these materials
and make them applicable for a wide range of applications. Lastly, an easy approach of
generating uniform metal oxide nanoparticles from MOF structures is investigated.
2.0 CRITICAL LITERATURE REVIEW

2.1 Nanoporous materials and metal organic frameworks

In the last few decades porous solids have been extensively studied for various applications including gas separation and purification, catalysis, biomedicine, and photovoltaic materials. Nanoporous materials are considered to be materials with pores of diameter of two nm or less, mesoporous materials with pores between two and 50 nm, and macroporous materials have pores higher than 50 nm in diameter [32]. One of the challenges scientists faced a while back is the lack of large pores among the properties of materials present at that time. Large pores (~10 Å) could be highly beneficial for catalytic applications and presented high potential for gas storage. The solution has come in the face of a new class of hybrid organic-inorganic materials, commonly known as metal organic frameworks (MOFs) [36, 79, 105]. These materials as well as any other porous materials have unique features such as pores suitable for storage, accessible inner surface beneficial for catalysis; these materials may also exhibit useful conductive, optical, and magnetic properties [36]. And due to the chemical tunability of those materials, if not present already, electric and physical properties can be introduced to these hybrid nanostructures.

2.1.1 History of metal organic frameworks

Before MOFs, there were two main classes of porous materials, inorganic and organic. Some representatives of inorganic class were aluminosilicates (zeolites), aluminophosphates, and activated carbons of organic class [53]. The hybrids between inorganic and organic materials, also known as porous coordination polymers (PCPs) or metal organic frameworks (MOFs) first appeared in the period of mid-late 1990s [53].
Since its discovery, the novelty of MOFs and its applications have become a fast growing research area. Several reviews on the topic have been published in recent years by pioneering researchers in this field, Ferey [34], Kitagawa [52], Rowsell [94]. To this date the number of identified MOFs has reached hundreds [21].

The main structure of metal organic frameworks consists of connectors and linkers that make up the main crystalline 3D compounds (Figure 1) [51]. The connectors are usually represented by the metal ions which could have multiple functional sites and depending on the oxidation state of the metals there could be up to 7 of sites for connections. The linkers are usually represented by organic molecules which could also posses multiple sites for linking to the connectors, or metal ions. There are also other components such as solvent molecules that could be present in the frameworks and could occupy metal-connectors sites. Usually after removal of the guest solvent molecules, the metal sites are open and could improve gas adsorption, catalytic properties, and sensing properties of the resulting compounds [52]. Due to the variety of the existing metal ions and organic ligands with multiple connecting sites, various combinations of metal organic frameworks could be potentially obtained.

The underlying science behind design of the MOF structure is reticular chemistry which studies design of materials constructed from secondary building blocks (SBUs) [105]. Cationic metal containing polyhedra, clusters, nodes, chain layers structures usually constitue SBU's and represent inorganic part of MOFs. Organic part is generally represented by polycarboxylates, polyphosphonates, imidazolates, polypyrazolates, and polytetrazolates which have anionic O or N donors [35, 105]. Due to high selection of
building blocks and linkers, different constructions are possible based on their nature and assembly [79].

The unique properties of MOFs that make them outstanding over other porous materials (zeolites, mesoporous silica, etc.) include crystallinity, high permanent and uniform porosity (BET surface area of 1000-3000 m²/g), accessibility of pores, and furthermore ease of chemical tunability. Physical and chemical properties could be manipulated according to the specifications of the targeted application. Here are the most common ways MOFs structures could be changed:

- by changing metal sites which could result in the change of coordination bonds
- by replacing organic linkers with longer or shorter organic ligands which could result in the pores of various sizes
- by adding functional groups to the main structure at either metal sites or organic ligand sites and by that introducing certain properties towards targeted applications

Kitagawa and Matsuda described structure of nanoporous materials as if they have walls composed of atoms and molecules that could be manipulated by changing their shapes and components [53].

Organic linkers could vary in sizes and chemistry creating infinite possibilities for potential MOF structures. Chemical versatility in this case could be both beneficial and broad giving a class of MOFs advantage over other nanoporous materials.

To give a general overview on currently known MOFs, few early reported and exceptionally highly porous materials will be discussed here.
Figure 1: The main constituents of metal organic frameworks [52]. Reprinted with permission from Ref. 52. Copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA.

Figure 2: Summary of various interactions that could exist between connectors and linkers within metal organic frameworks [52]. Reprinted with permission from Ref. 52. Copyright 2004 WILEY-VCH Verlag GmbH & Co. KGaA.
Some of the main routes of binding between connectors and linkers are coordination bonds. However as can be seen in Figure 2 other interactions like hydrogen bonding, metal-metal bonds, and the mixture of various other bonds (π-π interactions, CH- π) could be present within frameworks [52].

In 1999, Yaghi et al. reported a structure of highly porous and thermally stable MOF-5 framework, structure of which is shown in Figure 3 [31, 59, 78]. It was constructed from 1,4-benzenedicarboxylic ligands, which were connected to tetrahedron clusters of zinc (II) atoms. The material was stable when heated and kept isothermal at 300 °C for 24 hours while also having a density of 0.59 g/cm³. In addition, high porosity (Langmuir surface area: 2,900 m²/g) and high total pore volume (Dubini-Radukhvich model: 0.61-0.54 cm³/cm³) were reported overcoming properties of zeolites. MOF-5 was further extended by addition of functional groups resulting in materials with the same topology and cubic structure but highly suitable for methane storage [31].

Another highly porous MOF, MOF-177, showed high uptakes for hydrogen storage applications [111]. MOF-177 (Zn₄O (1,3,5-benzenetribenzoate)₂) is composed of octahedral Zn(II) clusters of atoms which has total of six coordination sites and connected to BTB organic ligands resulting in low density material with Langmuir surface area reaching about 4,500 m²/g and pore volume of 1.59 cm³/g (Dubini-Radukhvich equation) [12]. Highly porous nature of this material allowed incorporation of 16 dye molecules per unit cell occupying 40% of the crystalline material for one type of the dye, but not allowing another dye molecule indicating high potential for separation processes by molecular size. Other early MOFs designed by Ferey et al. in 2002, chromium (III) dicarboxylates named MIL-53 MOF derivatives. MIL-53ht and MIL-53lt
were reported to have permanent porosities with Langmuir surface areas of 1500 m$^2$/g and 1150 m$^2$/g from nitrogen adsorption isotherms, respectively [83, 96]. A little later in 2005, another material, MIL-101, based on Cr metal center was synthesized by the same group. This MOF was made out of chromium metal centers connected by H$_2$BDC organic linkers resulting in cubic cell structure with cell volume of about 702,000 Å$^3$ and Langmuir surface area of about 5900 m$^2$/g [37]. Accessible pores allowed the introduction of anions into the structure therefore creating a charged MIL-101 MOF opening up opportunities for the future uses in gas storage and drug delivery [37]. These are only few examples of highly porous MOFs.

![Figure 3: A crystal structure of MOF-5 where metal sites of Zn are shown in blue tetrahedral units and C and O atoms are in gray and red, respectively, and H atoms were omitted for clarity [78]. Reproduced from Ref. 78 with permission of the Royal Society of Chemistry.](image-url)
2.1.2 Synthesis of metal organic frameworks

In practice, most of the nanosized materials are built by chemical self-assembly and result in organized structures. Metal organic frameworks are also self-assembled by coordination bonds under mild conditions. In terms of strength, coordination bonds are in between covalent bond and hydrogen bonds [53]. Metal organic frameworks also sometimes called porous coordination polymers (PCPs) or inorganic-organic hybrids polymers.

For the choice of metals, usually transition metals used a lot due to the presence of multiple functional sites available for coordinative attachment to the ligands. In 2007, Gerard Ferey published an introductory review about metal organic frameworks, its synthesis routes and perspective applications [34]. He describes how MOFs can be obtained by using di-, tri-, or tetravalent cations. In the synthesis of MOFs few factors are critical in order to obtain high quality crystalline material. Temperature of the reaction can considerably affect coordination of metal sites, nucleation rates, and dimensionality of the resulting material. For instance, dimensionality of cobalt (II) succinates increased with increase in reaction temperature. Starting materials for synthesis evidently carries importance, metallic salts differ only in the anion of the salt can change the nature of the resulting material. In other words, foundational nature of the ions in the metal salts based on their acidity or basic character could define the resulting structure in greater way than the choice of organic ligands.

Many different organics have been considered for the choice of organic linkers. Depending on the targeted application the choice can become limited. For example, for
bio applications, materials biologically stable and acceptable could be chosen: amino acids and peptides have been considered for such applications [13].

Design of MOFs, as mentioned previously, is based on reticular chemistry. O’Keeffe [88] proposed an augmented nets, while Ferey [33] approached it through the secondary building units (SBUs). But chemical tunability of MOFs not only comes from the variety of components to choose from, but also from various modifications of the structure with functional groups. Due to high permanent porosities of MOFs, functionalities could be added onto the pore surfaces after synthesis of the main structure of MOF. Such modification has been investigated after porous structure of MOF was achieved and is called post synthetic modification.

Synthesis of MOFs is quite tricky. Certain conditions that would result in a crystalline material and would preserve integrity of the building blocks are required. The most commonly used synthetic route to make MOFs is hydrothermal synthesis. In this synthesis, metal salt and organic component undergo reaction under anywhere from room temperature to 250 °C from 12 to 48 hours [61]. The solution is heated under autogenous pressure, which is provided by putting the mixture inside Teflon-lined stainless steel container, commonly Parr bombs are used. It should be noted that even slight changes in concentration, pH or temperature could produce low quality crystals. Another important aspect in the synthesis of MOFs is removal of solvent molecules from the frameworks without damaging materials structure. Scientists were also able to obtain MOFs crystals through microwave synthesis, sonochemical and mechanochemical synthesis, but hydrothermal synthesis still stays to be a predominant route for generation of high quality MOF crystals.
2.2 Metal Organic Frameworks for Carbon Dioxide Capture

Carbon dioxide is one of the greenhouse gases and was recognized as a significant contributor to the rise in average global earth temperature causing climate change [76,92]. Furthermore the United Nations Intergovernmental Panel of Climate Change claims that a significant reduction by 50% of current carbon dioxide emissions is required to avoid global average temperature rise of 2-2.5 °C by the year of 2050 [76,92]. Carbon capture and storage (CCS) showed to be one of the most promising technologies to reduce future CO₂ emissions. Currently there is an urgent need to show CCS in action and take it to the large scale [76]. This technology mostly applies to the large CO₂ emissions sources such as coal fired power plants, refineries, and other large industrial plants [76]. Physical adsorption onto solid porous materials is one of the technologies used in CCS for the CO₂ capture from flue gas after combustion process and MOFs were and still are considered as strong candidates [63].

Adsorbents operating mainly on physisorption processes are known to be the most economical and perspective for capture and separation of greenhouse gases, such as CO₂ and CH₄. Other porous solids such as zeolites, activated carbon, and mesoporous silica have been considered as well, but these materials faced constrains of low CO₂ uptake capacities and demanding conditions for material regeneration [70].

Keskin [49], Ferey [35], D’Alessandro [22, 103], Li [60], Wang [109], Jones [46], Bae [5] all published excellent review papers describing performance of metal organic frameworks for carbon dioxide capture applications. With the variety and depth of research on this subject, few distinctive groups of MOFs have become the most promising.
The question about how adsorption and storage processes happen in the frameworks was discussed in the paper by Ferey et al.[35]. Properties for an ideal adsorbent were described and included the following: stability towards thermal stress, presence of humidity, cyclic operations of adsorption and desorption, presence of accessible pores, high specific surface areas and furthermost available adsorption sites; synthesis under mild and economically affordable conditions. It could be seen that metal organic frameworks with some structural manipulations and additional stability tests might just become an ideal candidate for this application. Some other issues to be addressed include selectivity of CO₂ gas molecules over N₂ molecules, which also partially constitute flue gas stream after combustion processes.

There is one other unique feature, which makes some MOFs more applicable for gas storage than others. Some frameworks possess unsaturated metal centers (UMCs), also sometimes referred to as coordinative unsaturated metal sites (CUSs) [69]. The CUSs provide adsorption sites for guest gas molecules and also present a site for various functionalizations which could be performed without changing the main structure of MOFs [39]. Dietzel et al. showed through X-ray diffraction and IR-spectroscopy studies on Ni₂(dhtp) MOF that CO₂ molecules do indeed strongly bond to the open Lewis acid sites of nickel metal centers [29]. These open metal sites are usually generated after the material activation step, where solvent molecules or axial ligands of metal atoms are removed [71].

Carbon dioxide appears in the flue gas at low partial pressures constituting about 3-16% by volume at ambient conditions creating a requirement for good gas selectivity during adsorption [115]. CO₂ capture by MOFs was both analyzed at high and low
pressures. Yaghi et al. first screened nine materials at the pressures of up to 42 bar where MOF-177 showed exceptionally high capture [84]. MOF-177 at 35 bar outperformed zeolite 13X and activated carbons, which are commonly referred to as benchmark materials in physisorptive adsorption of CO$_2$. Nevertheless, the point of interest in the pressure range is not 35 bar but rather atmospheric pressure with low CO$_2$ partial pressure, about 0.1 bar. Yazaidin et al. in 2009 screened 14 MOFs for CO$_2$ capture at low pressures [115]. Interestingly, it was found that materials that showed high CO$_2$ capacity at high pressures performed quite poorly at low pressures, some examples for those being the same MOF-177 and IRMOF-1. Rather materials with open metal sites, HKUST-1, UMCM-150 and M/DOBDC, performed well at the pressure point of interest.

Specifically, M/DOBDC series of MOFs, with metal centers of Mg, Co, and Ni and dioxybenzenedicarboxylate (DOBDC) organic linker presented competitive capacities at 0.1 bar and temperatures between 273-298 K. Caskey et al. in 2008 has synthesized a new metal organic framework, Mg/DOBDC from M/DOBDC series by switching previously used transitional metals (Ni, Co, Zn) with Mg metal site [11]. To this day, Mg/DOBDC MOF still is the best CO$_2$ adsorbent from the flue gas at low partial CO$_2$ pressures [9, 28, 77, 106, 112, 115] as can be seen in Figure 4. One of the reasons believed why this material performs so well is highest availability of unsaturated metal sites at Mg$^{2+}$ metal centers [9, 11, 28, 67, 101]. A few recent nuclear magnetic resonance (NMR) studies have been performed to study the interactions between Mg/DOBDC and CO$_2$ molecules [57, 65, 72]. In one such study on CO$_2$ dynamics in the Mg/DOBDC framework, a strong physical adsorption onto the framework was observed via NMR experiments, where CO$_2$ molecules bonded with Mg$^{2+}$ sites via end-on coordination.
through one of its oxygen atoms [9, 57]. Another interpretation of NMR results suggests CO₂ hopping movements between metal sites, which could affect diffusion of CO₂ through the framework [65].

![Graph showing CO₂ uptake by various MOF frameworks](image)

**Figure 4**: Experimental CO₂ uptake by various MOF frameworks at 0.1 bar and 293-298 K [117]. Reprinted with permission from Ref. 117. Copyright 2009 American Chemical Society.

Adsorption capacity is one of the most important criteria for the evaluation of CO₂ adsorbent. It refers to amount of gas adsorbed at the specific CO₂ partial pressure, and in order to be competitive with current benchmark materials, MEA chemical absorbents, capacity should be about 3-4 mmol/g or higher.

Another important aspect for the adsorbent is its ability to capture CO₂ over other gases such as N₂, CH₄, SO₂, NOx, and others, which are present in both flue gas and ambient air. An adsorbent’s selectivity for CO₂ gas molecules over other gases is
important and could also affect the choice of metal ions in the framework. For instance, interactions between quadrupolar molecules of CO$_2$ and N$_2$ and the polar groups present in the material will affect the heat of adsorption and amount of CO$_2$ captured by the material.

A more recent screening of eight MOFs was reported by Han et al.[42]. In this study, an emphasis was put on CO$_2$ adsorption performance in terms of selectivity over other gases and their stability against corrosive gases, SO$_2$ and NO$_2$ present in the flue gas streams. While most MOFs screened didn’t show decrease in CO$_2$ uptake after exposure to the 79% relative humidity air stream, exposure to acid gases had dramatically worsened performance. About 54-55% decrease in CO$_2$ uptake was reported for Zn/Co-BTEC MOF and 10-20% reduction was reported for ZIF-90, ZIF-8, ZIF-7, Co-NIC, and Ni-HF MOFs in both CO$_2$ capacities and selectivity over N$_2$ gas. Out of these materials, ZIF-90 and Zn/CO-BTEC MOFs showed material degradation in structure. The only Zn-TTC showed a minor increase in the uptake but the material based on XRD results might have structurally changed after acid gases exposure [42].

2.2.1 Structural modifications of MOFs for improved CO$_2$ capture

One of the biggest advantages of metal organic frameworks is the chemical and physical tunability of their structures, which can be altered by changing the synthesis conditions or initial counterparts used to generate MOF. This allows for the structure to be optimized for the application of interest. However, it is also possible to change the chemical and physical properties of the material through post-synthetic modifications. Post-synthetic modifications have an advantage of preservation of the main topology of the framework, so in other words modification could be done without changing main
properties of the material too much. In the case of carbon capture, the performance of a specific MOF can be further altered by the introduction of functional groups into the structure of the framework.

Alkanolamine-based materials are currently considered to be benchmark materials for CO₂ capture from flue gas due to their high affinity towards CO₂ gas molecules. These aqueous amines remove CO₂ from flue gas streams through absorption and stripping processes. During regeneration the amines are exposed to water vapor at high temperatures (100-120 °C) [92]. The good performance of these materials could be attributed to the interactions in the chemisorption regime between the absorbent material and absorbate gas. Monoethanolamine (MEA) is one of the most commonly used aqueous amine currently used for CO₂ capture and its reaction with CO₂ is shown in Figure 5. It can be seen that as a result of the reaction, a C-N bond is formed resulting in carbamate. One of the drawbacks of this approach is further regenerability of the amines, since this type of chemisorption requires a high-energy input to break the newly formed bond and release CO₂ molecules.
Depending of the type of the amines used in the presence of water molecules, bicarbonates and carbonates may form which would involve more CO₂ molecules resulting in the higher CO₂ capture uptake [109]. As shown in Figure 5 to capture one molecule of CO₂, only one molecule or triethanolamine (TEA) is required as opposed to two molecules of monoethanolamine (MEA).

While CO₂ capture might be effective due to chemisorption, the high energy input required to regenerate aqueous solutions of amines due to the high heat capacity of water (4.2 kJ/(kg-K) present in the mixture leads to the need for a more energy efficient capture system [17]. Amines are also susceptible to thermal and oxidative degradation which could lead to corrosion problems and material volatilization [92]. Porous solid adsorbents are less energy-intensive for regeneration and have the potential to be just as effective as amine solutions for the adsorption of CO₂. In order to combine amines high affinity for CO₂ with the benefits of using porous solid adsorbents for capture, amine functional
groups are often used for impregnation and modification of different nanoporous solids including metal organic frameworks [103, 119].

Demessence et al. grafted a pendant alkylamine group, ethylenediamine, onto the unsaturated metal centers of Cu$^{II}$ in the H$_3$[(Cu4Cl)$_3$- (BTTri)$_8$] MOF [25]. Compared to its non-functionalized derivative, en-MOF (ethylenediamine incorporated MOF) reached capacity of 0.366 mmol/g versus 0.277 mmol/g at low pressures of up to 0.06 bar, but reverse behavior observed above 0.1 bar. At low loadings higher heats of adsorption has been observed for modified framework (90 kJ/mol) indicating strong interactions of amines with CO$_2$. In addition, during cyclic processes of adsorption and desorption modified framework of Cu-BTTri showed stable CO$_2$ capacity under mixed gas stream flow (15% CO$_2$ in N$_2$) for adsorption and desorption under nitrogen gas only [25].

An enhanced capacity for carbon capture was observed in the amine functionalized CuBTTri (H$_3$BTTri = 1,3,5- tri(1H-1,2,3-triazol-4-yl)benzene) material. In this study, the N,N’-dimethylethylenediamine (mmen) molecule was incorporated into the structure. The resulting material exhibited a high porosity and CO$_2$ capacity of 2.38 mmol CO$_2$/g (9.5 wt%) at 25 °C under 0.15 bar CO$_2$/0.75 bar N$_2$ mixture. This incorporation resulted in a 3.5 times improvement in carbon dioxide capacity compared to the non-functionalized material [80]. The same MOF was functionalized with ethylenediamine by Long et al., leading to an increase in the CO$_2$ adsorption, with an uptake of 1.6 wt% versus 0.92 wt% uptake for the original material at a pressure of 0.06 bar [25]. The observed high heat of adsorption, about 90 kJ/mol, was indicative of chemisorption, which benefits selectivity towards CO$_2$ gas molecules. In addition, the
functionalized material maintained constant capture over a number of adsorption and regeneration cycles.

Another mmen-functionalized material, mmen-Mg\(_2\)(dobpdc) (dobpdc\(^{4-}\) = 4,4’-dioxido-3,3’-biphenyldicarboxylate), was reported to have good adsorption capacities both at ambient air conditions of 2.0 mmol/g (8.1 wt%) (0.39 mbar and 25 °C) and 3.14 mmol/g (12.1 wt%), and at flue gas capture conditions (0.15 bar and 40 °C) [81]. A related material, Mg/DOBDC, has also undergone surface functionalization with a similar molecule, ethylenediamine (ED), and has a reported stable capacity of 1.51 mmol CO\(_2\)/g under simulated ambient air conditions (400 ppm CO\(_2\)) over four adsorption/desorption cycles, compared to the non-functionalized material which showed a significant degradation of capacity over continued regeneration cycles [19].

In all three of these cases, amines are incorporated onto the uncoordinated metal sites of the framework, where one of the amine groups binds directly to the metal while the other amine group is free within the pore. This unbound amine is then free to interact with gas adsorbate molecules, which are introduced into the pore. Based on this principle, Cu\(_3\)(BTC)\(_2\) (BTC= 1,3,5- benzenetricarboxylate) metal organic framework has also been functionalized with ethylenediamine, 3-picolylamine and 4-picolylamine compounds to enhance the interaction of the framework with carbon dioxide molecules. It was observed that the 3-picolylamine and 4-picolylamine functionalized materials exhibit a higher adsorption at low-pressures than the ED-enhanced material. It was proposed that carbon dioxide molecules simultaneously interact with the amine groups and neighboring metal ions through acid-base Lewis interactions, holding CO\(_2\) molecules in the framework and thereby enhancing capture [85].
Functionalization with polar groups such as NH₂, OH, COOH, and CF₃ affect CO₂ capture in different ways depending on whether they are introduced during or after the synthesis of the original framework, as well as the characteristics of the MOF to be functionalized. Overall the incorporation of polar functional groups positively enhances CO₂ uptake ability by allowing for additional interactions with guest molecules, and the most commonly used and most effective polar groups for functionalization are NH₂ and COOH. When introducing functional groups into the pores of MOFs, one should also remember and account for potential decreases in pore volume, which could negatively affect CO₂ capture.

2.2.2 Effect of the presence of water and corrosive gases on the performance of metal organic frameworks

Stability towards humidity is vital for carbon dioxide capture from flue gas or dilute ambient air. Flue gas composition roughly consists of nitrogen, water, and carbon dioxide in the following weight ratios, N₂:H₂O:CO₂ = 6.5:1:1. In addition, depending on the nature of the flue gas, corrosive gases may also be present. In this section, important effect of the presence of humidity will be evaluated.

There are two different views established in the literature on the effects of water. Yazaydin et al. found that water molecules competitively adsorb onto open metal sites of MOFs, which then increases further CO₂ adsorption in Cu-BTC (HKUST-1) at 4 wt. % of water loading [116]. It was also found that when water loading is increased to 8 wt. %, the CO₂ capacity drops to less than CO₂ capacity achieved with dry sample. This was explained by pore blocking effect by water molecules. However the authors suggest, that small amount of pre-loaded water molecules could be optimized for the best CO₂ capture
scenario [116]. It was found that electrostatic interactions occur between CO$_2$ gas molecules and H$_2$O increasing not only capture uptake but also CO$_2$ selectivity over N$_2$ and CH$_4$ gases [116]. Another work by Liu et al. showed a small increase in CO$_2$ capacity as can be seen in Figure 6 when a small amount of water is pre-loaded onto the sample, and H$_2$O loadings up to 3.4 mol/kg do not have any effect on the CO$_2$ capacity [71]. On the other hand, for Ni/DOBDC a gradual decrease in capacity is observed with increasing H$_2$O loadings as can be seen in Figure 7 and dramatic decrease is observed for both frameworks at higher water loadings [71].

![Figure 6: CO$_2$ isotherm at 25 °C for HKUST-1 with different pre-loaded amounts of H$_2$O][71]. Reprinted with permission from Ref. 71. Copyright 2010 American Chemical Society.
Figure 7: CO$_2$ isotherms at 25 °C for Ni/DOBDC samples with different pre-loaded H$_2$O loadings [71]. Reprinted with permission from Ref. 71. Copyright 2010 American Chemical Society.

There is also a possibility that during exposure to water molecules, a bond between metal and organic ligand breaks initiating hydrolysis. As a result, ligand could be replaced by water resulting in the material degradation. Low et al. found that strong bond between metal oxide cluster and coordinated to it organic linker could improve hydrothermal stability of MOFs [73]. Greathouse and Alendorf demonstrated MOF-5 lattice collapse after exposure to 3.9% water via molecular simulations. This work identifies few routes for structure collapse with water exposure: H$_2$O comes in contact with Zn metal center replacing oxygen atoms from MOF framework with oxygen atoms from water molecules therefore decreasing coordination numbers of metal site and potential hydrogen bonding between water and the metal clusters [40].

Balbuena et al. studied through molecular modeling why sometimes water has positive effect (in case of HKUST-1 MOF) and other times negative effect (Mg/DOBDC
MOF) on the carbon dioxide capture. It was found that final uptake is defined by the competition of interactions between CO$_2$ and metal center and CO$_2$ and water molecule. For instance, in HKUST-1 CO$_2$ attracted to water more due to the presence of Coulombic interactions, but in Mg/DOBDC MOF CO$_2$ adsorption decreases with water introduction [118].

In additional experimental breakthrough experiments where mix of nitrogen, carbon dioxide, and water adsorbed onto Mg/DOBDC MOF porous solid, it was found that after exposure to 70% relative humidity CO$_2$ capture uptake decreases by about 85% for this material as can be seen in Figure 8. Another M/DOBDC MOF, Ni/DOBDC, demonstrated better stability by capturing 60% of the capacity captured in dry conditions [54].

Figure 8: CO$_2$ capacities of the dry Mg/DOBDC framework and regenerated samples after hydration of different levels [55]. Reprinted with permission from Ref. 55. Copyright 2011 American Chemical Society.
In different study by Liu et al., Ni/DOBDC again showed to retain its CO$_2$ capacity after the first breakthrough experiment to 94% of the initial capacity achieved. Worth noting that after breakthrough experiment with the mixed flow of N$_2$ and CO$_2$, adsorbent was regenerated by He purge flow without additional heating or pressure increase. Water effect was also investigated in the same study by breakthrough experiment where adsorbate gas was 15% N$_2$ and 85% CO$_2$ mixture which was pretreated with slight amount of water vapor. CO$_2$ capacity did decrease after humid gas exposure possibly due to the hydrophilic nature of Ni/DOBDC MOF [70]. Nonetheless, another MOF based on Cu-complex, water adsorption was shown to be almost fully regenerable without degradation in material structure and only with an insignificant decrease in carbon dioxide capacity [16].

According to the studies described above and some other studies about MOFs and their performance for CO$_2$ capture in the humid conditions in most of the times, water effect is important and could affect adsorption in negative ways. Since most of the MOFs are hydrophilic, tendency to adsorb water instead of desired gas is high. Therefore a new way to create hydro stable MOFs is required and would be vital for further consideration as adsorbent material to capture CO$_2$ from flue gas.

While there are quite a large amount of reports available about CO$_2$ adsorption under dry conditions, few under humid conditions, very minimal is known about materials degradation and their CO$_2$ adsorption performance under present traces of corrosive gases, such as SO$_2$. Belmabkhout and Sayari evaluated performance of amine functionalized porous adsorbent, mesoporous silica, by first exposing material to pure SO$_2$ gas at constant temperature, desorbing the same material under vacuum and then
introducing mix of CO\textsubscript{2}/N\textsubscript{2} gas to check for material integrity in CO\textsubscript{2} capacity [8]. The adsorbent has captured 3.9 wt % of CO\textsubscript{2} (versus 6.9 wt % for non-SO\textsubscript{2} treated fresh sample). It was postulated that incoming SO\textsubscript{2} gas might be coming in contact with amine groups and forming salts assigning to lower SO\textsubscript{2} capacity [8].

A more recent screening of eight MOFs was reported by Han et al. [42] In this study, an emphasis was put on CO\textsubscript{2} adsorption performance in terms of selectivity over other gases and their stability against corrosive gases, SO\textsubscript{2} and NO\textsubscript{2} present in the flue gas streams. While most MOFs screened didn’t show decrease in CO\textsubscript{2} uptake after exposure to the 79% relative humidity air stream, exposure to acid gases had dramatically worsened performance. About 54-55% decrease in CO\textsubscript{2} uptake was reported for Zn/Co-BTEC MOF and 10-20% reduction was reported for ZIF-90, ZIF-8, ZIF-7, Co-NIC, and Ni-HF MOFs in both CO\textsubscript{2} capacities and selectivity over N\textsubscript{2} gas. Out of these materials, ZIF-90 and Zn/CO-BTEC MOFs showed material degradation in structure. The only Zn-TTC showed a minor increase in the uptake but the material based on XRD patterns might have structurally changed after acid gases exposure [42].

While not much is currently known about corrosive gases influence on the integrity of MOFs, from these few reports available a negative effect was observed. Therefore, further studies required on the MOFs stability towards corrosive gases and investigation of routes for flue gas treatment prior to the CO\textsubscript{2} capture step.

2.3 Layered metal organic frameworks

A subclass of metal organic frameworks, layered metal organic frameworks, has recently gained attention due to the new potential chemical functionalities widening the
chemistry of metal organic frameworks more and opening potential for various applications.

### 2.3.1 Current examples of layered metal organic frameworks

There are currently few pillar-layered frameworks are known. Xuan et al. synthesized few frameworks where 1,1′-biphenyl-2,2′,6,6′-tetracarboxylic acid (H₄bpta) was used as a part of the layer, and bipyridine ligands of N-(4-pyridyl)-isonicotinamide (4-pna) and 1,2-bis(4-pyridyl)ethane) (bpy-ea) were used [114]. It was found that framework with 4-pna as a pillaring ligand showed higher surface area (413 m²/g for 4-pna based framework, and 51 m²/g for bpy-ea based framework) and CO₂ uptake than framework with bpy-ea potentially due to the framework flexibility of the latter. The better CO₂ capture uptake of the first framework was attributed to the presence of acylamide functional groups within the structure of the pillaring ligand which possibly make the framework more rigid and prevent flexibility [114].

Aggarwat et al. recently reported two frameworks where two dimensional layers were formed by Cd(II) ions and organic linker of terephthalate (tp) for framework 1 or 2-aminoterephthalate (atp) for framework 1 [1]. The 2D layers are pillared by the organic ligands of 4,4′-bipyridine. A transformation from non-interpenetrated framework to interpenetrated framework was observed after activation of framework 1 at 150 °C under dynamic vacuum based on the obtained XRD patterns. Such phenomena were attributed to the availability of space after guest solvent molecules are removed which creates potential for interpenetration. It was also mentioned that if solvent molecules support the framework by coordinating to the metal sites for example, upon removal molecules
undergo structural rearrangement. The initially generated coordination bonds could assemble or disassemble when solvent molecules are removed and coordination chemistry around metal site could be changed completely. For framework 2, the same transformation was observed at temperature of 270 °C which was attributed to the presence of amino group within the structure of 2-aminoterephthalate [1].

2.3.2 Applications of layered metal organic frameworks

There are many potential applications of layered metal organic frameworks. One of such application is MOF/polymer composites or mixed matrix membranes for gas separation. There are currently exist pure inorganic and pure organic membranes, and some cases of mixed matrix membranes (MMM) but only few studies on the MMM where metal organic frameworks are used. Some of the advantages of using MOFs for this application are presence of organic units, which could create good adhesion to polymers, presence of channels for selective gas diffusion, and fabrication of thin layers of the resulting membrane materials, which would increase gas permeability.

One of the examples of MMM with MOFs is ZIF-8 and PEBAX-2533 (polyether block polyamide (PEBA) resin) composite. ZIF-8, Zn(methylimidazolate)$_2$, was chosen due to its high stability and the presence of pores of 3.4 Å matching well with the kinetic diameter of CO$_2$ [86]. The resulting membrane was found to have a polymer layer with scattered inorganic particles and inorganic-based layers connected by polymer chains [2, 86]. The new structural configuration was observed to have increased permeability of CO$_2$ for both dry and humid feed gases with increased loadings of ZIF-8, but also showed a slight decrease in CO$_2$/N$_2$ selectivity [86]. At this stage, the development of MOF
membranes for carbon dioxide capture has yet to mature [61]. Most of the results are based on calculations and simulations, and it is yet to be seen if experimental results will confirm these findings [2, 4, 58]. For mixed matrix membranes to become the next adsorbent materials for carbon dioxide capture, very high surface area membranes with high permeability are needed [2, 30]. This could be achieved potentially through the incorporation of microporous and flexible metal organic frameworks.

While there are some examples of MMMs with MOFs, there are no reports of the incorporation of layered MOFs into MMM. However, there is a report of other nanoporous layered silicates AMH-3 embedded into a cellulose acetate (CA) [51]. A small thickness and high aspect ratio embedded into a polymer composite could provide improved features such as better separation of gases with a minimum amount of nanoporous layered material used. Because of the high aspect ratio of the layers, where the length of layer is much higher than the thickness of the layer, the diffusion of larger molecules would inhibited and would be forces to travel around the edges of the layers. At the same time, molecules of the smaller size would be allowed to diffuse through the pores present within the layers, as pictured in Figure 9 [51]. The fabricated membrane with exfoliated layers of AMH-3 showed an improved CO₂/CH₄ separation with only about 2-6 wt% loading of nanoporous AMH-3. The small loadings of AMH-3 particles could also eliminate the possibility of particle aggregation and enhance interactions between polymer and incorporated particles [51].
Combination of unique properties of layered structures, introduction of pore channels, and organic nature of metal organic frameworks establishing good interactions with polymers makes for a potentially highly effective membrane for gas separation.

Another application of layered metal organic frameworks are graphene/MOFs composites. Graphene materials are known for the their structural, mechanical, and electronic properties. Graphene layers consist of carbon atoms uniformly arranged into a 2D sheet generated from the bulk graphite. However oxidation of graphite causes graphene layers to exhibit defects due to the presence of oxygen atoms and vacancies. Graphene-MOFs composites could create a highly conductive materials, could be applied in adsorption processes and heterogeneous catalysis because of the presence of transition and noble metals in metal organic frameworks [90]. Petit et al. in 2009 fabricated one of the first MOF-graphene composites based on the MOF-5. The potential structure or growth of the resulted composite is presented on Figure 10. It can be seen from the Figure 10 that metal organic framework is first attached to a single layer of GO by the epoxy groups present on the surface of the GO layer. The further attachment of another
GO layer could be due to the epoxy groups and carboxylic acid groups also present on the surface of GO. It was also found that BET surface area of the MOF-5 is preserved with a slight decrease at higher GO loading [90].

Figure 10: Schematics of the potential structure of graphene-metal organic frameworks composite (MOF-5-GO).[90] Reprinted with permission from Ref. 90. Copyright 2009.

There are currently more studies available on MOF-graphene composites and addition of layered metal organic frameworks-graphene composites would open up new opportunities and applications. It is believed that thin layers of MOF material could be grown on the layers of graphene sheets.
2.4 Metal oxides and applications

Metal oxides have been intensively studied for their chemical and physical properties and potential applications in sensor, catalysis, and energy conversion [64, 74]. The unique properties of oxides involve large specific surface area, good electronic conductivity and showed good potential as catalytic materials [99]. There are generally two main ways to obtain well-defined nanostructures of metal oxides: bottom up and top-down. The “bottom-up” approach involves forming a larger structures from small building units while “top-down” approach involves decomposition of larger materials into smaller structures [99]. Usually the “top-down” approach is easier to implement with lower cost requirements and better efficiency. One of the ways to implement such approach to generation of metal oxides is to decompose larger superstructures of metal organic frameworks. For examples Das et al. studied generation of Cu/CuO, Co/Co$_3$O$_4$, ZnO, Mn$_2$O, MgO, and CdS/CdO nanoparticles where various metal organic frameworks were used as precursors or templates. The authors found relationship between dimensionality of the frameworks and the resulting size of the nanoparticles: 3D frameworks led to larger nanoparticles for Co/Co$_3$O$_4$ nanoparticles. The resulting metal oxides also showed relatively high surface areas among oxides of about 133.4 and 94.8 m$^2$/g for CuO and Co$_3$O$_4$, respectively [23].

Another recent work by Zhang et al. describes generation of CuO/Cu$_2$O porous composites from Cu-BTC MOFs where copper metal centers are linked by the organic ligands of 1,3,5-benzenetricarboxylic acid. The resulting particles took various shapes such as cubic, octahedral, rod-like and wire-like configurations when factors like temperature, choice of solvents and additives were varied [120].
Li et al. have achieved cobalt oxides starting from ZIF-67-Co MOF with an open framework structure [62]. The calcination of ZIF-67-Co was performed in air to result in the honeycomb-shaped Co$_3$O$_4$ oxides as shown in Figure 11 (A) [62]. The BET surface area reported for these particles was about 47.8 m$^2$/g with the presence of type IV isotherm indicating presence of mesopores. A higher surface area of 148 m$^2$/g was achieved by Salunkhe et al. also from ZIF-67 MOF but under different calcination conditions [95]. The conditions involved heating under nitrogen flow at 500 °C for 30 minutes and further heating at 350 °C for 2 hours.

![Figure 11: SEM micrographs of different shapes possible cobalt oxide nanoparticles](image)

*Figure 11: SEM micrographs of different shapes possible cobalt oxide nanoparticles [95, 113]. Reprinted with permission from Ref. 95. Copyright 2015 American Chemical Society. Reprinted with permission from Ref. 113. Copyright 2009 John Wiley and Sons.*

There are some few different shapes that were observed for the morphology of cobalt oxide nanoparticles, some examples are shown in Figure 11, where polyhedronds, nanosheets, and microspheres could be seen. These oxides were all obtained using different synthesis routes which is most likely why the morphology of these materials is so different. While some amount of work is already available on the conversion of MOFs into metal oxide nanoparticles using “top-down” approach, it is still challenging to obtain uniform nanoparticles with high surface area. Although some research works state the benefits of obtaining agglomerated metal oxide nanoparticles [66]. Also it seems some
kind of relationship between the dimensionality and structure of the starting material and the shape/morphology of the resulting particles exists. Therefore, it would be interesting and useful to further expand this research area by converting layered metal organic frameworks into metal oxide nanoparticles.
3.0 EXPERIMENTAL

3.1 Materials synthesis and characterization

In this section, the synthesis techniques used to generate metal organic frameworks studied in this work will be presented. In addition, post-synthetic functionalization techniques will also be described. For both types of frameworks, hydrothermal synthesis techniques were used. Also, an overview of each of the characterization techniques and instruments will be discussed in this section.

3.1.1 Hydrothermal synthesis of Mg/DOBDC MOF

The first step of this project was to synthesize a nanoporous platform, which will then be used for further pore surface functionalization. An Mg/DOBDC metal organic framework was chosen for this purpose based on the previous available reports of high CO$_2$ capture capacity in the low partial pressure ranges (0.1-1 bar) relevant for postcombustion and ambient air CO$_2$ capture. The main goal of this project is to show that metal organic frameworks can be optimized to improve their properties, in this case, to enhance the stability of Mg/DOBDC MOF in a humid environment. This MOF was synthesized based on a slightly altered synthesis procedure from the originally reported recipe to obtain higher amounts of the material [18]. Mg/DOBDC MOF was synthesized via hydrothermal synthesis at mild temperature of about 120 °C and autogenous pressure. The resulted crystalline material was characterized using X-ray diffraction, pore size analyzer, Fourier Transform Infrared Spectroscopy, and thermo-gravimetric analysis. Once a successful synthesis procedure was established and high quality crystals of Mg/DODBC framework were obtained, further pore surface functionalization with
ethylenediamine groups was performed. Materials were then put to a test by prolonged exposure to steam, characterized, and tested for carbon dioxide capture.

### 3.1.1.2 Experimental procedure for hydrothermal synthesis of Mg/DOBDC

The Mg/DOBDC crystals were obtained by hydrothermal synthesis using Mg salt (Mg(NO$_3$)$_2$ 6H$_2$O) as a source for metal sites, and 2,5-dihydroxyterephthalic acid (H$_4$DOBDC) as the organic linker, pictured in Figure 12. The metal ion of Mg is locked in the middle of carboxylate groups and form rigid metallic rod like structures. These metal carboxylate units act as secondary building units (SBUs), take and have terminal points on their axes that can link to other metallic rods through the organic units, with covalent bonds between the metal rod groups and benzene groups of the DOBDC linker.

About 0.888 g of H$_4$DOBDC and 3.8 g of Mg(NO$_3$)$_2$·H$_2$O were mixed in 400 ml of a solvent solution of DMF, ethanol, and water in a 15:1:1 ratio by volume. Hydrothermal synthesis took place in an oven at 125 °C for 20 hours. After the mixture was taken out from the oven, yellow crystalline material was observed to have formed on the bottom and the walls of the bottle. The mother liquor was immediately decanted while the mixture was still hot. The formed material was then let to cool in air for about three hours to ensure room temperature was achieved. After cooling, the bottle was filled with methanol and shaken to knock out any material on the walls and the bottom of the bottle. This was done to ensure a thorough rinsing of the sample with methanol. Methanol rinsing is done to remove any other solvent molecules that were used during synthesis such as water, ethanol, and dimethylformamide from the porous structure. Methanol replacement was repeated four more times over the next two days and each time fresh methanol solution was added. After the last replacement the material was left to dry
completely in air. Activation of the surface then took place, where all of the collected powder was heated under dynamic vacuum at 250 °C for 5 hours. This step is done to further remove any methanol or solvent molecules still free within the framework, opening the porous channels within the framework and allowing for further characterization. The material was then transferred into a vial and stored under vacuum to prevent any contamination from air or exposure to ambient water, which has been shown to degrade the Mg/DOBDC crystals. In the end, about 800 mg of the yellow crystalline material was obtained per batch.

Figure 12: Organic linker source, 2,5-dihydroxterephthalic acid (H₄DOBDC)

3.1.2 Modification of the Mg/DOBDC framework with functional groups for enhanced CO₂ capture

The choice of the amine functional group and further procedure for post-synthetic functionalization of Mg/DOBDC MOF will be discussed in this section.

3.1.2.1 Choice of functional groups

A primary amine group, ethylenediamine (ED) molecule was used as a functional group for surface modification of Mg/DOBDC. This specific molecule was chosen based on the simplicity of the molecule, it is linear, and possesses amine groups on both sides. It was hypothesized that one end of the amine group can bind to the coordinatively
unsaturated metal site of Mg which is revealed after activation step while another end would be free within the pore of the framework ready to interact with incoming guest CO\textsubscript{2} molecules. Amines are also known to be very effective in CO\textsubscript{2} capture and currently implemented as liquid amine scrubbers therefore such combination of physical adsorbent platform, such as metal organic framework, and grafted amine groups could generate a highly efficient adsorbent for carbon dioxide capture.

In addition, due to the hydrothermal synthesis of metal organic frameworks, after removal of solvent molecules (e.g. water, dimethylformamide, ethanol) from the pores of the frameworks, MOFs become hydrophilic. There are reports present that suggest MOF crystals degradation after exposure to humid conditions, which are relevant for post-combustion flue gas CO\textsubscript{2} capture, and further decreased performance of MOFs as CO\textsubscript{2} adsorbents. It is proposed to shield metal sites of MOFs with covalently bonded functional groups, such as ethylenediamine. This way, amine functionalized MOFs should be more stable towards humidity and therefore show constant CO\textsubscript{2} capacity before and after water exposure. It should be noted that various amine groups can be used for this purpose, but amine loadings should be optimized to avoid a complete pore blockage.

3.1.2.2 Experimental procedure for amine functionalization

Amine functionalization was performed as follows. About 1 g of ED was added to 200 mg of the activated material and mixed in 40 ml of anhydrous toluene under reflux for 12 hours. The resulting material was filtered and washed with 100 ml of water and then 100 ml of ethanol to remove any ED molecules that might have been appended on the surface of the MOF. The sample was then dried at room temperature for 16 hours.
3.2 Synthesis of layered metal organic frameworks

The detailed conditions for the hydrothermal synthesis of metal organic frameworks of CoBDC-ED, CoBDC-HD, and CoBDC frameworks will be described in this section. The frameworks were synthesized based on the cobalt metal sites and terephthalic acid organic linkers to make up a layer structure of the materials. Simple organic ligands of ethylenediamine and 1,6-hexanedi amine were used to play a role of pillaring ligands. The crystals obtained with ethylenediamine and 1,6-hexanedi amine were named CoBDC-ED and CoBDC-HD in this work, respectively. The layered framework composed of only cobalt metal sites and terephthalic acid organic ligands was named CoBDC in this work.

3.2.2 Synthesis of CoBDC-HD MOF

Synthesis procedure for crystalline material CoBDC-HD where 1,6-hexanedi amine was used as a secondary linker will be discussed in this section.

3.2.2.1 Experimental procedure for hydrothermal synthesis of CoBDC-HD

The CoBDC-HD crystalline material was obtained via hydrothermal synthesis using Co(NO$_3$)$_3$ 6H$_2$O as the source for metal sites, and organic molecules of terephthalic acid and 1,6-hexanedi amine acting as co-linkers. Both of these molecules can be seen in Figure 14. The synthesis proceeded in a solvent mixture of dimethylformamide and acetonitrile in a 3:1 volume ratio. It is believed that the organic ligand of terephthalic acid
participated in the formation of the 2D layers of the framework and 1,6-hexanediamine served as a pillarizing linker resulting in a 3D framework of layers stacked one on top of the other.

![Molecular structure of organic ligands](image)

**Figure 14: Molecular structure of organic ligands of terephthalic acid (a) and 1,6-hexanediamine (b) used in the synthesis of NEU-3 framework**

A separate solution of 1,6-hexanediamine was first prepared. For this solution 24 ml of dimethylformamide (DMF) and 8 ml of acetonitrile were mixed. About 2.347 g of 1,6-hexanediamine was then slowly added to the solution. The mixture was stirred for 24 hours at room temperature. In a separate beaker, a solution of cobalt metal source and layering organic ligand was prepared. For this solution, 12 ml of DMF and 4 ml of acetonitrile were mixed. About 0.268 g of Co(NO_3)_6H_2O was then slowly added to the mixture. The mixture was left to stir until cobalt salt was completely dissolved. The solution took on a bright purple color. Then, about 0.056 g of terephthalic acid (H_2BDC) was added to the solution and stirred overnight. After 24 hours of stirring the mixture of DMF/Acetonitrile/ Co(NO_3)_6H_2O /H_2BDC was added to the amine solution in a dropwise fashion. The mixture was again left to stir for 1 hour to become homogeneous. The final solution was of a dark brown color with a pH of around 12. The solution was separated into 20 ml vials, with 6 ml of solution in each of the vials. The vials were then tightly sealed by placing PTFE tape around the necks and capped, then placed into an oven at 80 °C for 5 days. After 5 days, the vials were taken out of the oven and placed
into a chemical hood to cool down to room temperature. The light brown/light purple color solid could be seen to have accumulated on the bottom and walls of the vials. Once cooled, the solid was washed with DMF a number of times and filtered using vacuum filtration. Once filtered and dried, the solid was collected. The methods of activation, or removing solvent molecules from the framework, will be discussed in Chapter 4.

3.2.2.2 Modified experimental procedure for hydrothermal synthesis of CoBDC-HD

The modified recipe of CoBDC-HD framework involved first making a solution of DMF/CH$_3$CN (16 ml, 3:1 volume ratio) to which about 1.46 g of 1,6-hexanediamine was added. A separate solution of DMF/CH$_3$CN was also made to which about 0.131 g of Co(NO$_3$)$_6$H$_2$O and 0.150 g of H$_2$BDC (terephthalic acid) were added. Both solutions were well mixed on the magnetic stir plate. After about Co(NO$_3$)$_6$H$_2$O /H$_2$BDC has become homogeneous, it was added to the amine solution in a dropwise fashion. The final solution was left to mix for another hour and the contents of the solution were then separated into four 20-ml vials. The vials were tightly sealed and placed into the oven at 80 °C for 5 days. After 5 days light pink solid resulted in all four vials and was further washed with fresh DMF few times. After vacuum filtration, the final light pink solid was collected and ready for characterization.

3.2.3 Synthesis of CoBDC-ED MOF

Crystals of the CoBDC-ED framework were prepared in a similar way to those of CoBDC-HD MOFs. The main difference here was the choice of ligand serving as pillaring linker: instead of 1,6-hexanediamine, a shorter molecule of ethylenediamine (ED) was used. The synthesis of CoBDC-HD was optimized for a proper scale up of the material. First, about 117 ml of DMF and 34 ml of acetonitrile were mixed together until
a homogeneous mixture of two was obtained. About 1.95 g of ED was added to the mixture with stirring. Once homogenous, about 0.3515 g of Co(NO₃)₆H₂O was added to the solution. After about 15 minutes, 0.1807 g of terephthalic acid was added to the solution. The mixture was left for vigorous stirring at room temperature for 1.5 hours and the final pH of the solution was recorded to be 13. The mixture was then placed into a 500 ml Pyrex bottle that was tightly sealed with a stirring bar inside. The bottle was placed into the oven preheated to 80 °C on a stirring plate. The mixture was kept stirring in the oven for 2 days. After 2 days the bottle was taken out and the solution was left to cool down to room temperature. Once cooled, the yellow solid could be seen settled on the bottom of the bottle. It was further washed with DMF, filtered, and collected.

### 3.2.4 Synthesis of CoBDC complexes in dimethylformamide

The samples of CoBDC complexes were prepared by dissolving about 0.126 g of Co(NO₃)₆H₂O and 0.724 g of terephthalic acid in the solution of dimethylformamide (DMF). When all of the components were dissolved after mixing at room temperature, the solution was transferred into a 125-ml Pyrex bottle and placed in the oven at 110 °C for 1, 2, 3, and 4 days. Samples obtained after 1, 2, 3, and 4 days were named as CoBDC-1, CoBDC-2, CoBDC-3, and CoBDC-4, respectively. The resulting solids were of bright purple color and were thoroughly washed in the fresh DMF. After vacuum filtration, samples were ready for characterization.

### 3.2.5 Ligand introduction to CoBDC complexes and further recrystallization

First solution of dimethylformamide (DMF) and 1,6-hexanediamine was prepared where about 1.472 g of 1,6-hexanediamine and 18 ml of DMF was used. After solution was mixed on the magnetic stir plate for 1 hour and has become well-mixed, about 0.050
g of CoBDC-3 (synthesized after 3 days) was added to the solution. The mixture was left to stir at room temperature for 3 hours. When mixture has become well-mixed, the contents were separated into 3 20-ml vials where 6 ml of the solution was poured into each of the vials. The vials were then capped and wrapped with Teflon tape to ensure well-sealed containment. Vials were then placed into the oven at 110 °C for 24 hours. After vials were taken out of the oven, they were left to cool at room temperature. The resulted solid was in light-pink color and was thoroughly washed with fresh DMF and further vacuum filtered. The solid was then collected and ready for characterization.

3.2.6 Calcination trials for conversion of MOFs to metal oxide nanoparticles

Calcination trials of CoBDC-HD were performed by placing about 100 mg of the material into the oven for 24 hours under continuous nitrogen flow. The resulting material was then collected. Calcination temperatures tested were 200 °C, 250 °C, 300 °C, 450°C, and 500 °C with a heating rate of about 3 °C/min. Similar tests were performed for CoBDC layered MOFs at 270 °C and 450 °C.

3.3 Characterization techniques

Due to the crystalline nature of metal organic frameworks, all of the solid materials used in this work were characterized using X-ray diffraction (XRD).

3.3.1 Structural characterization using X-ray diffraction (XRD)

X-ray diffraction is commonly used for the analysis of atomic arrangements in crystalline materials. X-rays diffract from the surface of the material, or more precisely, from the diffraction centers or repetitive planes of these diffraction centers, that are spaced uniformly from each other. If these periodic planes are spaced in such a way that
the diffracted beams undergo constructive interference, the resulting x-ray beam can be
analyzed to provide information about the periodicity of the structure. Braggs’ law
provides certain conditions that should be satisfied to create a diffraction pattern. If the
beam is coming in at a certain incident angle $\theta$, it is assumed that the beam will be
reflected at this same angle $\theta$, as can be seen on Figure 10. Braggs’ law is based on these
beams either undergoing constructive or destructive interference of the diffracting beams,
where constructive rays result when the beams are regularly spaced in a way that they
have the same wavelength, while destructive rays result from a random grouping of
wavelengths that cancel each other out and appear as flat regions in the XRD patterns.
The equation that must be satisfied for XRD peaks to become detected is Braggs’ law,
given below:

$$ n \lambda = 2d_{hkl} \sin \theta \quad (2) $$

where: $n = \text{number of reflection}$

$$ d_{hkl} = \text{distance between two parallel planes} $$

In the XRD instrument, a radiation source with constant wavelength is used and
its position can be changed with time, allowing for the detection of diffraction patterns
that can be used to determine the identity and periodic structure of a sample crystal.
The resulting diffraction peaks from the collected XRD pattern represent constructive interference caused by periodic distances between diffraction planes in the crystal. These diffraction planes can be characterized by Miller indices (hkl), which describe the geometry of the unit cell and allow for each of the diffraction peaks to be assigned to a given periodic crystal distance. The indices represent reciprocals of the distances where the plane cuts each of the three crystal axes of the unit cell, as shown in Figure 16. This technique would be very important for the characterization and
assignment of Miller indices of the CoBDC-HD and CoBDC-ED frameworks since these materials were synthesized in this work for the first time. Based on the geometry of the unit cell, Miller indices can be calculated when distances of each of the sides of the unit cells are known. In the case of CoBDC-HD if for example the crystal structure is assumed to be monoclinic, with all three unit cell sides (a,b,c) having different lengths, two angles of 90 degrees, and one angle which is greater than 90 degrees. The distance in the a-direction is believed to be the distance representing the interlayer distance between 2D layers of the framework, with those in the b and c direction representing the crystallinity within the layers. Therefore, the a-distance should be different between MOFs within the CoBDC series, while the b and c parameters should stay unchanged.

The crystallinity of the material in this work was confirmed via X-ray diffraction (Rigaku Ultima IV X-Ray Diffractometer) with Cu-Kα radiation with a wavelength of 1.54 Å. Data was collected in the 5-50 degrees 2θ range with a step size of 0.1 degree and scan rate of 1 degree/min for 1 minute for Mg/DOBDC crystals and with a step size of 0.1 degree and scan rate of 1 degree/min for 4 minutes for CoBDC-HD crystals (5-40 degrees 2θ range).

3.3.2 Transmission Electron Microscopy (TEM)

In the characterization of the newly generated layered metal organic frameworks, transmission electron microscopy (TEM) technique was used to study structural properties at the nanometer scale. Specifically, it was an essential tool for observation of individual layers of the CoBDC-ED and CoBDC-HD frameworks. TEM imaging was performed using a high-contrast TEM JEOL JEM-1010 at Northeastern University, operating at 80 kV shown in Figure 17.
Ernst Ruska and Max Knoll designed the first transmission electron microscope in 1931. In current TEM machines highly excited electrons are generated in a cathode ray tube under vacuum and the stream of electrons is accelerated toward the sample of interest [110]. Electrons are able to penetrate through the sample depending on the thickness of the area of interest (50-100 nm). From the interactions of electrons with a sample, an image can be formed, magnified, and transformed onto an imaging device and then recorded by digital camera. The samples of the layered metal organic frameworks were placed onto standard copper TEM grids with a square mesh and a carbon film [110].

Different preparation methods were used for imaging. One of those methods includes distributing a sample in a solvent solution of ethanol and dispensing small amounts of the resulting solution on the copper mesh grids. While this method was used it was thought that ethanol, being a polar solvent, might be too strong for CoBDC-HD crystals and could disturb the structure of the framework. Therefore, in some cases the sample was dispensed directly on the copper mesh grid. It was also found that due to the high content of organic materials within the framework, crystals tend to move around a lot under exposure to the beam at high energy, making it difficult to take a high quality image.
3.3.3 Scanning Electron Microscopy (SEM)

To study the surface morphology of the formed crystals scanning electron microscopy (SEM) techniques were implemented. In this work a high-resolution field emission scanning electron microscope (FE-SEM) Hitachi S-4800 at Northeastern University was used.

Scanning electron microscope also uses electrons to generate images of the samples, as opposed to light that is used in conventional microscopes. Electrons are generated by an electron gun within an instrument and then focused using various lenses onto a sample. In this case, the electrons do not penetrate through the sample as they did
in TEM, but rather electrons and X-rays are ejected/diffracted from the sample. The signals from diffracted X-rays, backscattered electrons, and secondary electrons are collected by a detector and then translated into a black and white image [91].

As samples used here are not conductive, all of the samples were first coated with a 6 nm thick layer of platinum by sputter coating.

**3.3.4 Surface area and pore size analysis**

Generally porous solids can be classified into three classes based on the size of the pores present in those frameworks: nanoporous (pore size <20 Å), mesoporous (pore size between 20 Å to 500 Å), and macroporous (pore size > 500 Å). One of the most powerful tools for the characterization of the porous properties of materials is the collection of adsorption/desorption isotherms. Exposing a sample of material to a constant temperature bath, varying the gas pressure, and recording the amount of the adsorbate gas taken up by the sample results in adsorption/desorption isotherms. The physisorption in this case is non-destructive and is useful in the characterization of the microporosity of the adsorbent. Based on the information from collected isotherms, surface area, total pore volume, pore size distribution, and other porous properties can be obtained. Based on the shape of the adsorption/desorption isotherms, solid materials can be classified into various classes; with the behavior of each of the classes presented in Figure 18. Type I or type IV isotherms are usually characteristic of microporous solids because of the steep increase in adsorption when gas is first introduced, which is associated with a fast filling of the micropores present within the material [97]. The isotherms may then plateau and another uptake step at higher pressures can be observed, which is due to multilayer adsorption in mesopores. Type IV isotherms can be seen to
show both of these pore types, causing these solids to be defined as mixed micro and mesoporous sorbents [97].

**Figure 18:** Six classes of adsorption/desorption isotherms characteristic to solid materials (left) and types of hysteresis loops observed in types IV and V isotherms (right) [97]. Reprinted from Ref. 97. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

Based on this characterization, type I isotherms represent materials that are primarily microporous, a type II isotherm is representative of nonporous or macroporous adsorbent materials, types III and V represent materials where guest gas-gas interactions are stronger than gas-solid interactions, and a type VI isotherm is characteristic to a nonporous solid with uniform surface where stepwise multilayer adsorption occurs [97]. Type IV isotherms also exhibit a hysteresis loop occurring from different processes of adsorption and desorption in the adsorbent materials. The hysteresis loop is usually indicative of capillary condensation within the mesopores of the adsorbent. In Figure 18 some of the possible shapes of hysteresis loop are represented, with H1 and H4 being the
most common [97]. While H1 hysteresis loop is constant over the increasing gas uptake, the H4 loop is more constant over the increasing gas pressure range. An H4 hysteresis loop is indicative of narrow pores and in combination with Type I isotherm behavior is representative of a microporous material [97]. It is therefore important to perform full adsorption/desorption isotherms as isotherm shapes present additional information about porous characteristics of the solid materials.

For surface area calculations of microporous materials like metal organic frameworks, adsorption models such as Brunauer–Emmett–Teller (BET) and Langmuir are widely used. Brunauer-Emmett-Teller (BET) theory is based on multimolecular layer adsorption and is represented by the following set of equations where the rate of condensation of adsorbate gas molecules onto monolayer adsorption sites is equal to [97]:

\[
\frac{P}{V_a(P_0-P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \left(\frac{P}{P_0}\right)
\]

(3)

where: 

\(V_a\) = quantity of gas adsorbed at pressure \(P\)

\(V_m\) = quantity of gas adsorbed when the entire surface is covered with a monomolecular layer

\(P_0\) = saturation pressure of the gas

\(C\) = constant

\(C\) constant is defined by the following equation:

\[
C \propto \exp\left(\frac{q_1-q_L}{RT}\right)
\]

(4)

where: 

\(q_1\) = heat of adsorption of the first layer

\(q_L\) = heat of liquefaction of the adsorptive

\(R\) = gas constant

\(T\) = absolute temperature
Based on the theory, the C constant is exponential to the heat of adsorption of the first adsorbed layer. According to the Equation 3, a linear plot can be plotted of $P/[V_a (P_0-P)]$ vs. $P/P_0$ where $(C-1)/V_mC$ is the slope and $1/V_mC$ is the intercept. The straight line is usually obtained from the region of partial pressure $P/P_0$ between 0.05 and 0.3. From the graph, C and $V_m$ values can be calculated and specific surface area is obtained based on the information known about nitrogen molecule at 77 K and the following equation:

$$S = \frac{V_m\sigma N_A}{mV_0} \quad (5)$$

where: $\sigma$ = area of surface occupied by a single adsorbed gas molecule (16.2 Å² for nitrogen gas)

$N_A$ = Avogadro constant (6.022 x $10^{23}$ molecules/mole)

$m$ = mass of the adsorbing sample

$V_0$ = molar volume of the gas (22414 cm³)

For characterization of the porosity of materials generated here based on their average pore sizes, surface areas, pore size distribution, and total pore volume nitrogen gas was used as adsorbate gas and adsorption isotherms were collected by surface area and pore size analyzer Quantachrome NOVA 2200e shown in Figure 14. Prior to analysis, anywhere between 30-100 mg of adsorbent material is placed into a 9 mm in diameter specialized sample cell and outgassed at about 120 °C under dynamic vacuum for 24 hours to remove any impurities. The sample cell is then transferred to an analysis station where is it submerged into a constant temperature bath, in this case liquid nitrogen at 77K. The sample cell is held completely under vacuum until some inert gas, in this case nitrogen is introduced in small amounts. Inert gas is introduced in steps allowing for gas molecules to adsorb on the surface of the solid samples until the equilibrium pressure
reaches the saturation point. At first gas molecules form a monolayer on the surface of the adsorbent. Once more gas is introduced, multilayer adsorption then occurs. The surface area is then calculated based on the Brunauer–Emmett–Teller (BET) theory described above.

![Quantachrome NOVA 2200e pore size and surface area analyzer.](image)

**Figure 19: Quantachrome NOVA 2200e pore size and surface area analyzer.**

### 3.3.5 Fourier Transform Infrared Spectroscopy

To confirm the formation of chemical bonds, Fourier Transform Infrared Spectroscopy (FT-IR) will be used. The main goal of this instrument is to estimate or average the absorbance of the beams of various frequencies of light. Infrared waves are absorbed by the chemical bonds present in the material providing an IR spectrum for every sample. In this work, the FT-IR was used in ATR (Attenuated Total Reflectance) mode with Germanium crystal. The infrared spectrum can provide valuable information about whether or not ethylenediamine molecules were grafted on the metal sites of Mg/DOBDC crystals. In addition, FTIR spectra could give important information about the types of chemical binding present in CoBDC-HD and CoBDC-ED frameworks.
3.3.6 Thermo-gravimetric analysis (TGA)

For the estimation of organic content and overall decomposition profiles of frameworks, thermogravimetric analysis was executed with TA Instruments TGA Q500 available at Northeastern University. In this instrument, a small amount of sample is placed into a platinum pan. The sample then undergoes heating in TGA oven under the presence of purge gas, in this case nitrogen. As the heating proceeds, the weight changes are recorded. With a reference pan placed inside the instrument for balance, any weight changes can be monitored very precisely. Samples of Mg/DOBDC were heated from room temperature to 600 °C at a rate of 10 °C/min under nitrogen gas flow and samples of NEU frameworks were heated at the same rate to 800 °C. The weight loss between 100 °C and 150 °C was taken as points for calculations of ethylenediamine loadings (boiling point of ethylenediamine is around 120 °C) for ED-functionalized Mg/DOBDC MOFs.

3.3.7 Accelerated Steam Treatment Tests

In order to test the stability of Mg/DOBDC bare and functionalized derivatives, accelerated steam treatment tests will be performed. Accelerated steam treatment tests were performed previously on a number of materials considered for CO₂ capture. A schematic of the steam treatment set up is shown in Figure 20. A solid adsorbent was placed into a glass tube, which was further placed into a liner filled with water. The liner was then placed into a Parr reactor, tightly sealed and placed into the preheated oven at 110 °C for 48 hours. This set up allowed for water vapor to interact with solid sample rather than liquid water.
3.3.8 Carbon dioxide capture tests

Carbon capture tests were performed using thermogravimetric analysis instrument (TGA Q500). About 20 mg of each sample was measured for each run. In the experimental run, the material is first heated to 100 °C at a rate of 10 °C/min and kept there for three hours to draw out any guest molecules such as water. The sample was then cooled back to 25 °C at the same rate and equilibrated to 25 °C for 60 minutes. At this point, 100% carbon dioxide gas was introduced and was allowed to flow until pseudo-equilibrium was reached. It was assumed that the total weight gain observed after introduction of CO₂ gas is the overall CO₂ capture uptake.

3.3.9 Energy Dispersive X-ray Spectroscopy (EDS) on the SEM

In this work scanning electron microscope with energy dispersive x-ray spectroscopy analysis installed was used for chemical characterization of NEU metal organic frameworks. In EDS operation, a beam of X-rays is focused on the sample which consists of various atoms. Each of the atoms possesses electrons in different energy
levels. When the electrons become excited, some will be kicked out from the inner energy shells and electrons from the outer energy shells will fill their spaces as shown in Figure 21. When this occurs, the difference in energy has been lost by the formation of x-rays. Since every atom exhibits different atomic structure, based on the energies of the released X-rays chemical characterization and localized assignment of elements is possible [38].

In this work the samples used for EDS analysis were coated with a 2 nm thick platinum film before characterization. This was done to limit charging artifacts at the surface, although it caused platinum to become observed in the resulting EDS patterns.

![Figure 21: Representation of processes occurring during the EDS analysis to the atom and its electrons [38].](image)
4.0 RESULTS AND DISCUSSION

The main goal of this Ph.D. Dissertation is to demonstrate the flexibility in the structural modification and design of metal organic frameworks for targeted applications. The first goal of this work was to demonstrate the tunability of the frameworks by postsynthetic functionalization for targeted application of carbon dioxide capture in humid conditions. For such targeted application, it is important to impart resistance to humidity to the adsorbent material chosen for this purpose, in this case the Mg/DOBDC metal organic framework. Results obtained for postsynthetic functionalization, characterization analysis, and performance in carbon dioxide capture of the bare and functionalized MOF chosen for this test are covered in section 4.1.

Another part of this dissertation work involved design and construction of layered metal organic frameworks with controllable pore space for various applications such as in mixed matrix membranes for selective gas separation. The resulting framework, CoBDC-HD and its structure is described in section 4.2 with few cases made on the crystal structure of the obtained material. Similar frameworks have been also obtained based on the use of different constituents and the resulting structures are described in section 4.2.

Generation of metal oxides from metal organic frameworks synthesized in the second part of this work has also been performed. The obtained cobalt metal oxides are described in section 4.3.

Graphene/CoBDC-ED composites and their characterization analysis are presented in section 4.3 as an additional study.
4.1 Aim 1: Pore surface modification of metal organic frameworks for CO\textsubscript{2} capture in the humid conditions

In this section, an optimization of metal organic framework with amine functional groups will be described. While some well-known MOFs exhibit high crystallinity and permanent high surface areas, and good CO\textsubscript{2} capture capacity at practical CO\textsubscript{2} partial pressures, there are reports that show degradation of the framework in the presence of water and further loss of the capture capacity [44, 67, 71]. It is important to address this issue since no matter how efficient MOFs are in capturing CO\textsubscript{2}, these high capture properties could be lost in humid conditions and both ambient air and post-combustion flue gas exhibit water amounts of up to 7 vol %. Metal organic frameworks are unique materials due to their high versatility and chemical modifications that are possible for optimization of the materials properties. In this work, modification at the metal sites of MOFs was investigated and results presented.

The Mg/DOBDC MOF has been chosen as a platform metal organic framework to demonstrate pore surface modification to impart stability in humid conditions without causing a change to the main topology of the crystal itself. This specific material is also one of the most promising materials for carbon dioxide capture with the highest competitive CO\textsubscript{2} capacity uptake among currently known MOFs. Mg/DOBDC MOF was exhibits high CO\textsubscript{2} capture uptake (up to 8 mmol CO\textsubscript{2}/g) at 0.1 bar and 298 K [115].

Rosi et al. reported the first MOF of M/DOBDC series of frameworks in 2005 and since then many isostructural frameworks based on various metal sites (Co, Zn, Ni, etc.) have been synthesized [93]. The Mg/DOBDC framework was synthesized by Caskey et al. in 2008 and was found to have the highest CO\textsubscript{2} uptake at 1 bar among other
M/DOBDC series of frameworks [11]. Since that paper, much of research was focused specifically on this particular MOF studying its CO$_2$ capture kinetics and stability in the practical conditions. In addition, a lot of work is currently being done on the modification of the available pore space within the frameworks with functional groups for potential improvements in properties and gas separation or capture.

Liquid amines are known for their effectiveness in absorbing CO$_2$ gas, therefore it is believed the CO$_2$ capture ability of Mg/DOBDC can be improved with such functionalization. Another important aspect is stability under humid environment, which is applicable for real life conditions of CO$_2$ capture. Attachment or grafting of these functional groups directly onto metal sites is believed to shield metals from water molecules therefore providing better material stability. Such enhancement would bring Mg/DOBDC MOF one step closer to becoming an efficient physical adsorbent of carbon dioxide from post-combustion flue gas or ambient air. The original and modified frameworks were evaluated under strident steam conditions to test its stability to the highest degree. Specifically, the surface of the nanopores in Mg/DOBDC was decorated by functional groups such as ethylenediamine to prevent the direct contact of water molecules with open metal sites of the framework, using post-synthetic functionalization techniques [19]. The original and functionalized MOF samples and their potential degradation after steam treatment were evaluated with various characterization techniques such as X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), infrared spectroscopy (IR), etc. Most importantly, the CO$_2$ capture uptake of original and functionalized Mg/DOBDC MOFs upon exposure to humid environments were studied. This section discusses the main results obtained for post-synthetic functionalization of
metal organic frameworks with amine groups. Mg/DOBDC framework was initially synthesized as a physical adsorbent platform and further pore surface modification with amine groups was performed.

### 4.1.2 Structural and physical analysis of Mg/DOBDC metal organic framework

Mg/DOBDC framework is composed of Mg metal clusters connected by organic ligands of 2,5-dioxido-1,4-bezene-dicarboxylate (DOBDC) generating hexagonal pores as shown in Figure 22 [7]. The coordination spheres of the Mg(II) ions are associated with solvent molecules such as H₂O or DMF right after synthesis, which are then removed after solvent removal or framework activation. The solvent removal leaves behind coordinatively unsaturated sites (CUSs) on the metal sites, thus activating the materials with empty pore structures. The framework presents one-dimensional pore channels where metal clusters build infinite rods along the channels. For the removal of solvent molecules used in the initial synthesis of the material, such as dimethylformamide (DMF) and water with high boiling points, solvent exchange with methanol as a solvent over the course of few days has been performed. Upon solvent exchange, material was heated to remove exchanged molecules of methanol leaving material porous.
The structure of Mg/DOBDC was assessed through the obtained for it X-ray diffraction pattern shown in Figure 25 (b). Mg/DOBDC is a crystalline material and can be identified by the characteristic peaks, specifically by the first and second peaks clearly distinguishable around 6.8 and 11.8 degrees 2θ. The XRD pattern of the resulted material (Figure 25b) matched well with reference XRD obtained by Kong et al. (Figure 25a). The first and most intense peak in the pattern corresponds to a distance of about 13 Å. This distance is associated with (2,-1,0) plane slicing the unit cell of the framework in about half and corresponding to about the size of the pore opening. Figure 23 shows the unit cell of the framework and how the plane of (2,-1,0) slices the unit cell in half at the red line. A peak at 11.8 degrees 2θ corresponds to a distance of about 7.5 Å and represents (3,0,0) plane shown in Figure 24. These two peaks are characteristic to the framework of Mg/DOBDC mainly because of the relationship to the size of the pore opening within the framework.
Figure 23: Representation of the unit cell of Mg/DOBDC and the plane of \((2,-1,0)\) slicing the cell in half representing the pore size distance. (Image generated in Mercury software based on the Mg/DOBDC structure synthesized in Ref. 115).

Figure 24: Representation of the unit cell of Mg/DOBDC and the plane of \((3,0,0)\) slicing the unit cell in three equal distances represent the distance of the half of the pore opening. (Image generated in Mercury software based on the Mg/DOBDC structure synthesized in Ref. 115).
Figure 25: Reference XRD pattern of Mg/DOBDC MOF obtained by Kong et al.[56] (a) and XRD pattern of the material synthesized in this work (b). Reference inset figure reprinted with permission from Ref. 56. Copyright 2012 American Chemical Society.

The BET surface area of the material was about 1200 m$^2$/g, and this also confirms results from previous works on Mg/DOBDC. Nitrogen adsorption and desorption isotherms shown in Figure 26 exhibit a narrow hysteresis loop indicative of microporous material. Adsorption here happens very fast under driving force of low partial pressure where micropores within the material are filled first. The gas uptake then slows down with increasing relative pressure when all of the micropores are filled but continues to rise until pores of larger size are filled or multilayer adsorption occurs. Hysteresis loop is usually caused by the different processes involved into adsorption and desorption. A narrow hysteresis observed here indicates that processes are not distinctly different from
each other and pores are not distinctly different from each other in size indicating a material with uniform porosity throughout.

Figure 26: Nitrogen adsorption and desorption isotherms of as-synthesized Mg/DOBDC framework.

Fourier Transform Infrared Spectroscopy (FT-IR) has also been performed on the as-synthesized Mg/DOBDC framework. The obtained spectrum is shown in Figure 27 with all of the main peaks assigned. The presence of the 2,5-dioxido-1,4-bezene-dicarboxylate (DOBDC) organic linker is indicated by the strong peaks between 1400-1600 1/cm due to the stretching vibration modes of the C-C bonds of the aromatic ring and by the peaks between 800-1200 1/cm due to the C-H deformation vibration modes of the aromatic ring. A metal oxygen coordination bond is present based on the broad peak around 580 1/cm indicating metal coordination the organic ligand. Also absence of peaks at higher wavenumber region (3200-3500 1/cm) indicates there are no water molecules or –OH groups present in the framework.
Figure 27: Fourier Transform Infrared Spectroscopy (FT-IR) pattern of the as-synthesized Mg/DOBDC.

Based on the analysis of the obtained X-ray diffraction patterns, porosity measurements, and FT-IR spectra it can be concluded that good quality crystals of Mg/DOBDC framework were obtained. Therefore the obtained material can be further tested for amine functionalization and steam treatment.

4.1.3 Effect of amine functionalization on the crystallinity of Mg/DOBDC

After removal of solvent molecules, Mg/DOBDC MOF is left with the presence of open metal sites. Ethylenediamine (ED) functional group was used for grafting on these open metal sites. Ethylenediamine is a linear primary amine molecule. While one of the amine groups is attached to the metal, another amine group is free within the pore to interact with incoming adsorbate gas molecules. Such modification should not change the main topology of the material or affect the overall topology of the unit cell as seen in Figure 28, therefore the peak positions of the XRD patterns of the main framework should stay the same. It was indeed observed that after ED functionalization the crystal
structure stayed constant as can be seen in Figure 29, while some degradation in peak intensities at lower angles was observed [3]. After ED functionalization, the intensities of the characteristic peaks, specifically that of the first peak which corresponds to the diffracting planes within the pore and from which the pore size can be calculated decreased to some extent due to the shielding effect of the ethylenediamine molecules occupying the pore space of the Mg/DOBDC. On the other hand, there were no significant shifts in peak positions observed, which suggest overall topology of the original Mg/DOBDC was unchanged after functionalization. The representation of the ED functionalized Mg/DOBDC unit cell is shown in Figure 28 (b-e) with different ED loadings [3, 18].

![Figure 28: Schematics of the unit cell of Mg/DOBDC occupied with ED molecules with various loadings: a) 0 ED, b) 1ED, c) 3 ED, d) 6 ED, and e) 18 ED [18] Reprinted with permission from Ref. 18. Copyright 2012, American Chemical Society](image-url)
4.1.4 Effect of the amine functionalization on the porosity of the Mg/DOBDC

ED-Mg/DOBDC samples displayed lower surface areas initially from that of the bare Mg/DOBDC, which is suspected to be due to the occupancy of ED molecules within the pore space. This is further supported by the difference in surface area for samples of different amine loading. While pore properties of the functionalized material decreased, the resulting material still maintained some level of porosity with about 140 m²/g and 0.207 cm³/g for BET surface area and total pore volume, respectively. Figure 30 shows nitrogen adsorption-desorption isotherm for the ED-Mg/DOBDC sample and as it can be seen the behavior of a type I isotherm can still be observed: steep increase in adsorption at lower pressure and narrow uniform hysteresis loop.

Figure 29: XRD profiles of the bare Mg/DOBDC (bottom) and ED-Mg/DOBDC (top).
It should be noted that the total pore volume of the original Mg/DOBDC (0.536 cm$^3$ g$^{-1}$) decreases as amine loading increases: to 0.345 cm$^3$ g$^{-1}$ (Sample 1 with an amine loading of 0.763 mmol ED g$^{-1}$ adsorbent) and 0.167 cm$^3$ g$^{-1}$ (Sample 2 with an amine loading of 1.07 mmol ED g$^{-1}$ adsorbent) due to the ED molecules occupying the pore spaces of the framework.

![Nitrogen adsorption-desorption isotherm for ED-Mg/DOBDC MOF.](image)

**Figure 30: Nitrogen adsorption-desorption isotherm for ED-Mg/DOBDC MOF.**

### 4.1.5 FT-IR analysis of the amine functionalized Mg/DOBDC framework

Valuable information about functionalization of ethylenediamine molecules could be obtained from Fourier Transform Infrared Spectroscopy. Figure 31 presents IR spectra obtained for bare and functionalized Mg/DOBDC samples. The presence of ED molecules could be predicted based on the FT-IR spectra of its liquid phase, which shows peaks at about 2924 cm$^{-1}$ for $–$NH stretch and 2848 cm$^{-1}$ for $–$CH stretch [45]. In this study, IR spectra of ED-Mg/DOBDC shows weak developing peaks at 2950 cm$^{-1}$ and
2981 cm\(^{-1}\). A shift observed to the larger wavenumbers is due to the coordination to the metal sites \([45]\). Another developed peak was observed in ED-Mg/DOBDC at 1641 cm\(^{-1}\), which is indicative of the presence of primary amines. It is also interesting to observe that after CO\(_2\) adsorption ED-Mg/DOBDC sample loses peaks at 2950 cm\(^{-1}\) and 2981 cm\(^{-1}\) possibly due to the chemical binding of CO\(_2\) molecules to the –NH groups. This kind of behavior which was not observed after N\(_2\) adsorption, could be indicative of potential selective capture of CO\(_2\) over N\(_2\) by the amine functionalized frameworks of Mg/DOBDC.

![FT-IR spectra](image.png)

Figure 31: FT-IR spectra of the Mg/DOBDC, ED-Mg/DOBDC, and ED-Mg/DOBDC after carbon dioxide and nitrogen adsorption. The dashed lines mark the peaks indicating presence of amines across all four samples.

### 4.1.6 Effect of steam exposure on the crystallinity and porosity of bare and functionalized Mg/DOBDC samples

After steam treatment, the Bragg’s intensities of all peaks of the original Mg/DOBDC underwent drastic degradation, suggesting that the Mg/DOBDC has become less crystalline or suffered structural degradation upon exposure to steam. As it was
discussed in the literature review, it was observed in previous studies, MOFs are hydrophilic and degrade in the presence of water [54]. Specifically, it was observed that water molecules could replace organic linkers in the framework therefore collapsing the structure. XRD profiles of the bare sample before and after steam treatment are presented in Figure 32. Characteristic peak intensities of the ED-Mg/DOBDC have also become lowered after exposure to steam, possibly due to a harsh experimental conditions of the accelerated steam treatment employed in this work, but to a much smaller extent compared to that of the bare Mg/DOBDC. For instance, the relative intensities of the first characteristic peak of the Mg/DOBDC dropped after the steam treatment significantly by 72 %, while that of the ED-Mg/DOBDC decreased to a lesser degree (60 %) as can be seen in Figure 32 [3]. This implies less degree of the structural degradation for the ED-Mg/DOBDC sample, possibly being attributed to organically functionalized Mg(II) ions that may prevent direct adsorption of H₂O onto the open metal sites [3]. It is expected that the observed intensity decrease for the ED-Mg/DOBDC will be much less under practical CO₂ capture conditions, which is typically much milder than that of the steam treatment used in this work (e.g., post-combustion flue gas capture containing 5-7% of H₂O by volume at atmospheric pressure) [3].

Similar to the results observed in the XRD, the pore characteristics of the Mg/DOBDC have changed upon exposure to high temperature steam. Figure 33 (a) compares the changes of the BET surface area before and after the steam treatment, for the Mg/DOBDC and ED-Mg/DOBDC samples with varied amine loading. As it can be seen, the BET surface area of the Mg/DOBDC was 1200 m² g⁻¹ originally but exhibited a
drastic drop to 22 m$^2$ g$^{-1}$ after the accelerated steam treatment, corresponding to ca. 98% loss of the surface area. It can also be seen from Figure 33 (a) hysteresis is much wider and more pronounced than for bare material before steam treatment indicating presence of mesopores and pores of different shapes and sizes, or interconnected pores within each other. Such a large reduction of the surface area observed can be attributed to the loss of the material crystallinity upon steam exposure, as indicated by significant decreases in peak intensities evidenced in the XRD results. After the accelerated steam treatment, surface area values for the ED-Mg/DOBDC samples decreased as well but the extent of the surface area reduction is also smaller. For instance, the BET surface area of the ED-Mg/DOBDC sample containing 0.763 mmol ED g$^{-1}$ adsorbent (Sample 1) decreased from 195 m$^2$ g$^{-1}$ to 58 m$^2$ g$^{-1}$ after steam treatment, which corresponds to 70 % reduction in the surface area [3]. A similar reduction of about 67 % was observed in Sample 2 in BET surface area after steam treatment. Also as can be seen from Figure 33(b) the hysteresis of the adsorption-desorption isotherm for steam treated ED-Mg/DOBC is not as wide as

Figure 32: XRD patterns of the original Mg/DOBDC and ED/Mg-DOBDC before and after steam treatment. The full XRD pattern of Mg/DOBDC is also provided. [3] Reprinted with permission from Ref. 3. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA
it is for bare Mg/DOBDC, appearing much narrower indicating lesser degree of degradation and better preservation of some of the original pore sizes. Thus, despite some degree of the surface area loss upon accelerated steam treatment due to harsh conditions used here, the structural integrity of the ED-Mg/DOBDC is better preserved compared to the original Mg/DOBDC. These results support the data obtained through XRD analysis that showed retained intensities of the characteristic peaks for the ED-Mg/DOBDC samples [3].

The same trend was observed for total pore volume values as depicted in Figure 33(b). Values of the total pore volume were obtained via nitrogen adsorption tests on Mg/DOBDC and ED-Mg/DOBDC samples respectively, representing nitrogen uptake volume at the highest pressure point where the saturation to ambient pressure ratio is 1. Similar to the measurement results of the BET surface area, total pore volume of the bare Mg/DOBDC dropped considerably after exposure to steam from 0.536 cm$^3$ g$^{-1}$ to 0.0512 cm$^3$ g$^{-1}$, corresponding to a 91% reduction. On the other hand the ED-Mg/DOBDC samples showed no reduction in the total pore volume after accelerated steam treatment [3].

When bare Mg/DOBDC is functionalized with ED molecules the total pore volume values decreases since ED molecules now occupy the pore space, creating a steric hindrance effect and prohibiting the diffusion of nitrogen gas to some extent hence the smaller total pore volume values [3]. It is hypothesized that when ED-Mg/DOBDC is then exposed to steam the ED molecules that are grafted at the metal sites protect the open metal from the entering water molecules [3]. Based on the BET surface areas reported in this work, some surface area is retained after accelerated steam treatment on
ED-Mg/DOBDC suggesting that the structure is partially retained, as opposed to the dramatic decrease in porosity observed for bare Mg/DOBDC samples which shows complete structural degradation. However, since it is unlikely that all of the available metal sites have been grafted with ED it is expected that partial degradation of the structure can occur at these open metal sites, leading to the lower surface area as reported [3].

Due to this incomplete grafting of the available metal sites it is unclear how the structure of the material changes after the accelerated steam treatment. There are a number of possible degradation schemes that can occur depending on the number of ED sites loaded within the pore [3]. For example, if we assume every metal site within a pore has been grafted with ED then it is expected that the addition of water will not degrade this particular pore structure. However if ED has not been grafted to any sites within the pore, we can expect that the pore will completely collapse as seen in the case of the bare material. Between these two cases, it is unclear how the pore would be affected where ED grafting protects one or more metal sites, but not the entirety of the available metal sites in the pore.

The pores that have been partially loaded with ED may therefore be expected to show a number of different potential final structures upon steam treatment. It is expected that at the very least these pores should not completely collapse, retaining some pore volume and surface area. Complicating this discussion is the steric hindrance due to the addition of ED molecules observed even before steam treatment. As it was discussed above, we believe the pore blockage may be leading to the reported low pore volume values. With this steric hindrance effect already occurring, we may expect that even with
partial pore degradation we may still retain similar pore volumes with subsequent
decreasing surface areas, as the pores collapse to structures that are of different shape but
same overall volume. It could also be the case that given the collapse of the pore wall
between two semi-protected pores the formation of a larger mesopore may occur, giving
further high pore volume values even with lower crystallinity and surface area.

Therefore it is hypothesized that ED molecules play the role of protector of the
metal sites from the attack by water molecules but since not every metal site is grafted
with ED some degradation of the structure occurs, which either changes the geometry of
the pore channels or potentially creating mesopores resulting in lower surface area but
preserved total pore volume.

This fact could be attributed to the potential changes in the pore structure of ED-
Mg/DOBDC. The decrease in BET surface area after steam treatment may be explained
by partial framework degradation at the metal sites that were not functionalized with ED
molecules [3]. It is hypothesized that ED molecules protect the metal sites from
interaction with water molecules. Since not every single metal site is grafted with ED, at
the un-grafted metal sites the degradation occurs in a similar way to that observed in the
bare Mg/DOBDC. However what degree of degradation and how pore structure would
change after steam treatment is unclear [3]. It seems likely pores with at least one ED
molecule, the total collapse of the pore (and subsequent complete loss of pore volume
and surface area) may not occur. It may also be possible for larger pores to form, as
adjacent pores containing ED molecules partially collapse leaving behind only ligand-
metal connections that are protected by ED. These complicated degradation schemes may
explain why loss in surface area without significant decreases in total pore volume
occurs, although this can only be hypothesized at the current time. This result, in conjunction with those of the XRD and the BET surface area, suggests that amine-functionalization of the CUSs helps preserving the structural integrity of the Mg/DOBDC framework under the humid environment [3].

Figure 33: BET surface area (a) and total pore volume (b) values of the original Mg/DOBDC and two ED-Mg/DOBDC samples with different amine loadings before and after steam treatment. [3] Reprinted with permission from Ref. 3. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA
Figure 34: Nitrogen adsorption and desorption isotherms of steam treated Mg/DOBDC MOF (a) and steam treated ED-Mg/DOBDC samples (b).

4.1.7 Effect of steam exposure on the carbon dioxide capture in bare and functionalized Mg/DOBDC samples

The consequences of the structural changes upon steam treatment were evaluated in terms of the CO$_2$ adsorption characteristics of the Mg/DOBDC and ED-Mg/DOBDC,
respectively (Figure 35). The equilibrium adsorption capacities of these samples were measured using a TGA instrument under the flow of pure CO$_2$ at ambient temperature (Figure 35(a)). The results showed that the Mg/DOBDC undergoes a significant loss in the adsorption capacity from ca. 4.27 mmol g$^{-1}$ to ca. 1.71 mmol g$^{-1}$ after the steam treatment, regaining only 40% of its equilibrium adsorption capacity. We assert that this considerable reduction of the adsorption capacity observed in Mg/DOBDC after steam treatment can be attributed to the degradation of the crystallinity and the pore characteristics as evidenced by the XRD and the BET analyses discussed above. In bare Mg/DOBDC sample, the main adsorption sites for carbon dioxide molecules are coordinatively unsaturated metal sites of Mg. When ED is grafted onto the metal site, it is possible that metal site is now blocked from carbon dioxide molecules and the particular metal site may not anymore serve as an adsorption site. However, since ED molecule possesses amine groups on both ends of the molecule, a new adsorption site at the other end of amine unbounded to the metal site is formed and able to capture carbon dioxide molecule. Basically, the adsorption site at the metal site is now replaced by the adsorption site at the amine group. It is believed that in this case ED contributed to carbon dioxide capture based on the similar carbon dioxide capture capacity as in bare Mg/DOBDC. If ED molecules block the adsorption sites of metal but the capacity stays constant after ED grafting, ED molecules must contribute to the carbon dioxide capture capacity [3]. One of other ways to prove this concept could be functionalization of the framework with a group where only one end possesses amine group. In that case, amine group would be blocking the metal site from CO$_2$ adsorption and CO$_2$ capacity should be decreased since there are no other amine groups available as adsorption sites. Another way to test
importance of ED in the CO$_2$ adsorption would be to increase ED loading and observe whether or not CO$_2$ capture capacity increases or decreases. From those results it would be possible to conclude whether or not ED adsorption site is able to capture more CO$_2$ than the adsorption site at the metal. Compared to the original Mg/DOBDC, the ED-Mg/DOBDC samples recovered a considerable portion of the initial adsorption capacity after steam treatment. For example, the ED-Mg/DOBDC with a loading of 0.763 mmol ED g$^{-1}$ adsorbent (Sample 1) that showed an initial capacity of 4.26 mmol g$^{-1}$ marked the capacity of 4.35 mmol g$^{-1}$ after accelerated steam treatment, preserving its capture capability completely. Same trend was confirmed in the Sample 2 with a loading of 1.07 mmol ED g$^{-1}$ adsorbent, of which the capacities before and after steam treatment were 4.66 mmol g$^{-1}$ and 4.47 mmol g$^{-1}$, respectively [3].

The CO$_2$ capture kinetics, often represented by the initial adsorption rate and/or the adsorption half time, is another important characteristics of the adsorbents defining their capture performance. The initial adsorption rates of the Mg/DOBDC and ED-Mg/DOBDC were determined in terms of the amounts of the CO$_2$ captured during the first 10 seconds of the adsorption experiments in order to identify the effect of structural changes onto their CO$_2$ capture performance upon functionalization and steam treatment (Figures 35(b) and 36). After steam treatment, the initial adsorption rate of the original Mg/DOBDC decreased significantly from 14.9 mmol g$^{-1}$ min$^{-1}$ to 0.10 mmol g$^{-1}$ min$^{-1}$, which corresponds to a more than 95% reduction in rates. Such a considerable deterioration of the initial adsorption rate may be ascribed to the loss of the crystallinity and porosity occurred within Mg/DOBDC sample after steam treatment, as evidenced by the XRD and the BET analyses. The initial adsorption rates of the ED-Mg/DOBDC were
slightly lower compared to the bare Mg/DOBDC, e.g., 14.8 mmol g\(^{-1}\) min\(^{-1}\) (Sample 1) and 12.1 mmol g\(^{-1}\) min\(^{-1}\) (Sample 2) [3]. This may be another indication of the ED molecules occupying the pore space of the framework and therefore reducing the effective pore dimensions of the adsorbents while affecting diffusional transport of CO\(_2\) molecules toward the internal adsorption sites (amine groups) [3].

Compared to the bare Mg/DOBDC that showed more than a 95% decrease in the initial adsorption rate, the sorption kinetics of the ED-Mg/DOBDC were much less influenced by the accelerated steam treatment. Specifically, the initial adsorption rate of the ED-Mg/DOBDC was lowered to 10.8 mmol g\(^{-1}\) min\(^{-1}\) (Sample 1) and to 11.2 mmol g\(^{-1}\) min\(^{-1}\) (Sample 2), corresponding to reduction by about 27% and 8%, respectively [3]. The differences in the degree of the initial rate reduction observed for these two samples could be attributed to their differences in amine loadings, implying that materials stability of the Mg/DOBDC adsorbents under humid conditions could be further enhanced by increasing the amount of the amines added to the framework. Based on these results, it is also thought that almost no ED molecules escape or leak from the framework during steam treatment. Otherwise, the same level of degradation in structure and in CO\(_2\) capture capacities observed in Mg/DOBDC would have been observed in ED-Mg/DOBDC samples [3].
Figure 35: CO$_2$ adsorption capture capacity (a) and initial CO$_2$ adsorption rate (b) of the original Mg/DOBDC and two ED-Mg/DOBDC samples before and after steam treatment. [3] Reprinted with permission from Ref. 3. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA
Figure 36: Initial CO\textsubscript{2} adsorption capture curves of Mg/DOBDC and ED-Mg/DOBDC before and after steam treatment. [3] Reprinted with permission from Ref. 3. Copyright 2015 WILEY-VCH Verlag GmbH & Co. KGaA

4.1.8 Conclusions and significance

In this work it was shown how simple modification at the open metal sites of MOF structures could improve materials stability in humid conditions and retain their CO\textsubscript{2} capture capacity. These results are highly significant in the field of practical applications of metal organic frameworks as porous solid adsorbents for CO\textsubscript{2} capture. Specifically, the framework of the metal organic framework, Mg/DOBDC, was organically functionalized to generate ED-Mg/DOBDC by coupling its coordinatively unsaturated sites (also known as open metal sites) with ethylenediamine molecules [3]. The stability of the Mg/DOBDC and ED-Mg/DOBDC MOFs in the presence of humidity was assessed through the examination of the changes to the structure and CO\textsubscript{2} adsorption
characteristics of these materials after the accelerated steam treatment. The results from
the XRD and porosity measurements showed that the bare Mg/DOBDC suffers from
significant degradation in its crystallinity and pore characteristics after steam treatment.
In contrast, while showing some degree of degradation possibly due to the harsh
conditions of the accelerated steam treatment, the crystal structure and the pore properties
of the ED-Mg/DOBDC seems to be less influenced by humidity. These differences in the
material stability of the Mg/DOBDC and ED-Mg/DOBDC lead to major differences in
terms of the CO$_2$ adsorption performance described by CO$_2$ adsorption capacity and
kinetics. For instance, compared to the original Mg/DOBDC that revealed 61% reduction
in the adsorption capacity as well as more than a 95% drop in initial adsorption rate after
exposure to steam, the adsorption capacity and kinetics of the ED-Mg/DOBDC are
considerably improved. These results suggest that amine functionalization of the
 coordinatively unsaturated sites within the MOF framework is a promising technique for
preservation of material stability as well as material adsorption properties in a humid
environment, which is closer to the CO$_2$ capture conditions found in flue gas or ambient
air. There are currently many reports that exist where metal organic framework materials
are functionalized with amine groups. An accelerated steam treatment test performed in
this work is a fast method to test materials stability in the humid conditions, which is
important for future consideration of the material in the practical conditions. It is
considered that the accelerated treatment causes the maximum degradation of the
structure possible in steam, and therefore can be used to predict the final state of the
sorbent after multiple rounds of humid capture in practical conditions. This may be a
useful tool therefore to determine quickly if a material should be investigated for long term studies of capture in industrial flue gas conditions.

On the topic of using amine groups (in this case ED groups) as pore stabilizer or protector of metal sites from the attack from water molecules, this approach could be applied to any of the current metal organic frameworks reporting promising CO$_2$ capacities at atmospheric pressure where coordinatively unsaturated metal sites are present. The MOFs materials with pore size of about 10 Å and higher would also be advantageous for higher possible ED loadings.

4.2 **Aim 2: Design, synthesis, and characterization of layered metal organic frameworks**

In this section the design, synthesis and characterization results of layered metal organic frameworks will be discussed. The results encompass morphological and structural information of the synthesized MOFs, as well as the analysis of the composition.

4.2.1 **Synthesis and characterization of CoBDC-HD framework**

As described in the literature review, the structure of metal organic frameworks can be manipulated post-synthetically or new frameworks can be synthesized using different organic ligands or metal sites. For a synthesis of new frameworks there are many operating conditions that have to be taken into account, such as solubility of the ligands, and the chemical and thermal stability of the constituents. In order to eliminate or reduce the number of variables, it would therefore be beneficial to use already known structures and interchange the constituents post-synthetically generating new frameworks of similar shapes but different pore sizes. This could be achieved by interchanging the
organic linker molecules with ones with similar chemistry but longer or shorter lengths, which would result in the manipulation of the pore size in the final framework. In this work, a series of layered pillared metal organic framework were generated with potentially interchangeable organic ligand molecules. There are currently few reports that describe the synthesis of layered three-dimensional MOFs based on this “pillaring” strategy [14, 15, 27, 48, 89, 108]. The strategy implies starting with a known two dimensional MOF structure and further pillaring it with rigid organic ligands to generate a final 3-dimensional crystal [26, 27, 41, 108]. In general for the construction of such a pillar-ligand based MOF, neutral pyridyl N,N’ donor ligands are used. As a result, these frameworks usually possess rigid structures that allow for high surface area and permanent porosity. This rigidity however also makes the frameworks chemically stable, and therefore they are not often viable candidates for post synthetic linker exchange. Here, a novel metal organic framework was constructed using an aliphatic amine chain organic linker of 1,6-hexanedi amine to serve as one of the constituents and potentially directing the construction of 2D sheets pillared with either solvent molecules or amine linkers. The new framework was denoted as CoBDC-HD (or NEU-3). It was attempted to show here that besides the commonly used neutral pyridyl N,N’ donor molecules used as pillaring linkers, it is also possible to use molecules with end –NH₂ groups to obtain layered structures. The 1,6-hexanedi amine molecule was chosen because it possesses two coordination modes, which would allow for the interaction with metal sites, and because it is a linear molecule to obtain a large interlayer spacing and hence large pores in between the layers. Once synthesized and the first well-defined XRD pattern was obtained the main question was to solve the structure of the new material and determining
whether or not it was indeed a metal organic framework. Further tests also have been done in attempts to introduce other organic linkers into a framework by post-synthesis transformation, which would allow for control over pore size and dimensionality of the material.

4.2.1.1 Synthesis trials of CoBDC-HD framework

The first few synthesis trials of CoBDC-HD resulted in a bright purple color in a powder form following the main synthesis. Through a careful manipulation of synthetic conditions, it was found that good quality crystals were formed at 80 °C after 5 days. Initial synthesis run was performed where amine solution was first prepared in dimethylformamide/acetonitrile mixture, and then one by one the cobalt source and terephthalic acid were added to the main mixture. It was later found that pre dissolving 1,6-hexanediamine in DMF/acetonitrile solvent solution and pre dissolving the cobalt source and terephthalic acid in DMF/acetonitrile solvent solution separately followed by mixing of the two solutions until a completely homogeneous mixture is obtained results in a more crystalline material based on the XRD patterns (Figure 37-1) and uniformly shaped rod-like crystals based on the SEM micrographs as shown in Figure 38. The recipe used for generation of crystals with XRD profile shown in Figure 37-1 would be called original recipe for synthesis of CoBDC-HD.
Synthesis proceeded in the presence of a solvent mixture of dimethylformamide and acetonitrile under hydrothermal conditions. The crystal structure was assessed via X-ray diffraction pattern of the resulted framework presented in Figure 37-1. From the overview of the pattern, it can be said that the resulted material is crystalline based on the intense peaks present in the pattern. The structural analysis based on the XRD profiles of the obtained crystals will be presented later in this chapter with four different potential structures of CoBDC-HD (Cases 1-3).

Scanning electron micrographs shown in Figure 38 reveal the surface morphology of generated CoBDC-HD crystals obtained after all of the components were pre-dissolved (Figure 37-1). As it can be seen, crystals take the form of long rods of about 1-2 mm in
width. These rods seem to generate from the middle of the node and grow outwards. No other shapes were observed across multiple samples of CoBDC-HD indicating the uniformity of generated crystals.

When synthesis conditions were slightly altered and higher amount of terephthalic acid was used, the XRD pattern of the obtained framework was similar in terms of peak positions but appeared to be significantly more crystalline. The conditions for each of the synthesis runs along with the original recipe conditions are summarized in Table 1. With higher concentration of terephthalic acid in the initial solution, the first three peaks appeared significantly more intense while peaks between 15-20 degrees 2θ stayed approximately of the same intensity. When the molar concentration of terephthalic acid in the initial synthesis solution was almost twice as much as the concentration of the metal nitrate hydrate (Co (NO₃) 6H₂O), the first peak at 7.2 degrees 2θ was almost three times of the intensity of the peak at the same position from the original recipe (Figure 39). The increase of intensity of peaks with increase of TPA content indicates that terephthalic acid is a limiting reactant in the reaction that generates NEU-3 crystals and nucleation.

SEM micrographs of the new synthesis runs are shown in Figure 39 and reveal different morphology compared to the crystals from the original recipe. A uniform separated rods of about 10-15 micrometers long and about 5 micrometers wide for synthesis with 0.5:1 Co:BDC ratio (Figure 39, A and B) can be seen. A ratio of 0.748:1 resulted in thin sheets of also about 10 micrometers long and 3-5 micrometers wide as can be seen in Figure 39 (C and D).
Figure 38: SEM micrographs of CoBDC-HD crystals at different magnifications.

Table 1: Summary of the synthesis conditions used to obtain CoBDC-HD frameworks.

<table>
<thead>
<tr>
<th></th>
<th>Original recipe</th>
<th>0.74:1 molar ratio Co (NO$_3$)$_6$H$_2$O : H$_2$BDC</th>
<th>0.5:1 molar ratio Co (NO$_3$)$_6$H$_2$O : H$_2$BDC</th>
<th>Co-BDC complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (NO$_3$)$_6$H$_2$O</td>
<td>0.45 mmol (0.131 g)</td>
<td>0.45 mmol (0.131 g)</td>
<td>0.45 mmol (0.131 g)</td>
<td>0.45 mmol (0.131 g)</td>
</tr>
<tr>
<td>H$_2$BDC (TPA)</td>
<td>0.164 mmol (0.0273 g)</td>
<td>0.602 mmol (0.1 g)</td>
<td>0.903 mmol (0.15 g)</td>
<td>0.903 mmol (0.15 g)</td>
</tr>
<tr>
<td>1,6-hexanediamine</td>
<td>12.6 mmol (1.468 g)</td>
<td>12.6 mmol (1.468 g)</td>
<td>12.6 mmol (1.468 g)</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 39: XRD patterns of the synthesis runs of CoBDC-HD with higher amounts of terephthalic acid.

In all of the Cases 1-3 described later in this chapter about the potential structure of CoBDC-HD, the material is composed of two dimensional sheets formed between inorganic clusters of cobalt connected by the organic linkers of terephthalic acid groups. Therefore, it is possible that in the original recipe where amount of cobalt nitrate hexahydrate was predominant and almost three times as high as the amount of terephthalic acid, the two dimensional sheets would be formed but with an excess of metal source which further participates in a reaction with 1,6-hexanediamine therefore creating an extra phase. However when higher amount of terephthalic acid is added, the crystallinity of the overall material improves which could be due to the formation of more of the 2D sheets material forming a more crystalline and periodic structure.
Figure 40: SEM micrographs of CoBDC-HD synthesis runs with 0.74:1 molar ratio (A and B) and 0.5:1 molar ratio of Co (NO$_3$)$_2$ 6H$_2$O: H$_2$BDC.

4.2.1.2 Structural characterization of CoBDC-HD framework

Before we get into the potential cases of the structure of CoBDC-HD MOF synthesized in this work, the common structural characteristics will be described first. In frameworks generated from reactions between cobalt nitrate hexahydrate and terephthalic acid, usually cobalt takes an octahedral coordination environment or binds to six different ligands. In most cases it was reported that trinuclear metal clusters are generated where central metal is coordinated to six carboxylate oxygens of the separate benzene – 1,4-dicarboxylic acid (BDC or terephthalic acid, TPA) groups and the two terminal metal centers coordinated to four oxygens of the terephthalic acid groups each and the other two coordination sites are occupied by either solvent molecules or any other additional organic ligands available. It was observed in other frameworks, such as Mg$_3$(bdc)$_3$(DMA)
MOF that Mg-bdc 2D layers are usually formed. Similarly, it is thought that reaction between cobalt and terephthalic acid also generates 2D layers which are supported or pillared by additional molecules. The structure of 2D layers is shown in Figure 49b on the example of the Mg$_3$(bdc)$_3$(DMA) [24]. In all cases presented later in this chapter, the 2D layers are further pillared by either solvent molecules, 1,6-hexanediamine ligands, or formed due to the reaction cations. A simplified schematic of the proposed structure of CoBDC-HD is presented in Figure 41. Each case will be described and the information supporting each case would be presented. Since instrumentation for the single X-ray diffraction analysis was not available to us, the structural analysis in this work is based on the powder X-ray diffraction results, TEM micrographs, and thorough literature search for similar frameworks.

Figure 41: Schematics of the hypothesized structure of CoBDC-HD framework.
a) Case I: 2D layers pillared by ligands of 1,6-hexanediamine

The first hypothesis made about the structure of the obtained framework which is here denoted to as CoBDC-HD MOF, consists of 2D layers stacked in [1,0,0] direction. The 2D layers are made out of cobalt clusters connected by the organic ligands of the terephthalic acid as described earlier. Based on the Case I presented in this section, the 2D layers are further pillared by ligands of 1,6-hexanediamine groups. Based on this hypothesis the layers in CoBDC-HD are composed of cobalt metal sites connected by benzene-1,4-dicarboxylic acid groups used here as a primary organic linker. The secondary building unit of the cobalt cluster contains three Co atoms where the middle atom is coordinated in an octahedral fashion to six oxygens of the surrounding carboxylic groups. The cluster made out of three cobalt atoms is formed with the Co atoms connected to each other through the O atoms of the benzene – 1,4-dicarboxylic acid groups. The other two symmetrical cobalt atoms are then positioned on either side of the 2D layer and are each coordinated to the four O atoms of benzene-1,4-dicarboxylic acid molecules, one O atom from dimethylformamide, and to the molecule of 1,6-hexanediamine via N atom. It is hypothesized that 1,6-hexanediamine binds with its end –NH₂ group to the metal sites and sits between the layers, hence playing the role of a pillaring linker between the 2D sheets. If there are two molecules of 1,6-hexanediamine present between the layers the Miller indices of potential representative planes could be assigned and XRD peaks identified as shown in Figure 42. For this assignment, the unit cell was assumed to be monoclinic based on the previous literature reports. For example, Han et al. reported a MOF based on the same 2D layer of cobalt metal centers connected by the terephthalic acid (benzene 1,4-dicarboxylic acid or BDC) [41]. In their work the 2D layers were pillared with larger and bulkier organic ligand, but the unit cell was found
to be monoclinic. If based on that example and Case I, the unit cell is also monoclinic and
distance of b and c parameters are known along with an angle beta, then new Miller
indices could be assigned for unique length of a-parameter (approximate length of two
1,6-hexanediamine molecules).

The first interlayer peak, also the strongest in the pattern, was assigned to the
[3,0,0] plane representing a repetitive distance between diffracting planes of 12.4 Å. This
would mean that the distance for the [1,0,0] plane could be calculated to be 37.4 Å. The
obtained distance supports the hypothesis of two layers of 1,6-hexanedianime molecules
between the layers, and the a-parameter of the unit cell within the crystal corresponds to a
thickness of two layers and two 1,6-hexanediamine molecules.

![XRD pattern](image)

**Figure 42:** XRD pattern of the as-synthesized CoBDC-HD framework with
interlayer peaks assignments.
b) **Case II: 2D layers pillared by the solvent molecules of DMF and/or dimethylammonium cations**

Case II described in this section inscribes also formation of 2D layers composed of cobalt metal sites and organic ligands of terephthalic acid as described earlier. In Case II, it is hypothesized that formed 2D sheets are pillared by the solvent molecules of dimethylformamide which are coordinated through their O atom to the terminal metals of cobalt. If this is true then it is also assumed that 1,6-hexanediamine molecules do not play any role in the structure of CoBDC-HD. To investigate this further, synthesis runs without addition of any amine molecules have been performed and results are shown and analyzed here. The first run was repeated with the same conditions where same amounts of cobalt metal source, terephthalic acid (0.15 g), dimethylformamide, and acetonitrile but no 1,6-hexanediamine were used. This solid obtained from this specific synthesis run will be denoted here as the CoBDC-A (Cobalt-terephthalic acid) complex. After 24 hours, two different solids were observed with different colors, specifically a brown and a purple solid precipitate as can be seen in Figure 45. The XRD patterns of these two solids are presented in Figure 45 as well. It can be seen that the XRD profile is completely different from that of CoBDC-HD. The peaks around 8.8, 14, 15.7, and 17.7 degrees 2θ could be representative peaks of the layer structure itself. Based on the TEM and HRTEM images taken of the CoBDC-A complex (Figures 46 and 47), definite layered structures are observed. In this case, it is important to understand how cobalt metal site is binded to the terephthalic acid, in what type of coordination and whether or not the 2D sheet created here is the same type of layer formed in the CoBDC-HD framework. There have been works previously reports on cobalt and terephthalic acid pairings. In one of the
earliest works is by Rosi et al. MOF-71 was made out of [-O-Co-] infinite rods that were further connected to each other via organic molecules of terephthalic acid as shown in Figure 44 [93]. However, based on the XRD pattern of the MOF-71 it does not correspond well with patterns of any of the obtained solids of CoBDC-A or CoBDC-HD. The XRD pattern of MOF-71 does show only some similar peaks with the most crystalline derivative of CoBDC-HD. The lengths of both terephthalic acid and 1,6-hexanediamine are approximately the same, about 7 Å. It is therefore possible that infinite rods made out of cobalt metal sites and oxygen atoms of the terephthalic acid are further connected to each other either by terephthalic ligands as in MOF-71 (Figure 44) creating a 2D sheet and further pillared by 1,6-hexanediamine explaining peaks at 7.2 degrees 2θ in the NEU-3 XRD profile. Figure 43 shows the comparison between two XRD patterns and it is observed that the peaks assigned to the interlayer peaks, at 7.2 degrees 2θ for [3,0,0] plane and 9.8 degrees 2θ for [4,0,0] according to Case I are unique only to CoBDC-HD framework.
Figure 43: Comparison of the XRD patterns between MOF-71 and CoBDC-HD frameworks. The red arrows indicate the matching peaks and CoBDC-HD characteristic peaks are in black.

Figure 44: The structure of MOF-71 composed of infinite rods of metal-oxygen-metal complexes which are further connected to each other by a benzene ring of the terephthalic acid generating a 3D structure shown on the right [93]. Reprinted with permission from Ref. 93. Copyright 2005 American Chemical Society.
Figure 45: XRD patterns of brown and purple solids of Co-BDC complex formed after 48 hours in the oven at 80 °C.

Figure 46: Transmission electron micrographs (TEM) of CoBDC complex. Layered structures with 3-4 nm interlayer distances are observed on the micrographs.
Figure 47: High-resolution TEM (HRTEM) images of the layers observed in CoBDC-1 complex.

Again to answer the same question of whether or not layers formed from this synthesis are the same layers that are present in CoBDC-HD framework, few more synthesis runs were performed under different conditions.

In order to shine light into the structure of CoBDC-HD, few attempts of the formation of isostructural MOFs with Mg or Cu metal sites instead of Cobalt have also been performed. Since the MOF structures of MgBDC and CuBDC are known and have been reported in the literature it was thought to be helpful in determining the structure of CoBDC-HD. The first synthesis runs were performed without 1,6-hexanediamine and in the presence of only terephthalic acid (also called benzene 1,4-dicarboxylic acid) and cobalt nitrate hexahydrate in the solution of only dimethylformamide (DMF) at higher temperature of 110 °C heating in the oven for 1 day. These conditions were repeated from the conditions at which MgBDC and CuBDC frameworks are usually obtained. While the synthesis run without 1,6-hexanediamine has been performed previously and its XRD
pattern did not match any of the CoBDC-HD profiles observed, the absence of acetonitrile and the increase in the synthesis temperature to 110 °C resulted in crystals with different XRD profile. The new complex will be denoted to as CoBDC-1 in this work for the CoBDC framework synthesized using only DMF and heated at 100 °C. As observed in Figure 48, XRD profiles of CoBDC-1 and of MgBDC-1 are very similar with stars indicating similar peaks in two patterns. It could be possible that both of CoBDC-1 and MgBDC-1 complexes form the same crystals with similar unit cell parameters and geometry differing only in the metal center. Since both cobalt and magnesium are known to exhibit octahedral coordination environment and tend to form trinuclear units of three metals where central metal is coordinated to six carboxylate oxygens of the terephthalic acid and the terminal metal centers coordinated to four oxygens of the acid and other two coordination sites are occupied by the solvent molecules of either dimethylformamide or water.

Davies et al. generated a framework, Mg₃(bdc)₅(DMA)₄ made out of two dimensional layers (Figure 49) with solvent molecules of dimethyl acetamide (DMA) in between [24]. In this framework, the layers of trinuclear clusters connected by the terephthalic acid are stacked along the b-direction. Due to the presence of DMA molecules coordinated to the metal sites of magnesium, this framework at this form is not porous. Also the layers are offset from one another in the b-direction. In the tests performed in this work, XRD pattern obtained after 2 days of synthesis of MgBDC complex (will be denoted to as MgBDC-2) is very similar to that of Mg₃(bdc)₅(DMA)₄. The difference between MgBDC-2 and Mg₃(bdc)₅(DMA)₄ is the solvent molecule used for synthesis. In MgBDC-2 DMF with a lower steric requirements than DMA was used,
therefore small deviations in peak positions is possible. Nevertheless, the XRD patterns of those two materials are very similar therefore it is possible that generated here MgBDC-2 framework has the structure as $\text{Mg}_3(\text{bdc})_3(\text{DMA})_4$ but with molecules of DMF coordinated to the terminal magnesium metal sites and occupying interlayer space. From the known structure of $\text{Mg}_3(\text{bdc})_3(\text{DMA})_4$ the characteristic peaks of MgBDC-2 were indexed with the first peak corresponding to $[1,0,-1]$ plane and second peak to $[1,0,1]$ plane which represents the two dimensional layer but not the interlayer distance since the layers are stacked in b-direction. All of the peaks appear to be shifted slightly to a higher angle $2\theta$, which could be due to the smaller interlayer distance due to the presence of DMF molecules, which are smaller than the DMA molecules. As it can be seen as well, the MgBDC-1 complex (after 1 day of synthesis) also exhibits the first peak around 7 and 14.1 degrees $2\theta$ for the respective reflections of $[1,0,-1]$ and $[2,0,-2]$ planes corresponding to the formation of the two dimensional layers. Therefore it is possible the same peaks observed in the XRD pattern of CoBDC-1 complex at 7.3 and 14.4 degrees $2\theta$ in Figure 43 also represents the plane cutting two-dimensional layer along the a-c direction. Hence it can be said that CoBDC-1 and MgBDC-1 are isostructural MOFs based on almost identical XRD patterns shown in Figure 48 with the only difference in metal centers.
Figure 48: XRD patterns of CoBDC-1, MgBDC-1, and CuBDC MOFs after 1 day of hydrothermal synthesis in the solvent solution of dimethylformamide at 110 °C.

Figure 49: Structural representation of the Mg$_3$(bdc)$_3$ layers parallel to the [1,0,1] plane (a) and the views of stacked layers along the b-axis (b). Orange polyhedral represent octahedral coordination of the magnesium metal sites. DMA molecules are not included. [24] Reproduced from Ref. 24 with permission of The Royal Society of Chemistry.

After two days of synthesis, MgBDC-2 complex was resulted where two dimensional layers were stacked along b-axis similar to the complex of Mg$_3$(bdc)$_3$(DMA)
reported in the literature and with the solvent molecules of dimethylformamide occupying space in between the layers. Based on the indexed peaks of the known structure of Mg$_3$(bdc)$_3$(DMA), the peaks of MgBDC-2 complex were also indexed. As mentioned earlier, the first peak around 7.1-7.3 degrees 2θ represents a distance within the 2D layer with a plane [1,0,-1]. Also peak at 14.1 degrees 2θ in MgBDC-1 complex could be indexed as [2,0,-2] and also shows up in MgBDC-2 complex but at slightly larger angle 2θ of 14.4. It is possible that after 1 day of synthesis MgBDC-1 complex has not crystallized fully and allowing longer reaction time at high temperature could result in a more structured material. Synthesis was further performed with reaction time of 3 days in the reaction oven and the resulted XRD pattern can be seen in Figure 50(d). Indeed, it can be concluded from the XRD profile that MgBDC complex stays the same in structure after 2 and 3 days of synthesis but becomes more crystalline after 3 days and few peaks around 10 degrees 2θ start to develop after 2 days of synthesis but not after 1 day. It should be again noted that two the most intense peaks (at 7.1 and 14.1 degrees 2θ) are representative of the 2D layers themselves. Hence, it is possible that as reaction time increases the crystals grow more of the 2D layer material with less stacking occurring.

Similar synthesis runs with varying reaction times in the oven were performed with CoBDC complexes. The XRD profiles of the obtained materials are presented in Figure 53. It can be seen that peaks very similar to the peaks of the Mg$_3$(bdc)$_3$(DMA)$_4$ are observed in CoBDC-2, CoBDC-3, and CoBDC-4 complexes with the most similar peaks marked with stars. Hence, it can be said that CoBDC complexes crystallized after 2, 3 or 4 days of synthesis are also isostructural to the Mg$_3$(bdc)$_3$(DMA)$_4$ and to the MgBDC complexes. This would mean CoBDC after 2 days of synthesis most likely forms 2D
layers of cobalt-terephthalic acid with solvent molecules of DMF in between the layers. A very recent study by Bagherzadeh et al. showed that the hypothesis made above about the structure of 2D layers and about MgBDC and CoBDC complexes being isothermal is true by synthesizing a new framework with Co-carboxylate building units, \( \text{Co}_3(\text{BDC})_3(\text{DMF})_2(\text{H}_2\text{O})_2 \) [6]. This specific MOF is 2D-periodic and composed of infinite chain supported by covalent bonding. This framework also forms layers along (1, 0, 1) plane, with one of the cobalt centers coordinating to six oxygens from carboxylic acid groups, and another distinguishable cobalt site coordinates to five oxygens from carboxylic groups and one oxygen of dimethylformamide as shown in Figure 51 (a). Structure of the layer is shown in Figure 51 (b). The XRD profile of this 2D MOF matches very well with the XRD profile of the CoBDC complex synthesized in this work after 2, 3, and 4 days. Due to such a good match in XRD profile, it could be seen that obtained framework is indeed isostructural to Mg\(_3\)(bdc)\(_3\)(DMA) framework with a cobalt center instead of magnesium.
Figure 50: XRD patterns of the MgBDC complexes after 1 day (b), 2 days (c), and 3 days (d) of synthesis. The XRD profile of Mg$_3$(bdc)$_3$(DMA)$_4$ is also presented for comparison (a). Similar characteristic peaks with the reference profile are indicated with a star.

Figure 51: A representation of one layer with shown DMF molecules coordinated to terminal cobalt centers (a), and a view in the (1 0 1) plane where cobalt clusters shown as polyhedrons connected via benzene rings og 1,4-benzenedicarboxylate ligands (terephthalic acid ligands).[6] Reprinted from Ref. 6 with permission from Elsevier.
Figure 52: XRD profiles of the reported in the literature Co$_3$(BDC)$_3$(DMF)$_2$(H$_2$O)$_2$ (a) and CoBDC-3 complex synthesized in this work.

As can be seen from SEM micrographs on Figure 54, the crystals take shape of hexagons anywhere between 20-40 micrometers wide. The closer look at those crystals reveals layering sheets as shown in Figure 54B.
Figure 53: XRD patterns of the CoBDC synthesized for 1 day (b), 2 days (c), 3 days (d), and 4 days (e). XRD profile of the Mg$_3$(bdc)$_3$(DMA)$_4$ complex is also shown for comparison.

Figure 54: SEM micrographs of the CoBDC-3 complex at high and low magnifications.
Structural transformations of the MgBDC and CoBDC-HD frameworks

It is known that magnesium carboxylate framework materials are able to undergo structural transformation upon loss of solvent molecules and back to the original state upon solvation of the materials [24]. For example the Mg₃(BDC)₃(DMA)₄ framework turns into Mg(bdc) complex after heating at 200 °C for 12 hours which is amorphous. This particular complex then turns into a Mg(BDC)(H₂O)₂ framework after exposure to air due to the highly hygroscopic nature of MgBDC. In a similar way, Mg₃(BDC)₃(DMF)₄ synthesized here showed to turn into a Mg(BDC)(H₂O)₂ when soaked in ethanol and was let to dry under air at room temperature. Also another way the Mg(BDC)(H₂O)₂ was obtained was via the same synthesis used to obtain Mg₃(BDC)₃(DMA)₄ but the resulting solid was vacuum dried and left to dry in air at room temperature. The framework of Mg(BDC)(H₂O)₂ consists of layers of terephthalic acid ligands connecting the rods of metal centers of magnesium [47]. Each of the Mg metal centers is connected to two oxygens of the terephthalic acid and water molecules occupy two other coordination sites. The XRD profiles of all three materials are presented in Figure 55.

One of the questions that arise here is that if Mg₃(BDC)₃(DMF)₄ can undergo such dramatic structural transformation, would CoBDC-HD also undergo a similar transformation. If it does then it is possible that CoBDC-HD possesses the same or very similar structure to Mg₃(BDC)₃(DMF)₄. As described Mg₃(BDC)₃(DMF)₄ turns into Mg(BDC)(H₂O)₂ and to observe any potential transformation, CoBDC-HD framework was also resolvated in ethanol solution and then air dried. The XRD profiles comparing original CoBDC-HD framework and ethanol resolvated/air dried CoBDC-HD are
presented in Figure 56. As can be seen no dramatic changes were observed and the peaks were almost the same in the resolvated sample. The only difference is the shift to lower values of degrees 2θ, which could indicate increased distances between diffracting planes within the sample due to the addition of ethanol molecules. But no structural transformation similar to the Mg₃(BDC)₃(DMF)₄ to Mg(BDC)(H₂O)₂ transformation was observed for CoBDC-HD.

Figure 55: XRD profiles of the Mg₃(bdc)(H₂O)₂ complexes obtained via vacuum drying of the MgBDC-2 complex (b) and via resolution of MgBDC-2 complex in ethanol and air drying (c). The reference XRD profile is also presented (a).
Figure 56: XRD patterns of the CoBDC-HD sample (a) and resolvated CoBDC-HD sample in ethanol and then dried in ambient conditions (b).

Davies et al. has also demonstrated transformation of Mg₃(BDC)₃(DMA)₄ to Mg(bdc) complex which is amorphous, and further back to Mg₃(BDC)₃(DMA)₄ after soaking it in DMA solution [24]. Same experiment was performed with CoBDC-HD where it was first heated at 200 °C for 24 hours and then solvated in DMF solution. Figure 57 provides comparison of the XRD profiles at each step in this experiment. As can be seen from the figure, CoBDC-HD did not take its original form Figure 57(a) after the sample was resolvated in DMF Figure 57(c). The structure degraded after heating at 200 °C (Figure 57(b)) and a strong peak has emerged at 27.8 degrees 2θ after resolvation in DMF (Figure 57(c)). Also it should be noted that the first peak in CoBDC-HD framework disappears after heating indicating some kind of transformation taking place within the structure of the layers themselves.
Figure 57: XRD patterns of the CoBDC-HD (a), heated at 200 °C CoBDC-HD (b) and further resolvated in DMF CoBDC-HD (c).

From these results it could be concluded that CoBDC-HD most probably does not possess the same structure as Mg₃(BDC)₃(DMA)₄. Similar test was performed on the crystals of the CoBDC-3 or CoBDC-4 frameworks which were isostructural to Mg₃(BDC)₃(DMA/DMF)₄ frameworks. Figure 58 presents XRD profiles before and after CoBDC-3/4 complexes were resolvated in ethanol and then dried in air. As it can be seen from Figure 58 CoBDC-3/4 complexes degrade after this test and does not undergo reversible transformation to Co(BDC) form or takes another form with water molecules in between the layers as it happens in magnesium complex. This could be due to the different nature of metals (cobalt versus magnesium) affecting the coordination environment and instantaneous water uptake only occurs in Mg based materials. It should be however pointed out that while CoBDC-3/4 complexes degrade almost completely after the test, CoBDC-HD framework maintained its structure almost fully after similar
test (Figure 57). This indicates differences in the structures between the two materials and that addition or presence of 1,6-hexanediamine has an effect on the final structure of CoBDC-HD making it less susceptible to the solvent resolvation tests with ethanol.

Figure 58: XRD profiles of CoBDC-3 complex before (a) and after (b) resolvation in ethanol and drying in air.

Another conclusion from these tests is that CoBDC-HD and CoBDC complexes do not have the same structure. While there are DMF solvent molecules present between the layers in CoBDC complexes, it is less likely to be the case in CoBDC-HD material. While there still could be DMF molecules in between the layers in CoBDC-HD, other ligands or molecules must also be present to support the structure making it more stable. Additionally, CoBDC and CoBDC-HD exhibit different XRD profiles but with few similarities in some of the peak positions.
Role of 1,6-hexanediamine in CoBDC-HD framework

A question that is left to answer is what is the role of 1,6-hexanediamine in CoBDC-HD? Does it somehow facilitate coordination of terephthalic acid groups to cobalt or does it serve as one of the constituent of the framework?

One of the potential scenarios is formation of dimethylammonium cations which are formed as a result to the well established reaction of decarbonylation of dimethylformamide (DMF) in the presence of base and heat. When heated, DMF results in carbon monoxide and dimethylammonium guests in the presence of base [100, 107]. It was found that in Fe- based MOF these guests also formed as well where pyridine was added to the reaction mixture and resulted dimethylammonium guests acted as counterions to the anionic Fe polyhedral clusters [100]. In addition to decarbonylation, hydrolysis of DMF also could be occurring as shown in Scheme 1 [10]. But since along with the base formed from the DMF, 1,6-hexanediamine molecules are also present in the solution, it all could contribute to the generation of higher amounts of the dimethylammonium cations, NH$_2$R$_2^+$. In that case, it is possible that instead of just DMF molecules present between the layers, the dimethylammonium cations could also be present along with DMF solvent molecules.

Scheme 1: Hydrolysis reaction of DMF in the presence of water and following formation of dimethylammonium cations [10].

\[
\text{HC(O)NR}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_2\text{H} + \text{HN}_2\text{R}_2 \rightleftharpoons \text{HCO}_2^- + \text{H}_2\text{NR}_2^+  \\
R = \text{Me, Et}
\]
Another interesting observation was made when Mg$_3$(bdc)(H$_2$O)$_2$ sample obtained after vacuum filtration and air drying (Figure 59b) was heated to 350 °C for 24 hours under nitrogen flow, a pattern very similar to the CoBDC-HD was generated as can be seen in Figure 59. It could be then that CoBDC-HD and MgBDC-2 complex heated at 350 °C are also isostructural materials with the difference in metal sites. It is interesting that in CoBDC-HD no heating was needed to achieve the specific structure with specific XRD profile while Mg$_3$(bdc)(H$_2$O)$_2$ complex was heated at high temperature. This further suggests that DMF undergoes hydrolysis. If in the Mg$_3$(bdc)(H$_2$O)$_2$ form some residual DMF molecules are still present under applied heat DMF hydrolyzes in the presence of water and forms the dimethylammonium cations yet again. Those cations further play a templating role in the crystallization of MgBDC (350 °C) and in the same way in CoBDC-HD. Such structural templating effect then results in isostructural materials with Co metal site for CoBDC-HD and with Mg metal sites for MgBDC. It is however still unclear, what type of structure results. Do dimethylammonium cations reside in the between 2D layers or result in a different structure completely?
Figure 59: Comparison of XRD profiles of the calcined at 350 °C Mg₃(bdc)(H₂O)₂ complexes and CoBDC-HD MOF. Stars indicate similar peaks.

Additional test on the influence of 1,6-hexanediamine molecules on the structure of CoBDC-HD has been performed. It was thought that if CoBDC complexes either after 3 or 4 days of synthesis (those are the same materials) are composed of 2D layers with DMF molecules inside, would the structure change in the presence of additional 1,6-hexanediamine? A separate solution of 1,6-hexanediamine in DMF was first prepared to which CoBDC-3 was added. The solution was well-mixed and then was placed in a 20 ml vials and heated to 110 °C for 1 day. Figure 60 presents results of this test. It can be seen that indeed after addition of 1,6-hexanediamine to CoBDC-3 complex and reheating just for 1 day resulted in crystals that have identical XRD profile (Figure 60(c)) as CoBDC-HD (Figure 60(d)) framework. The identical peaks are marked with stars and some Miller indices are marked from the known structure of Mg₃(bdc)₃(DMA)₄ (Figure 60a) to which CoBDC-3 complex is isostructurial. It can be seen that peaks corresponding to the peaks of 2D layers also show up in the pattern of both CoBDC-3 with added amine groups and
in CoBDC-HD. This may indicate that while layering structure did not change within the crystal, but the interlayer distance did due to the addition of 1,6-hexanediamine. The interlayer distance could be now occupied by the dimethylammonium cations formed as discussed earlier or by other molecules due to the structural transformation of CoBDC into CoBDC-HD after addition of amine groups.

When the same test of addition of 1,6-hexanediamine to the CoBDC-3 complex was performed but only in the solution of acetonitrile and not in dimethylformamide, material of different structure was obtained. The XRD profile of the resulted material is shown in Figure 61 (c) and for comparison along with the profile of the synthesis trial performed in DMF and the original profile of the CoBDC-3. As it can be seen when 1,6-hexanediamine is added in the solution of acetonitrile and not dimethylformamide, the resulting XRD profile (Figure 61(c)) is not similar to the one of CoBDC-HD. This further indicates that dimethylformamide does undergo decarbonylation in the presence of base (1,6-hexanediamine) when heated and potentially forms dimethylammonium cations. When base (1,6-hexanediamine) is added in different solution from DMF, no such reaction occurs resulting in a different material.

In conclusion to Case II, the structure of CoBDC-HD is templated based on the 1,6-hexanediamine molecule. The amine molecule could play role in the reaction of decarbonylation of DMF encouraging formation of dimethylammonium ions. So in Case II, it is hypothesized that along with some DMF solvent molecules present in between the layers, so do the dimethylammonium cations which balance the anionic layers of the framework and also occupy the interlayer space. It is expected then that in monoclinic unit cell the distance between the layers would change and so would the angle beta.
Figure 60: XRD profiles of CoBDC-3 complex before (b) and after (c) addition of 1,6-hexanediane and reheating. Profiles of CoBDC-HD (denoted as NEU-3 in the figure) and Mg$_3$(bdc)$_3$(DMF)$_4$ are also shown for comparison.
Figure 61: XRD profiles of CoBDC-3 (a), CoBDC-3 to which 1,6-hexanediameine was added in the solution of DMF (b) and in the solution of acetonitrile (c), and of CoBDC-HD (denoted as NEU-3 in the figure).

c) **Case III: 2D layers of CoBDC pillared by organic linkers of terephthalic acid**

Burrows et al. reported a framework which involved zinc(II) nitrate and 1,4-benzenedicarboxylic acid (terephthalic acid) as main constituents synthesized in the solution of DMF or DEF [10]. In this specific framework, anions of terephthalic acid are linking trinuclear linear clusters of Zn metal sites generating layered structure with triangular pore windows. The layers of zinc-bdc$^{2-}$ were further linked via deprotonated ligands of bdc$^{2-}$ generating a 3D framework. In this case pores of the framework are occupied by molecules of DEF and NH$_2$Et$_2^+$ (diethylammonium cation) which is formed from decarbonylation of DEF in the presence of heat and a base [10]. In the framework these diethylammonium cations are balancing out anionic layers of zinc-bdc$^{2-}$. Based on this research and other works reporting same formation of those cations, it could be possible that CoBDC-HD is also composed of anionic layers of Co-bdc$^{2-}$ just as it was
described in Cases I and II, where cobalt clusters are trinuclear. In the ZnBDC MOF such configuration of structure was observed only when diethylammonium cations were formed after hydrolysis of DMF. Similar to the framework of ZnBDC, it could be that layers of Co-bdc$^2-$ are pillared by the additional organic ligands of terephthalic acid, as shown in Figure 63. Since the atomic radii of cobalt and zinc are different, the thickness of the 2D layer itself would be different and the distance of terephthalic acid in the interlayer space, therefore using reflections observed in ZnBDC framework, new peaks for the same reflections with corrected interlayer distance values could be recalculated. Since in this case, the pillars are very stable in the form of terephthalic acid groups, the angle $\beta$ for the monoclinic form is much smaller than in the monoclinic form of Mg$_3$(bdc)$_3$(DMF)$_4$.

When the expected peak reflections were recalculated, it showed that NEU-3 framework has a lot of those expected peaks as shown in Figure 62. The pores of interlayer volume are still could be occupied by the dimethylammonium cations. Such nature of coordination where ligands of terephthalic acid support the layers could be due to the presence of dimethylamine groups which could also form from the hydrolysis of DMF. In that case hydrogen bonding could form between hydrogens of the dimethylamine groups or even dimethyformamide molecules and oxygens of the terephthalic acid groups hence templating the structure in a certain way. The hydrogen bonding from the following dimethylamine ligands and from DMF were observed in a Cu-BDC and Zn-BDC complexes by Hawxwell et al. and Clausen et al. [20, 43].
Figure 62: Comparison of the XRD profiles of CoBDC-HD and ZnBDC with peaks indicated for ZnBDC as they are and recalculated Miller indices for CoBDC-HD if terephthalic acid is in between the layers.

Figure 63: Structural configuration of Zn(bdc) complex where 2D layers are pillared with organic ligands of terephthalic acid [10]. Reproduced from Ref. 10 with permission of The Royal Society of Chemistry.

In case III for the potential structure of CoBDC-HD, 1,6-hexanediame plays templating role and encourage the structure where 2D layers of CoBDC are pillared by
the additional BDC organic ligands in the presence of 1,6-hexanediame in the main reaction. Such behavior would result in a stable rigid framework. It is also possible that dimethylammonium ions formed during the reaction still occupy the pore volume of the framework and are held there by ionic interactions.

4.2.1.3 Attempts of activation of CoBDC-HD framework

The synthesis of CoBDC-HD crystals occurs via self-assembly in the solvent mixture of dimethylformamide and acetonitrile. As a result, directly after synthesis, the pores of the framework are occupied either by solvent molecules of DMF or acetonitrile and/or by formed dimethylamine ligands. In order to investigate whether or not CoBDC-HD framework exhibits permanent porosity, the pore blocking species need to be removed. This is usually referred to activation of MOFs, or freeing the pores from solvent or guest molecules. One of the most common methods of activation of MOFs is activation by heating under vacuum. In the case of the CoBDC-HD framework, some physical properties of the constituents should be taken into account to carefully activate the framework without degrading or collapsing the framework itself. The boiling point of 1,6-hexanediame is about 200 °C while the boiling point of dimethylformamide is 150 °C. If, as it is mentioned in Cases I and II, solvent molecules of dimethylformamide are coordinated to the cobalt metal sites, meaning a temperature higher than 150 °C should be applied to proficiently remove the molecules, although temperatures near 200 °C could lead to destruction of the pillared framework.

a) Activation by heating

The boiling points of dimethylformamide and 1,6-hexanediame molecules are very close making it hard to optimize conditions for activation without disturbing the
main structure of the CoBDC-HD. However it is also unknown if the removal of guest molecules would degrade the framework. This could happen if guest molecules support the overall structure as it was discussed in Cases II and III. Temperatures for activation at 150 °C, 180 °C, 200 °C, 210 °C, 220 °C, and 230 °C were tested. The XRD patterns before and after heating at some of the tested temperatures are provided in Figure 64. It can be seen that after 200 °C the peaks shift, especially the first characteristic peaks. Decreases in the Braggs’ intensities have been observed at all temperatures but shifts in the positions were observed only at temperatures higher than 200 °C. The nitrogen adsorption and desorption isotherms are shown in Figure 65 and the porosity characteristics at each of the temperatures are provided in Table 2. The highest BET surface area values increased with increasing temperature of activation with the highest value of about 106 m²/g reported at 210 °C. After this point the surface area decreases, indicating that the changes in the structural characteristics observed in the XRD patterns lead to subsequent decreases in the porosity of the material. In addition, the surface area reported at 210 °C may not be a true representative of the actual porosity of the material since the sorbent is believed to degrade at temperatures above 200 °C, therefore making the observed surface area of 106 m²/g potentially inconclusive.

Table 2: Summary of porosity properties of CoBDC-HD samples activated at various temperatures.

<table>
<thead>
<tr>
<th>Activation Temperature</th>
<th>BET Surface Area (m²/g)</th>
<th>Langmuir Surface Area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 °C</td>
<td>26.470</td>
<td></td>
<td>0.066</td>
</tr>
<tr>
<td>180 °C</td>
<td>41.677</td>
<td>61.758</td>
<td>0.403</td>
</tr>
<tr>
<td>200 °C</td>
<td>75.794</td>
<td></td>
<td>0.424</td>
</tr>
<tr>
<td>210 °C</td>
<td>106.013</td>
<td>155.075</td>
<td>0.633</td>
</tr>
<tr>
<td>220 °C</td>
<td>53.016</td>
<td>77.670</td>
<td>0.291</td>
</tr>
<tr>
<td>230 °C</td>
<td>66.635</td>
<td>89.435</td>
<td>0.594</td>
</tr>
</tbody>
</table>
Figure 64: XRD patterns of the as-synthesized CoBDC-HD before activation and after activation at four different temperatures. All temperatures were kept constant for 24 hours under vacuum.
Figure 65: Nitrogen adsorption and desorption isotherms of CoBDC-HD samples activated at six different temperatures under vacuum. Adsorption isotherms are presented in solid lines and desorption in dashed lines.

The nitrogen adsorption and desorption isotherms show the presence of micropores based on the flat region between 0.1 and 0.4 P/Po indicating the slow filling of micropores as shown in Figure 65. The narrow hysteresis loop from 0.8 to 1 P/Po also indicates type IV isotherm and indicates presence of mesopores, which could be representative of pores present between the layers. The surface area based on the
Brunauer-Emmett-Teller model (BET) was 76 m$^2$/g with a total pore volume of about 0.5 cc/g after the material was exposed to dynamic vacuum at 200 °C for 24 hours.

**b) Activation by solvent exchange**

Aside from the emptying the pores of solvent molecules by heating under vacuum, another strategy for the evacuation of the pore space is known as solvent exchange was implemented. Solvent exchange takes place after the final product of CoBDC-HD crystals is obtained. The material was soaked in various solvent solutions to physically replace solvent molecules of dimethylformamide and acetonitrile. The solvents were chosen based on their low boiling points (lower than 150 °C). Another consideration in the choice of solvent molecules was the polarity of the solvent and whether or not more or less polar molecule should be chosen to be able to replace dimethylformamide molecules. Since polarity refers to the dipole moment of the molecule, it is important for the interactions occurring between dimethylformamide/acetonitrile solvent molecules and the framework to have been overcome for solvent exchange to be successful. For instance, it could be that since dimethylformamide is a polar molecule, it is more attracted to the metal sites. Therefore, a range of solvent molecules with various polarity indexes was chosen for solvent exchange. Table 3 shows all the different solvents used for solvent exchange and their corresponding polarities. Table 4 summarizes the porosity characteristics after each of the solvent exchange experiments.
Table 3: Summary of solvents used with their polarity values and boiling points for the solvent exchange experiments.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polarity index</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>6.4</td>
<td>153 °C</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>5.8</td>
<td>82 °C</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.1</td>
<td>61.2 °C</td>
</tr>
<tr>
<td>Methanol</td>
<td>5.1</td>
<td>64.7 °C</td>
</tr>
</tbody>
</table>

The experimental conditions for solvent exchange were as follows. About 200 mg of CoBDC-HD sample was measured out and added to the solvent solution. The solution was slowly stirred over a 12 hours period. After 12 hours the material was left to settle down and the top solution was decanted. The exchange with fresh solvent solution was done 4 times over two days. After the last exchange, the material was filtered and the obtained solid was dried at about 100 °C for 24 hours under vacuum to remove solvent molecules. The evacuation temperature in this case was chosen to be higher than the boiling points of the solvents used but not high enough to remove 1,6-hexanediamine molecules.

Acetonitrile, chloroform, and methanol were chosen as new solvents for exchange. Porous properties of the materials after each of the solvent exchange experiments are presented in Table 4. In addition, the XRD pattern of the sample exchanged with methanol is given in Figure 66. It can be seen that methanol exchange has resulted in structural degradation or potential exfoliation of the layers due to the high polarity of methanol, resulting in a much less intense profile. While acetonitrile and chloroform exchange showed no harm to the main structure of the framework based on the XRD patterns, the resulting surface areas were still quite low. This could be due to the low polarity of these solvents not allowing them to replace molecules of
dimethylformamide. These results also suggest that dimethylformamide molecules are not only physically present within the pores but are coordinated to the framework making it hard to replace or remove them without destruction of the crystal.

**Table 4: Summary of the pore characteristics after solvent exchange with various solvents.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Activation temperature</th>
<th>BET surface area (m²/g)</th>
<th>Langmuir surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>100 °C</td>
<td>27.18</td>
<td>40.06</td>
<td>0.190</td>
</tr>
<tr>
<td>Chloroform</td>
<td>100 °C</td>
<td>3.22</td>
<td>5.18</td>
<td>0.027</td>
</tr>
<tr>
<td>Methanol</td>
<td>100 °C</td>
<td>36.94</td>
<td>55.29</td>
<td>0.283</td>
</tr>
<tr>
<td>Methanol</td>
<td>180 °C</td>
<td>80.26</td>
<td>122.69</td>
<td>0.657</td>
</tr>
<tr>
<td>Methanol</td>
<td>(sonication) 100 °C</td>
<td>31.18</td>
<td>45.51</td>
<td>0.563</td>
</tr>
</tbody>
</table>

Among all of the solvents used, the methanol exchanged sample showed the highest surface area of about 37 m²/g after activation at 100 °C. But as shown in Figure 66 the XRD patterns the crystallinity of the CoBDC-HD has been compromised after exchange, specifically the first peak shows a significant decrease in intensity and a shift to a larger degrees 2θ. Methanol is the most polar molecule among the chosen solvent molecules. With a polarity closer to the polarity of the dimethylformamide, it is hypothesized that it could replace dimethylformamide molecules and even further may exfoliate the layers from each other. The methanol exchanged material was then heated at two different temperatures, 100 °C and 180 °C. Both of these temperatures are higher than the boiling points of methanol and dimethylformamide. The surface area of the sample activated at 180 °C was about 80 m²/g which is the highest BET surface area reported among other solvent exchanged samples in these experiments.
Figure 66: XRD patterns of the as-synthesized CoBDC-HD (denoted as NEU-3) and after methanol exchange and activation by heating at 100 °C and 180 °C.

c) Synthesis of CoBDC-HD crystals in ethanol or methanol solutions

Another attempt of eliminating solvents with high boiling points from the structure was performed where the material synthesis proceeded without the dimethylformamide solvent completely. Instead it was replaced with methanol for one synthesis run and with ethanol for another. Both of these solvents have boiling points lower than 100 °C, which it was hoped could be more easily removed and retain the structure of the CoBDC-HD crystal. Since this is quite a large change to the synthesis conditions, it was important to make sure the same crystals could be obtained from both synthesis runs. XRD patterns of the obtained frameworks are shown in Figure 67.
From Figure 67, it can be seen that materials synthesized in ethanol/acetonitrile and in methanol/acetonitrile solvent solutions did not yield highly crystalline materials. Also when compared to the crystals synthesized in DMF/acetonitrile solvent mixture, some of the main peaks representing interlayer distances are shifted and are of lower intensity. Based on these XRD results it appears that the CoBDC-HD frameworks could not be synthesized well under these conditions. However, these synthesis runs did not yield amorphous materials so synthesis in the new solvent mixtures could still be possible. Therefore, optimization of synthesis conditions is further required to achieve high quality crystals. From an environmental standpoint, it would be better to use solvents with low boiling points to require less energy for activation, as well as potentially using more environmentally benign molecules. Also these synthesis runs further indicate that presence of dimethylformamide is vital in formation of CoBDC-HD,
most probably due to the reactions it undergoes in the presence of heat and a base as discussed in Cases II and III.

In summary of the solvent evacuation experiments performed on CoBDC-HD, the activation by heating yielded higher surface areas than solvent exchange or solvent replacement in the synthesis step. The highest surface area was achieved by heating CoBDC-HD crystals at 210 °C for 24 hours resulting in the surface area of 106 m²/g. While the surface area reported was the highest, the XRD pattern showed degradation on the crystallinity of the material after heating indicating that loss of guest molecules could degrade the framework. The solvent exchange tests were not successful either: only methanol exchange sample being able to improve surface area to 80 m²/g but simultaneously compromising the structure of the material. It is still believed that CoBDC-HD framework is porous with mesopores present in the structure as it was shown by the behavior of the nitrogen adsorption and desorption isotherms. Further tests have to be performed to obtain the best method of removing solvent molecules from the structure. It is also possible that if the molecules of dimethylformamide are supporting the structure in some way, for example by coordinating to the cobalt metal site, when removed, it causes the structure to collapse. Another solvents could be used for future exchanges tests along with supercritical CO₂ drying.

4.2.1.4 Decomposition profile of CoBDC-HD framework

Thermogravimetric analysis performed on CoBDC-HD crystals synthesized based on the original recipe showed that the material is stable up to about 180 °C as can be seen in Figure 68. There was a slight weight loss of about 5% up to 180 °C which could be associated to the loss of one or two acetonitrile molecules from the supposed unit cell.
Between 180 °C and 250 °C, the weight loss was about 19% which is due to the evaporation of two coordinated dimethylformamide molecules and potentially one 1,6-hexanediamine molecule. The decomposition profiles of the synthesis run with 0.15 g of terephthalic acid before and after activation at 180 °C in the vacuum line are presented in Figure 68. It can be seen that the material synthesized with 0.15 g of terephthalic acid is more thermally stable, up to about 210 °C. It is also observed that all of the solvent molecules such as acetonitrile and dimethylformamide which could have been present after synthesis have been evaporated after degassing the sample at 180 °C. The better stability of the material could be due to the higher concentration of [-Co-O-] clusters formed within the material, which is more stable than organic components like 1,6-hexanediamine.

Figure 68: Decomposition profile of the CoBDC-HD synthesized using original recipe, and with 0.15 g of terephthalic acid before and after activation at 180 °C.
4.2.1.5 Chemical identification of CoBDC-HD

Energy dispersive X-ray spectroscopy (EDS) performed on CoBDC-HD crystals also showed presence of cobalt, oxygen, nitrogen, and carbon as can be seen on Figure 69. Platinum is also detected due to the previous coating of the samples with platinum during sample preparation for SEM/EDS analysis.

![Figure 69: EDS analysis of the CoBDC-HD crystals. The following elements were detected: cobalt, nitrogen, and oxygen. Platinum was also detected because of the platinum sputter coating used prior to the analysis.](image)

4.2.1.6 Fourier Transform Infrared Spectroscopy (FT-IR) analysis of CoBDC-HD

To assess the chemical bonding within the CoBDC-HD framework, FT-IR analysis has been performed. The obtained patterns of each of the constituents of the framework and of the synthesized CoBDC-HD and CoBDC frameworks are shown in Figure 70. Peaks around 2880 and 2930 1/cm observed in CoBDC-HD represent –CH and –NH vibrations from the 1,6-hexanediamine. Another amine associated peak appears
around 1676 \text{ cm}^{-1} \) which could represent \(-NH\) bend. This peak appears to be shifted to higher wavenumber in CoBDC-HD framework which could indicate binding of the amine group to the metal site of Co. Due to the presence of organic molecules in the structure, like terephthalic acid and 1,6-hexanediamine, sharp peaks are present between 1200 to 1600 \text{ cm}^{-1} \) attributed to the vibrations of benzene ring or carboxylic acid groups. As can be seen in Figure 71, a peak at 750 \text{ cm}^{-1} becomes more and more pronounced as the amount of terephthalic acid used in the solution increases while the peak does not appear in the profile of the pure terephthalic acid at the same intensity. This could indicate that the peak is due to the higher presence of [-Co-O] cluster in the framework, or higher presence of the 2D layers composed primarily of cobalt metal sites and organic linkers of terephthalic acid.

Figure 70: Fourier Transform Infrared Spectroscopy (FTIR) spectra of the as-synthesized CoBDC-HD, Co-BDC complex, each of the organic linkers used, and metal source.
Figure 72 represents FTIR spectra of CoBDC-HD samples after activation at different temperatures. It can be seen that most of the main peaks are preserved even after activation at 220 °C. Among all samples a peak at 3599 1/cm is preserved in all activated samples as well. This peak could be associated with metal-OH group vibration which has been observed in other MOFs like MIL-101 (where Al-OH vibration appeared at 3599 1/cm). In the case of CoBDC-HD, this peak could represent hydrogen bonding formed between O atom coordinated to the Co site from one of the terephthalic acid groups and H atom of the 1,6-hexanedianime if the Case I is correct.

Figure 71: FTIR spectra of the CoBDC-HD synthesized using original recipe, 0.1 g and 0.15 g of terephthalic acid.
Figure 72: FTIR spectra of CoBDC-HD samples activated at various temperatures.

4.2.1.7 Carbon dioxide capture by CoBDC-HD framework

Carbon dioxide capture tests were also performed on the activated samples of CoBDC-HD. Table 5 shows the results of CO$_2$ capture tests and it can be seen that the sample activated at 180 °C captured the most amount of CO$_2$, about 1.077 mmol/g, compared to other samples tested. While the capacity is not the highest out of those reported for other MOFs, it is competitive with other solid porous materials like lamellar silica materials. As has been shown previously the material evacuated at 180 °C does not degrade as much as it does after 210 °C evacuation. This could be the reason for the observed better capacity after 180°C, while evacuation at 150 °C still leaves solvent molecules behind inhibiting CO$_2$ diffusion through the framework. It also should be noted that surface area reported here is not very high but carbon dioxide adsorption capacities reach just as much as some porous materials with surface areas up to 500-700 m$^2$/g (for example some lamellar silica materials). Therefore it can be expected that if solvent molecules could be sufficiently removed from the framework and surface area
increases, a competitive carbon dioxide capture performance can be achieved in the future tests.

Table 5: CO₂ adsorption capacity values for CoBDC-HD materials activated at three different temperatures.

<table>
<thead>
<tr>
<th>Degas Temperature (°C)</th>
<th>CO₂ Adsorption Capacity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.565</td>
</tr>
<tr>
<td>180</td>
<td>1.077</td>
</tr>
<tr>
<td>210</td>
<td>0.924</td>
</tr>
</tbody>
</table>

4.2.1.8 Summary on the structure of the synthesized layered MOFs

In this work, at least two new metal organic frameworks were obtained, CoBDC and NEU-3. A thorough structural analysis was performed on CoBDC and CoBDC-HD. It was found that CoBDC framework is isostructural to previously reported by other groups, Mg₃(bdc)₃(DMA)₄ framework. Based on the known structure of the Mg₃(bdc)₃(DMA)₄ it was found that in CoBDC framework synthesized in this work, cobalt metal centers form secondary building units, cobalt-carboxylate units which are further connected by terephthalic acid groups (or benzene 1,4-dicarboxylic ligands) to form 2D layers. Cobalt metal sites take octahedral coordination nature, and there are two distinguishable cobalt centers that coordinate in two different fashions. While one of the metal sites is connected to six oxygens of the separate benzene 1,4-dicarboxylic ligands, another cobalt sites is coordinated to five oxygens of benzene 1,4-dicarboxylic ligands and to one oxygen of the dimethylformamide (DMF) solvent molecule. The DMF molecules occupy interlayer space in CoBDC framework. Under the same synthesis
conditions but in the presence of amine molecule, 1,6-hexanediame, a different crystalline material was formed, CoBDC-HD. It was hypothesized that in the presence of added base, decarbonylation and hydrolysis of DMF occurs when heat is applied, which is a well-established reaction. One of the products for this reaction are dimethylammonium cations which could balance out the anionic layers and sit in between the layers. It was also found that CoBDC could undergo a structural transformation from its form to the CoBDC-HD form when 1,6-hexanediame is added to CoBDC and reheated. This could indicate that dimethylammonium cations could be introduced in between the layers of CoBDC to form CoBDC-HD framework. Another potential scenario for the role of 1,6-hexanediame is its templating effect. Literature reports that in Zn-BDC analogue addition or presence of dimethylammonium cations templates the framework to be pillared by the benzene 1,4-dicarboxylic ligands (terephthalic acid ligands). If true, that kind of framework should be stable and porous. The framework of CoBDC-HD shows very good thermal stability of up to 200 °C however does not show very high porosity. While the solvent exchange tests were not successful, the highest surface area obtained was around 107 m²/g and adsorption/desorption isotherms showed wide hysteresis loop indicating the presence of mesopores. If the dimethylammonium cations are present in the framework and play role of supporting the structure, it is reasonable to say that as the sample is heated, structure degrades and low surface area is observed. However, if the 2D layers are pillared by additional terephthalic acid ligands, the structure should be stable. Since high porosity has not been achieved, it could be said that even if it is the case, the solvent molecules of DMF still support the structure or occupy the pores of the framework.
It is believed this framework can be further modified where pillaring ligands (dimethylammonium cations or benzene 1,4-dicarboxylic acid ligands for CoBDC-HD) could be easily exchanged for another longer or shorter linker or more complicated linker with certain functionalities. This would expand the chemistry of MOFs even further showing promising features for various applications.

The CoBDC-HD framework has shown CO\textsubscript{2} adsorption capacity of about 1.07 mmol/g, which could potentially be increased by functionalization with amine groups or by expanding interlayer space even further.

4.2.2 Synthesis of other layered MOF materials based on different linkers

As an attempt for the expansion of the new synthesized here CoBDC-HD metal organic framework, synthesis runs based on other pillaring ligands with end –NH\textsubscript{2} groups have also been performed and results will be presented in this section. It was found that layered framework can also be obtained with an organic ligand of ethylenediamine based on the obtained XRD patterns and also TEM micrographs. Here, crystals synthesized based on ethylenediamine (ED) molecules will be denoted to as CoBDC-ED (or NEU-1) and crystals based on 4,4’-diaminodiphenyldiamine as CoBDC-DD (or NEU-5).

4.2.2.1 Structural characterization of the CoBDC-ED framework

The CoBDC-ED crystals were obtained via hydrothermal synthesis conditions in the dimethylformamide/acetonitrile solvent solution in the oven at 80 °C after 2 days. The crystals were of a bright yellow color. The 2D layers of the framework are composed of cobalt metal sites and terephthalic acid in the same way the 2D layers of the CoBDC-HD frameworks are. The main difference from CoBDC-HD is the pillaring linker or
templating component in CoBDC-ED, a short primary amine molecule of ethylenediamine was used as opposed to longer chain of 1,6-hexanediarnine. The full XRD pattern of CoBDC-ED is presented in Figure 73 with assigned Miller indices representing diffraction planes in the vertical direction, or when 2D layers are stacked in a-direction. These Miller indices were assigned based on the assumption similar to that made in Case I for CoBDC-HD framework, where amine molecules pillar 2D layers. In CoBDC-ED the amine molecules are short molecules of ethylenediamine. In this case, the first peak around 11.5 degrees 2θ corresponds to a distance of 7.71 Å. This would result in a distance of 23 Å for the interlayer space of the hkl plane (1,0,0). This plane represents diffraction between 2D layers of the framework and the distance of 23 Å roughly corresponds to the length of two ethylenediamine molecules in between the layers.

![XRD pattern of CoBDC-ED with Miller indices assignments](image)

**Figure 73:** XRD patterns of the as-synthesized CoBDC-ED with Miller indices assignments.
The scanning electron micrographs of CoBDC-ED crystals are presented in Figure 75 and reveal rod-shaped crystals similar to the rods of CoBDC-HD. In this case, the rods are about 7-10 micrometers long and about 1 micrometer in width. Also, it can be seen that rods seem to evolve from the center outwards. The crystals are uniform throughout the material as can be seen at low magnification micrograph (50 micrometers) in Figure 75.

While SEM images give an idea of the surface morphology and overall shape of the bulk crystals, transmission electron microscopy (TEM) gives a better look at the unique structural properties of CoBDC-ED. TEM micrographs of the samples showed again large crystals with the rod-shaped ends and revealed well-ordered layers on the end of those rods as seen in Figure 76. Furthermore, from the TEM micrographs the average distances between layers was measured to be around 2.2-2.4 nm. This matches well with a length attributed to two ethylenediamine molecules present between the layers. The layers are believed to stack in the a-direction so X-Ray diffraction peaks corresponding to the expected planes ([1,0,0], [2,0,0], [3,0,0], etc.) were calculated. The crystal unit was assumed to be monoclinic as it usually is for Metal-BDC complexes and previous works with cobalt as metal site and terephthalic acid as organic component [41]. So TEM micrographs and the observed distance between layers match well with XRD predictions and the hypothesis of two ethylenediamine molecules between the layers as shown in a simple schematics in Figure 74.
Figure 74: Simple schematics of the potential structure of CoBDC-ED framework.

Figure 75: SEM micrographs of CoBDC-ED crystals at various magnifications.

Thermogravimetric analysis of the as-synthesized CoBDC-ED revealed that material is stable up to about 200 °C after which it is believed solvent molecules of dimethylformamide (DMF) and acetonitrile start to evaporate (Figure 77). Because the boiling point of ethylenediamine (120 °C) is close to the boiling temperatures of both
solvents used (150 °C for DMF, and 80 °C for acetonitrile), it is believed that weight loss between 210-342 °C corresponds to the loss of all three of these constituents. This loss accounts for about 38-40 wt% which agrees with the hypothesis of one ED molecule per Cobalt metal site (8 ED molecules per unit cell). Theoretical weight loss for this hypothesis was calculated to be 33.6 wt%. Further loss of the organic linker may be occurring between 342 and 510 °C, and finally after 510 °C the decomposition of residual cobalt metal takes place. The loss of components in such step-wise fashion also indicates that the structure is composed of various constituents, or that it is in fact a metal organic framework formed from initial reactants used in the synthesis.

EDS analysis of the CoBDC-ED crystals has also been performed where Cobalt (26.28 wt%), Oxygen (11.1 wt%), Nitrogen (9.6 wt%), and Carbon (40.4 wt%) were detected (Figure 78). Platinum is also detected due to the platinum coating of the sample prior to the analysis.
Figure 76: TEM micrograph of CoBDC-ED crystal clearly showing layers within the structure of the framework.

Figure 77: Decomposition profile of CoBDC-ED framework.
Figure 78: EDS analysis of CoBDC-ED. Cobalt, nitrogen, carbon, oxygen were detected. Platinum is also detected due to the platinum coating using prior to the analysis.

Because of the low boiling point of ethylenediamine of 120 °C, which is lower than boiling point of dimethylformamide (DMF), it is challenging to remove the solvent molecules from the framework without disturbing the structure. So far, when heating at about 150 °C the surface area of CoBDC-ED was found to be only about 10 m²/g. Such a low porosity could be explained by the presence of DMF and acetonitrile molecules within the framework.

In summary from this synthesis run with ethylenediamine, a new layered metal organic framework was obtained denoted here as CoBDC-ED. In this framework layered structures were obtained and could be clearly observed on the TEM images. The interlayer spacing was then measured and led to a hypothesis of two ethylenediamine molecules in between the layers. Based on the measured distance, XRD peak positions
were predicted for the diffraction planes in a-direction and Miller indices were assigned. Predicted peak positions matched well with peaks observed in the as-synthesized CoBDC-ED XRD pattern confirming the presence of two ED molecules in between the layers. It was also confirmed based on the elemental analysis by EDS analysis which showed weight percentages consistent with those predicted, in addition to the decomposition profile of the CoBDC-ED material. So far, the porosity of the material cannot be confirmed due to the challenge of removing solvent molecules of dimethylformamide from the pores of the framework.

It also could be that as in Case II that 2D layers are pillared by not only guest molecules of dimethylformamide but also by dimethylamine ligands or dimethylammonium cations formed as a result of decarboxylation of DMF. However, XRD profiles of CoBDC-ED and CoBDC-HD frameworks are different indicating that the length of amine molecules used in the synthesis play role in the final structures of those frameworks. This adds another value into the relevance of the Case II where if dimethylammonium cations are formed, they could be of various lengths depending on the nature of the base (amine) used.

4.2.2.2 Structural characterization of the CoBDC-DD framework

Another metal organic framework, based on the 4,4-dimethylphenylamine organic linker, was crystallized and denoted as the CoBDC-DD framework in this work. The XRD patterns of the as-synthesized CoBDC-DD crystals, degassed in the Schlenk line at 200 °C for 24 hours, and of a sample washed additionally in a solution of dimethylformamide are presented in Figure 79. It can be seen that this XRD pattern is yet again different from those obtained for the CoBDC-HD or CoBDC-ED frameworks. This
indicates that different crystals were formed in the presence of 4,4-dimethylphenylamine molecule. It can also be seen that as solvent molecules are removed either by activation at 200 °C or by additional washing with solvent molecules, the pattern becomes more crystalline where the first peak in particular shows significant increases in intensity. In this case, if the first peak represents the interlayer distance between the layers, the increase in its intensity indicates removal of solvent molecules from the interlayer space.

From thermogravimetric analysis and obtained decomposition profile, this material is the most stable out of other CoBDC MOFs: stable up to 210 °C with only about 3 wt% loss. Also based on the SEM micrographs shown in Figure 80 this material takes shape of rods of about 20 micrometers long and of various thicknesses.

![XRD patterns](image)

**Figure 79:** XRD patterns of as-synthesized CoBDC-DD framework, the sample after evacuation at 200 °C in the Schlenk line, and the sample additionally washed in the solution of dimethylformamide.
4.2.3 Ligand Exchange in CoBDC-ED/HD MOFs

For ease of notation, the CoBDC-ED and CoBDC-HD in this section will be denoted to as NEU-1 and NEU-3, respectively. Linker exchange is one of the routes of post-synthetic modification that are currently being explored by scientists to widen the chemistry and design of metal organic frameworks. In this work, linker exchange in both frameworks of NEU-1 and NEU-3 has been performed. In this section, linker exchange trials of ethylenediamine in NEU-1 to 1,6-hexanediame and of 1,6-hexanediame in NEU-3 to ethylenediamine molecules will be presented. Such modification techniques could allow for pore engineering or control over pore volume and the interlayer spacing distance between layers in NEU-1 and NEU-3.

4.2.3.1 Synthesis conditions and characterization of linker exchanged CoBDC-ED (NEU-1)

In order to expand the distance between layers within the NEU-1 framework, a longer amine molecule of 1,6-hexanediame was used as an exchanging ligand. Three different loadings of 1,6-hexanediame were used. The 1,6-hexanediame molecule was chosen due to its similarity to ethylenediamine where each of the ends of the molecules

Figure 80: SEM micrographs of synthesized CoBDC-DD.
are –NH₂ groups. The exchange was performed in a solvent solution of dimethylformamide and acetonitrile similar to the conditions of the original synthesis of the NEU-1 framework. Three different trials with various loadings of 1,6-hexanediamine have been performed.

The XRD patterns of the obtained crystals can be seen on Figure 81 along with XRD patterns of NEU-1 and NEU-3 frameworks for comparison. As can be seen from the XRD patterns obtained, the complete exchange of ethylenediamine to 1,6-hexanediamine did not occur since the obtained XRD patterns did not match completely to the XRD pattern of the NEU-3 framework. However, a partial replacement may have occurred since the new XRD profile does not match the profile of the original NEU-1. For example, it can be seen that a new peak around 6.5 degrees 2θ emerges in all of the linker exchange trials. This peak could represent an increased distance between the layers of the framework due to the incorporation of 1,6-hexanediamine molecule to some population of the layered structure. There were three trials performed with different loading of 1,6-hexanediamine molecule. Based on the XRD profiles, the lower loading leads to a more pronounced first peak (Exchange Trial 3). This could be due to the excess of 1,6-hexanediamine molecules being present in the trials 1 and 2 which could have led to the blocking of the interlayer distance and therefore less intense first peak. If there dimethylammonium cations present in between the 2D layers in NEU-1 framework or even if only DMF molecules are present, introduction of 1,6-hexanediamine could cause structural transformation. But here, the exchanged solutions were not heated again, therefore new dimethylammonium cations might not have formed since heat is required for such reaction to occur.
Figure 81: XRD patterns of linker exchange trials with NEU-1 (CoBDC-ED) showing evidence of structural change from the original material of NEU-1 (CoBDC-ED). XRD patterns of NEU-1(CoBDC-ED) and NEU-3 (CoBDC-HD) are also provided for comparison.

Exchange trials should be further repeated where new solutions would be heated at high temperatures in closed vessel to create autogenous pressure.

4.2.3.2 Synthesis conditions and characterization of linker exchanged CoBDC-HD (NEU-3)

The linker exchange trial of converting NEU-3 into NEU-1 framework has also been performed. There were two different methods used to achieve the exchange. In the first method, the NEU-3 powder was added to the pre-made homogeneous solution of the solvent material and ethylenediamine. Upon completion of the reaction, the brown and white solids were identified and separated. The XRD profiles of those solids are shown in
Figure 82 along with XRD profiles of NEU-1 and NEU-3. As can be seen the first few peaks assigned to the interlayer peaks in NEU-3 and NEU-1 are almost absent in the exchanged trials with only few small peaks occurring in the brown solids with a smaller ethylenediamine loading. In this case, it is hard to conclude whether or not any kind of exchange has happened.

The second method of the linker exchange involved adding ethylenediamine to the dispersed solution of NEU-3. The XRD profile of the obtained material can be seen in Figure 83. The XRD profile shows that some peaks of NEU-3 are still preserved but many more new peaks have appeared. Some of the new peaks could be assigned to the NEU-1 profile but some are completely new. This could indicate a partial replacement of 1,6-hexanediame with ethylenediamine molecules but further testing need to be performed.

In summary, it was shown that linker exchange is possible but might be more difficult for NEU-3 to NEU-1 exchange rather the NEU-1 to NEU-3 exchange. Also, further tests could be performed where ligand exchanged solutions are further reheated in the oven for at least one day.
Figure 82: XRD patterns of the white and brown solids resulted from the exchange trials of NEU-3 to NEU-1 along with patterns of NEU-3 and NEU-1 for comparison.

Figure 83: XRD profile of the NEU-3 linker exchange trial with ethylenediamine. NEU-3 XRD profile is also provided for comparison.
4.2.4 Conclusions and significance

In this part of the dissertation synthesis of layered metal organic frameworks was investigated. The layered geometry of the materials could potentially provide a control over dimensions of interlayer or gallery space within those materials. Longer ligands could be introduced into the interlayer space and potentially result in pores of larger dimensions. Such control over interlayer space was previously observed in mesoporous silica materials, and in this work was attempted with metal organic frameworks. Layered materials based on cobalt metal sites and organic linkers of terephthalic acid were obtained where layers were stacked on top of each other with solvent molecules of dimethylformamide (DMF) residing between the layers. It was proposed to use simple molecules of ethylenediamine and 1,6-hexanediamine as pillaring ligands between the layers. The metal organic framework based on ethylenediamine linker, CoBDC-ED exhibited clear layering structures as it was observed in TEM micrographs and the material was crystalline based on the collected XRD patterns. The porosity of the material was found to be very low possibly due to the presence of solvent molecules with high boiling point such as DMF. The CoBDC-HD framework where 1,6-hexanediamine was used as a potential pillaring ligand also showed high crystallinity and BET surface area reached about 100 m$^2$/g. The TEM micrographs in this case did not show layering structures, although those still could be present within the samples. Potential scenarios on the final structure of the CoBDC-HD were explained. One of the hypothesis made was based on the fact that 1,6-hexanediamine molecule binds to the metal sites of the layers on both sides and serves as a pillaring ligand. The presence of mesopores observed based
on the nitrogen isotherms could be indicative of the mesopores formed in between the layers of the material. Another hypothesis made was about the effect of solvent, specifically dimethylformamide. It was found that this solvent might be having a templating effect in the crystallization of CoBDC-HD. Dimethylformamide might undergo a process of decarbonylation in the presence of base when heated. In this case, a base of 1,6-hexanediamine linker is present and heat is applied during synthesis. The formed dimethylammonium ions could further be residing in between the layers or pores of the framework. In addition, dimethylammonium ions could facilitate further protonation of terephthalic acid linkers present in the layers of the framework or in any access. Such deprotonation could further lead to additional coordination of terephthalic acid linkers to the metal sites and serve as pillaring ligands. In that case, the framework should be quite stable and show higher porosity. The framework showed degradation in the structure when heated to temperatures higher than 200 °C and it is hypothesized that molecules of 1,6-hexanediamine are might be still present or stuck in the mesoporous space between the layers. It was also found that the same material of CoBDC-HD could be obtained using a two-step synthesis, where first layered MOF CoBDC is synthesized, and amine linker is introduced post-synthetically. This result is significant because of the potential it provides to introduce various organic ligands to known layered structures. Another important result of this work is that careful optimization of the amounts of dimethylformamide and amine molecules could lead to the potential deprotonation of organic molecules with carboxylic acid end groups, which could be further serve as pillaring linkers. While more studies need to be done on the more accurate picture on the structure of the obtained here material, CoBDC-HD, this work opened up possibilities for
expansion of this project to introduction of longer molecules such as 4,4’-
biphenyldicarboxylic acid as a primary linker and/or as a pillaring linker.

4.3 Aim 3: Conversion of metal organic frameworks into metal oxide nanoparticles

In this section, two metal organic frameworks previously synthesized in this work will be used as starting materials for generation of cobalt oxide nanoparticles. These two frameworks are CoBDC-HD and layered CoBDC complex. CoBDC-HD was chosen over CoBDC-ED due to the higher observed porosity and better stability. And CoBDC complex was chosen to compare the morphology of nanoparticles obtained using layered material.

4.3.1. Conversion of CoBDC-HD MOF into cobalt oxide nanoparticles

Metal oxides have been widely studied for their chemical and physical properties (magnetic, luminescent, and catalytic), which makes those materials promising in the applications of adsorption, catalysis, and energy conversion. Specifically metal oxides such as CuO, Cu$_2$O, Co$_3$O$_4$ have been studied for potential applications in solar cells, gas sensors, supercapacitors, and lithium ion batteries [23, 120]. Since one of the MOFs generated in this work involved a structure with cobalt as the metal constituents it was thought it would be interesting to investigate generation of cobalt oxides by decomposition of the available CoBDC-HD frameworks. One of the applications for cobalt oxide are supercapacitor applications due to low cost, good electrochemical stability, high capacitance values and they are also less harmful to the environment than other materials.
Recently one of the strategies of generating those metal oxides was to use metal organic frameworks as precursors. It is expected that MOFs will be advantageous to use due to several factors such as large variety of MOF structures available, the porous nature of MOFs allows for incorporation of additional phases such as polymers, relatively low thermal stability of MOFs, and controllable pore size and structures of MOFs which could lead to nanoporous metal oxides [98]. By using MOF structures as templates, potential particle agglomeration and impurities could be avoided. Different shapes of oxides could also be obtained depending on the dimensionality and the structure of the initial MOF structure. Some of the shapes already known could be nanowires, nanorods, nanoparticles, and nanosheets [98].

In this part of the project, the generation of cobalt oxides would be obtained from the initial structures of CoBDC-HD. Pure highly crystalline Co$_3$O$_4$ metal oxides of irregular shapes were synthesized using CoBDC-HD MOF as a template at 500 °C. As it can be seen from Figure 84, the first peaks of the Co$_3$O$_4$ nanoparticles has started to emerge after calcination at 250 °C for 24 hours under nitrogen flow. The first defined peaks appeared after 270 °C calcination with peaks at 19, 31.2, 36.8, 38.3, 44.7, 55.4, 59.3, 65.1, and 77.3 degrees 2 theta which correspond to reflections of cubic phase of Co$_3$O$_4$ nanoparticles (JCPDS file no. 09-0418) [62]. No other phases were observed after calcination at 270 °C indicating that resulted oxides are pure crystalline. The total weight loss in that run constituted to about 88 wt% of loss. From the thermogravimetric analysis performed on CoBDC-HD, the total weight of present metal oxide clusters was estimated to be about 7 %. Table 6 summarizes the weight loss from the initial material after each of the calcination runs. From Figure 84 it can also be seen that as temperature increases,
the nanoparticles become more crystalline with the most crystalline materials after 500 °C calcination. This could be due to the evaporation/decomposition of the organic phase present in the initial framework.

![XRD patterns of the CoBDC-HD (NEU-3) crystals used as a template for generation of cobalt oxides and calcination trials at six different temperatures. Peaks marked with a star belong to the cubic phase of Co₃O₄ nanoparticles.](image)

**Figure 84:** XRD patterns of the CoBDC-HD (NEU-3) crystals used as a template for generation of cobalt oxides and calcination trials at six different temperatures. Peaks marked with a star belong to the cubic phase of Co₃O₄ nanoparticles.

The scanning electron microscopy revealed that the resulted Co₃O₄ nanoparticles are of irregular shape. Figure 85 shows that the surface of the material first exhibits evaporation of organics as predicted and further formation of solid spherically shaped particles after calcination temperature of 500 °C (Figure 85 H). As already observed the initial CoBDC-HD samples take shape of separated rods as shown in Figure 86A. The SEM image shown in Figure 86B is of obtained Co₃O₄ nanoparticles after calcination or decomposition of NEU-3 at 250 °C. From Figure 85 images taken at low magnification reveal that overall structure of the rods is maintained at all four different calcination temperatures. This indicates that this type of heating (controlled heating under nitrogen flow) retains the original shape of the CoBDC-HD crystals. Such effect has also been
observed when ZIF-67 MOF was heated under nitrogen flow to yield Co$_3$O$_4$ crystals retaining overall polyhedral shape [95]. The surface of the calcined samples show drastic changes from the surface of CoBDC-HD particles. It can be seen that while CoBDC-HD samples possess smooth surface, the calcined samples show large degree of cracking and holes on their surfaces. Such effect could be explained by evaporation of the gases entrapped within the structures of CoBDC-HD such as CO$_2$, H$_2$O, etc. The calcined samples form these infinite curvy lines composed of nanoparticles as seen in Figure 85 B and D after 250°C and 300°C trials. And as temperature increases, the holes in between those nanoparticles disappear revealing dense closely packed nanoparticles (Figure 85 F and H). The elemental analysis performed by X-ray spectroscopy (EDS) revealed presence of Co and O within the obtained nanoparticles as shown in Figure 87. However, high content of C was also observed indicating incomplete evaporation of the organic phase at the temperature of 250°C. Summary of the chemical compositions of the metal oxide nanoparticles obtained after 250 °C and 450 °C is shown in Table 7. It is observed that as temperature increases less of organic phase is left as C presence decreases dramatically, and so does O content.
Figure 85: SEM micrographs of the CoBDC-HD samples after calcination at four different temperatures for 24 hours under nitrogen flow.
Figure 86: Comparison between SEM micrographs of the CoBDC-HD MOF before calcination (A) and after calcination at 250 °C under nitrogen flow (B).

Figure 87: Compositional analysis by EDS spectroscopy of CoBDC-HD sample treated at 250 °C.

Figure 88 shows detailed structures of the obtained nanoparticles as four different temperatures. TEM images better represent the difference in the shape and size of the resulted nanoparticles. It is observed that as nanoparticles crystallize they also increase in size while the shape of those particles stays irregular. The particles increase from being about 5-20 nm in diameter after calcination at 250 °C to being anywhere between 40-100 nm in diameter after calcination at 500 °C. These results agree with the literature reports.
where Co$_3$O$_4$ nanoparticles were reported to be in the size of about 150 nm from calcination of the three dimensional MOF-CJ4 at 900 °C and of 90 nm in size from calcination of the two dimensional Co-HFMOF-D also at 900 °C. [23] It seems that particles of larger size usually result from the three dimensional frameworks. In this work particles of such size were formed from calcination trial at lower temperature of 500 °C requiring lower energy input.

Table 6: Summary of weight loss after calcination of CoBDC-HD at different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Weight loss (wt%)</th>
<th>Particle size (nm) based on TEM micrographs</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>74.2</td>
<td>5-10</td>
</tr>
<tr>
<td>300 °C</td>
<td>87.8</td>
<td>12-20</td>
</tr>
<tr>
<td>450 °C</td>
<td>88.7</td>
<td>20-80</td>
</tr>
<tr>
<td>500 °C</td>
<td>90.6</td>
<td>40-100</td>
</tr>
</tbody>
</table>

The porosity of obtained samples was characterized by nitrogen adsorption-desorption isotherms. Figure 89 presents such isotherm for a sample calcined at 270 °C and its Baret-Joyner-Halenda (BJH) pore size distribution is also provided. For that particular sample BET surface area was about 32.18 m$^2$/g, which is consistent with some of the other cobalt oxide nanoparticles reported in the literature. The highest BET surface area was 48.11 m$^2$/g as can be seen in Table 8, however at that temperature other phase aside from cobalt oxide phase is present. From literature the highest BET surface area is about 148 m$^2$/g which is significantly higher however the resulting particles in that report
were of different shape (polyhedrons).[95] The pore size distribution shows that most of the pores appear to be mesopores with diameters around 40-60 nm. While the surface area obtained is not as high as previous literature reports it is still comparable. Surface area is important for metal oxides since the higher surface area would provide more surface for electrochemical reactions which would be beneficial for supercapacitor applications.

Figure 88: TEM micrographs of the CoBDC-HD samples after calcination at 250 °C (A), 300 °C (B), 450 °C (C), and 500 °C (D).
Table 7: Summary of chemical compositions of Co$_3$O$_4$ oxide nanoparticles after calcination of CoBDC-HD at two different temperatures.

<table>
<thead>
<tr>
<th>Element</th>
<th>Calcination Temperature</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>250 °C</td>
<td>47.65</td>
</tr>
<tr>
<td></td>
<td>450 °C</td>
<td>27.77</td>
</tr>
<tr>
<td>O</td>
<td>250 °C</td>
<td>16.78</td>
</tr>
<tr>
<td></td>
<td>450 °C</td>
<td>9.11</td>
</tr>
<tr>
<td>Co</td>
<td>250 °C</td>
<td>35.57</td>
</tr>
<tr>
<td></td>
<td>450 °C</td>
<td>63.12</td>
</tr>
</tbody>
</table>

The porosity of obtained samples was characterized by nitrogen adsorption-desorption isotherms. Figure 89 presents such isotherm for a sample calcined at 270 °C and its Barett-Joyner-Halenda (BJH) pore size distribution is also provided. For that particular sample BET surface area was about 32.18 m$^2$/g, which is consistent with some of the other cobalt oxide nanoparticles reported in the literature. The highest BET surface area was 48.11 m$^2$/g as can be seen in Table 8, however at that temperature other phase aside from cobalt oxide phase is present. From literature the highest BET surface area is about 148 m$^2$/g which is significantly higher however the resulting particles in that report were of different shape (polyhedrons).[95] The pore size distribution shows that most of the pores appear to be mesopores with diameters around 40-60 nm. While the surface area obtained is not as high as previous literature reports it is still comparable. Surface area is important for metal oxides since the higher surface area would provide more surface for electrochemical reactions which would be beneficial for supercapacitor applications.
As it was mentioned before the highest BET surface area of CoBDC-HD achieved was about 106 m$^2$/g after activation at 210 °C. At that temperature CoBDC-HD seem to start to degrade in crystallinity but the peaks of cobalt nanoparticles have not yet emerged. It should be mentioned that conditions for activation were different when obtaining those XRD profiles and BET results, the activation was performed under vacuum rather than under nitrogen flow as it was during calcination trials.

Figure 89: Nitrogen adsorption-desorption isotherm for a Co$_3$O$_4$ metal oxide sample calcined at 270 °C. The Baret-Joyner-Halenda (BJH) pore size distribution is also presented.
Table 8: Porosity characteristics of the cobalt oxide nanoparticles.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>BET Surface Area (m²/g)</th>
<th>Total Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 °C</td>
<td>48.11</td>
<td>0.105</td>
</tr>
<tr>
<td>270 °C</td>
<td>37.78</td>
<td>0.162</td>
</tr>
<tr>
<td>300 °C</td>
<td>26.08</td>
<td>0.132</td>
</tr>
<tr>
<td>450 °C</td>
<td>38.19</td>
<td>0.148</td>
</tr>
<tr>
<td>500 °C</td>
<td>11</td>
<td>0.266</td>
</tr>
</tbody>
</table>

4.3.2 Conclusion and significance

In conclusion, utilization of superstructures of metal organic frameworks as a template material and precursor for generation of metal oxide nanoparticles was investigated. It was demonstrated that a simple “top-down” approach could be applied to the synthesized framework of CoBDC-HD to generate crystalline cobalt oxide nanoparticles. This type of synthesis for metal oxides was shown to provide control over the particle size which was observed to increase with increasing calcination temperature. The pure crystalline phase was obtained at the highest temperature with the largest in size nanoparticles. In addition, it was found that overall morphology of the starting MOF material stays preserved resulting in the rod-shaped crystals where both mesopores and macropores were observed. The two types of porous regimes is advantageous for the use of metal oxides as heterogeneous catalysts. This type of synthesis also provides predictability over the morphology of the resulting materials, as most of the times there is a high variety in shapes for cobalt oxide nanoparticles. The fundamental properties of these materials are highly dependent on their phase, crystallite sizes, and specific surface
area. In this work, cobalt oxides were successfully obtained after 270 °C calcination and the highest surface areas achieved was about 40 m$^2$/g which is competitive among cobalt oxide nanoparticles synthesized using other methods, such as chemical precipitation, etc. This work is therefore significant as it shows a way of obtaining metal oxide nanoparticles with preserved initial morphology of the starting material which further could provide control over the size of macropores or mesopores in the resulting oxide nanoparticles. The ongoing work involves investigation how MOF also based on the cobalt metal sites but with organic linkers of 4,4-diphenylbenzoic acid which are longer than terephthalic acid organic ligands. It is hypothesized that due to the longer size of the organic linker present in the MOF, the larger nanoparticles would be formed with potentially larger mesopores and macropores.

This specific synthesis route involving a metal organic framework as a precursor or a template could also be applied to other frameworks with different initial structures. The resulted here nanoparticles with high surface area and purely crystalline phase could be useful in various applications such as electrochemical water splitting reactions, lithium ion batteries, and supercapacitors, and other applications [62].
4.4 Ongoing study: preliminary trials of fabrication of the graphene/MOF composites

Another secondary project as a part of this dissertation was to fabricate graphene nanocomposites using synthesized layered metal organic frameworks. Graphene represents a single layer of densely packed carbon atoms with several groups on the surface. In this work, preliminary testing of fabrication of graphene and layered metal organic frameworks composites is presented with an idea of demonstrating a growth of MOF on the surface of the graphene layer. Such configuration of materials could generate larger structures where properties of single graphene layers would be translated into larger materials therefore being useful in different applications such as optoelectronics, conductive materials, and energy storage.

In this section, the initial tests on the fabrication of graphene/MOF composites are described. The synthesized framework of CoBDC-ED was used here for preliminary testing to mix with single layers of graphene sheets to generate composite materials.

In order to extend the electronic and adsorption properties of graphene, nanocomposites with other solid materials are currently widely studied. Graphene oxide layers usually possess epoxy and hydroxyl groups on the edges of the sheets, however the oxidation of graphene layers causes defects and breaks in the structure. Metal organic frameworks, while currently widely studied for gas capture and separation, still show a lack of the ability to encapsulate small molecules at ambient conditions within their structures. To overcome this, graphene composed of densely packed atoms mixed with metal organic framework material could create an ideal nanocomposite framework for the capture and storage of small molecules.
In this work, ammonia functionalized graphene was used to fabricate composites with the CoBDC-ED framework. Two different trials were performed, one in the presence of ethylenediamine and another without. It was hypothesized for the second trial that ammonia groups available on the surface of graphene would be allowed to bind with layers of CoBDC-ED and grow individual sheets. For the first trial, it was hypothesized that the same growth may occur, however it was expected that the presence of ED would provide additional –NH$_2$ groups which would facilitate formation of the 2D layers on the surface of graphene oxide sheets. XRD patterns of both trials compared to the XRD pattern of just CoBDC-ED are provided in Figure 90 and low angle data (between 5 and 20 degrees 2theta) are given in Figure 91.

![XRD patterns of two graphene/CoBDC-ED (NEU-1 in the figure) composites compared with XRD profile of CoBDC-ED only.](image)

**Figure 90:** XRD patterns of two graphene/CoBDC-ED (NEU-1 in the figure) composites compared with XRD profile of CoBDC-ED only.
Figure 91: Low angle XRD pattern of graphene/ CoBDC-ED (NEU-1 in the figure) trials compared to the XRD profile of only CoBDC-ED and of synthesis run without amine completely.

From the XRD patterns provided in Figures 90 and 91, it can be clearly seen that Trial 1 showed peaks characteristic to CoBDC-ED indicating the presence of CoBDC-ED crystals. The intense peak around 26.5 degrees 2θ observed in both trials is a characteristic graphene peak and represents the thickness of the graphene layer and so indicates the presence of graphene in both trials. Trial 2 where no ED was added showed an XRD pattern similar to the XRD pattern of the synthesis run for CoBDC-A complex where no amine was used discussed previously. This might suggest that crystals were formed between Cobalt metal sites and terephthalic acid but there was no indication of peaks from CoBDC-ED. Since no extra peaks were found in the pattern, it is possible that Co/H₂BDC particles are in physical mixture with the graphene material.

The surface texture of the formed composites can be seen on SEM micrographs of presented in Figure 92. It can be seen form the Figures that for both trial 1 and trial 2,
among many flakes of graphene, larger crystals are formed. When EDS analysis was performed on these specific large particles, Cobalt was detected indicating potentially the presence of formed MOF material in both trials.

Since there are also epoxy and carboxyl groups present on the graphene layer, it is possible that cobalt cluster might attach to those instead of the amine groups present. It is still unclear whether or not graphene and metal organic framework materials exist in only physical mixture or are attached to each other chemically. To further investigate this, loadings of MOF material into graphene could be manipulated and infrared spectroscopy could be performed to fully assess the structure of the fabricated nanocomposites.

In addition, for these trials commercial ammonia functionalized graphene platelets were used. It is unclear what is the loading or concentration of amine groups available on the surface of the graphene sheets. For the future tests in this area, it would be beneficial to perform functionalization of graphene sheets with amine groups in the lab where amine loading could be controlled and then proceed to fabrication of MOF/graphene nanocomposites.
Figure 92: SEM micrographs of ammonia functionalized graphene (A,B), graphene/CoBDC-ED trial 1 without ED (C,D), and graphene/CoBDC-ED trial 2 with ED (E,F)
5.0 Conclusion

Metal organic frameworks are currently widely studied in the area of CO\textsubscript{2} capture from post combustion flue gas and ambient air. In this work, Mg/DOBDC was successfully synthesized and further modified with ethylenediamine groups at the open metal sites resulting in ED-Mg/DOBDC. Such modification was done to improve stability of Mg/DOBDC MOF under humid conditions relevant for practical CO\textsubscript{2} capture conditions. To test material stability all of the samples were tested under accelerated steam treatment where samples were exposed to steam conditions for two days. ED-Mg/DOBDC showed less structural degradation than bare Mg/DOBDC, preserving some level of the original porosity, while bare Mg/DOBDC has degraded in crystallinity and has become almost nonporous. Carbon dioxide capture was also tested and it was observed that CO\textsubscript{2} capacity was almost completely regained for functionalized MOF after steam treatment, while it has decreased by about 50\% for bare MOF. These results suggest that amine functionalization at the metal sites of the MOF is able to make Mg/DOBDC withstand harsh steam conditions after which it preserves CO\textsubscript{2} capacity uptake. Such functionalization provides a shielding effect: shielding of open metal sites from the adsorption of water molecules. Such stability is very important since both post combustion flue gas and ambient air contain moisture. Further tests on the stability under corrosive gases should be performed to completely evaluate the performance and properties of the functionalized Mg/DOBDC MOF. Steam treatment tests performed in this work proved to be an easy and quick test for materials stability under very harsh humid conditions and could be applied to other porous adsorbents considered for CO\textsubscript{2}
capture applications. In addition, a simple amine functionalization at the metal sites could be applied to other metal organic frameworks, which show high CO\(_2\) capture capacity.

Another part of this dissertation work investigated synthesis and structural analysis of layered metal organic frameworks. A layered metal organic framework composed of cobalt-carboxylate building units connected by organic ligands of benzene 1,4-dicarboxylic acid (also called terephthalic acid) was synthesized, CoBDC-2/3/4. The same material resulted after 2, 3, and 4 days of reaction time of the hydrothermal synthesis. It was found that an organic ligand of 1,6-hexanediocmine could be introduced into the structure of the CoBDC after synthesis and de novo. The final structure was found to be unchanged based on the XRD data analysis. The resulting framework was denoted to as CoBDC-HD and it is hypothesized that 1,6-hexanediamine ligand plays either templating role in the framework and facilitates decarbonylation reaction of one of the solvent components, dimethylformamide. As a result of this reaction, dimethylammonium cations are formed which could reside in the pores of the framework and balance anionic 2D layers. In order to precisely assess structure of the NEU-3, single crystal X-ray diffraction analysis should be performed in the future work. Based on the literature reports of similar framework with different metals one case where the same 2D layers as in CoBDC were formed but further pillared by benzene 1,4-dicarboxylic acid creating a rigid framework with dimethylammonium cations in the pores. These cations played a templating role in the crystallization of that certain framework. The case was discussed in respect to the CoBDC-HD framework, but it was found that material is not highly porous with about 107 m\(^2\)/g after heating the sample under vacuum at 210 °C. It is possible that removal of dimethylammonium cations degrades the framework therefore
making those cations important for maintaining material crystallinity. One of the
directions for future research on this framework is removal of cations by ion exchange
first. A replacement of cations and 1,6-hexanediamine ligands with larger molecules to
increase interlayer volume and the surface area of the material could also be performed.
While the reported here surface area of CoBDC-HD is not highly competitive with other
MOFs reported in the literature, the carbon dioxide capture capacity of this material
reached about 1.07 mmol/g which could be compared to the capacities of other porous
solid materials such as layered silica materials. If larger ligands could be introduced and
the surface area increased, higher carbon capture capacities are expected. This work was
the first step and important in the sense that additional organic ligand was introduced into
the structure of the 2D layered metal organic framework potentially controlling the
interlayer distance of the material. While there were previously reported layered pillared
frameworks, most of them were based on the rigid molecules binding to the layers via \(-N\)
atom of the pyridine group. In this work, we have attempted to build a pillared structure
based on the molecules that could be easily exchanged for longer or shorter molecules
which would allow for control over interlayer distance between the layers. Another
framework based on a shorter amine ligand, ethylenediamine (ED) was also generated,
CoBDC-ED. A crystalline material was obtained and defined layered structures were
observed in CoBDC-ED on the TEM micrographs.

Further, few attempts of exchanging the interlayer pillaring linker to a shorter or
longer molecules have been addressed. In the preliminary results it was found that
exchange from CoBDC-ED to CoBDC-HD shows the most promise with few
characteristic peaks of CoBDC-HD appear after the exchange. In the future work, it is
recommended to apply heat or reheat the exchanged solutions to facilitate decarbonylation reactions. It is expected that at those conditions, a full transformation of CoBDC-ED to CoBDC-HD could be achieved.

Layered metal organic frameworks could become highly promising materials for size selective separation of CO₂ from mixed gas streams either as a part of the pure MOF membrane or mixed with polymeric materials membranes. The micropores within the layers of the frameworks might provide channels for diffusion of CO₂ only which could further be trapped in the mesoporous space in between the layers, which could be modified with additional amine groups for chemical adsorption of CO₂. In addition, the chemistry of metal organic frameworks could be widely expanded with a potential of variety of molecules of different lengths and properties to be introduced into the interlayer space.

Another study on the generation of metal oxides using metal organic framework superstructures as a template was performed. It was found that highly crystalline and porous cobalt oxide nanoparticles could be obtained from CoBDC-HD framework with the characteristic peaks appearing at temperatures as low as 250 °C and reaching a highly crystalline state at 500 °C. It was also found that metal oxides retained the overall structure of the CoBDC-HD, staying in the rod-shaped configuration forming metal oxide nanoparticles densely packed on the surface of those rods. There are many different shapes of cobalt oxides that have been reported in the literature and it would be interesting to investigate the electrical properties of the nanoparticles obtained in this work. It was also found that as temperature of the calcination increases, the size of the particles also increases as observed in TEM micrographs. While some particles looked
agglomerated, it is something that needs to be investigated on the benefits of disadvantages of such agglomeration in the related applications.

A fabrication of graphene-layered metal organic frameworks has also been attempted in this work with CoBDC-ED framework. It was hypothesized that ammonia functionalized graphene sheets would allow for growth of the 2D sheets and further stacking of the CoBDC-ED framework. It was found that it does not necessarily occurs in the absence of ethylenediamine and it has to be added to the solution mixture. Once obtained, characteristic peaks of CoBDC-ED were observed in the graphene-CoBDC-ED composites but it is unclear whether or not it exists as a physical mixture or is truly grown on the sheet of grapheme material.

In summary, this dissertation work evaluated various ways of manipulation of the structure of metal organic frameworks. The post synthetic modification was achieved with Mg/DOBDC MOF with amine functional groups generating a steam stable porous adsorbent material for carbon dioxide capture applications. The construction of new layered metal organic frameworks has also been attempted and three frameworks were obtained. Another post-synthetic modification, in this case replacement of one of the organic linker to a longer/shorter molecule potentially allowed for control over mesopores present in the framework. More tests need to be performed to investigate influence of the amine ligands in the structure and if introduction of even larger molecules would be possible and would lead to highly porous material. Lastly, synthesis route for metal oxide nanoparticles using metal organic frameworks as a template was investigated.
6.0 Recommendations

The results obtained in this dissertation are useful in expanding the knowledge about structural modification of metal organic frameworks. However there are still aspects of the carbon dioxide capture using metal organic frameworks that are left to answer:

1. How does introduction of ethylenediamine affects the binding strengths of CO$_2$ to the multiple adsorption sites now present in the ED-Mg/DOBDC framework?

2. Would additional trials of steam treatment degrade the amine functionalized Mg/DOBDC framework even further?

3. Could larger or shorter than 1,6-hexanediamine molecules be introduced into the interlayer space of CoBDC complex?

4. How could the porosity and carbon dioxide capture capacity be increased for the CoBDC-HD and CoBDC complexes?

Few recommendations for the future research regarding open questions provided above would be described here.

**Recommendation 1: Investigate the role and strength of ethylenediamine as a CO$_2$ binding site in comparison to the open metal sites.**

In the carbon dioxide capture results with ED-Mg/DOBDC frameworks, no decrease in capacity and even a slight increase in one of the samples was observed compared to the bare Mg/DOBDC material. In the discussion on the role of ethylenediamine molecule inside the framework, it was stated that ED coordinates to the unsaturated metal sites and hence protects it from the attack from water molecules when exposed to humidity. If the metal sites, which are the main adsorption sites in the framework, are now occupied, how
does ED functionalized framework captures almost the same and slightly higher amount of carbon dioxide. In the discussion provided in the dissertation it was stated that the end amine group –NH₂ replaces the adsorption site of the metal and chemically adsorbs CO₂ molecules. An ethylenediamine molecules possesses two such amine groups and one of the N atoms is coordinated to the metal therefore it is blocked for CO₂ adsorption. The future study could be done on this where Mg/DOBDC could be functionalized with a group which would possess only one amine group to coordinate to metal site. In that case, CO₂ adsorption capacity would be much lower than the one for bare material since some of the metal sites would be occupied with functional group which do not carry additional adsorption sites, such as –NH₂. Another test that could be done to test for the role of ED and how if affects carbon dioxide capture is to increase the loading of ED. Since amine functionalized samples synthesized in this work did not occupy every unsaturated open metal site available but the CO₂ capture capacity matched the on without ED molecules at all, what would happen if the ED loading is increase and CO₂ could be chemically adsorbed only to the amine groups. Would the CO₂ capture increase or decrease due to the pore blocking that could occur at higher loadings? The maximum loading that would not interfere with diffusion of CO₂ into the pores and which would provide the highest CO₂ capacity and shield metal sites from the water molecules would make for a highly promising material for practical carbon dioxide capture. The heat of adsorption could also be measured for capture with bare and functionalized Mg/DOBDC to study the strength of binding which would be highly useful in determining the requirement for further desorption process.
Recommendation 2: Investigate the effect of cyclic steam treatment tests on the stability of functionalized Mg/DOBDC MOFs and further CO₂ desorption.

In this dissertation work, only one steam treatment test was performed. The work provides initial investigation on the stability of the functionalized material. While the material was exposed to a very harsh condition of steam treatment, it is still unclear what is the level of degradation would occur if the steam conditions were mild instead, for example at 10% of humidity. In this work material was tested to the maximum degradation level, however it is unknown how low-humidity gas stream would affect stability and carbon dioxide capture capacity of the functionalized framework. It would also be interesting to investigate in more detail steam treatment as a process for material regeneration. This type of regeneration process would allow to recycle waste steam usually available at the power plants and would not require high energy input.

Recommendation 3: Introduction of longer and shorter organic ligands into the interlayer space of CoBDC.

One of the frameworks obtained in this dissertation work was MOF, CoBDC, composed of 2D layers of cobalt-carboxylate building units connected by organic ligands of benzene 1,4-dicarboxylic acid. The 2D layers were pillared by solvent guest molecules of dimethylformamide (DMF). Upon introduction of long amine molecule of 1,6-hexanediamine to CoBDC, a framework of different structure was formed. It would be interesting to study introduction of shorter or longer chain molecules to the CoBDC complex to introduce control over the structure and potentially the pore sizes of the frameworks. Also while ligand exchange trials were performed with CoBDC-HD, the solutions were not reheated. Therefore another tests that could be performed are the
exchange of 1,6-hexanediamine linkers in CoBDC-HD to a shorter or longer molecules and further crystallization under hydrothermal conditions in the reaction oven at high temperature. In addition, to fully assess the structure of the obtained CoBDC-HD a single crystal X-ray diffraction analysis needs to be executed. Such analysis would provide an exact information on how amine ligands participate in the structure of CoBDC-HD and where if present dimethylammonium cations are located within the structure itself.

**Recommendation 4: Ligand replacement with larger molecules for increased permanent porosity and CO$_2$ capture.**

As it was found in this work, neither CoBDC-HD nor CoBDC complexes exhibit high surface area. This could be attributed to the blockage of the pores with solvent molecules. In both of these frameworks, a benzene 1,4-dicarboxylic acid organic ligand was used as a primary linker to connect cobalt clusters. It is proposed for the future research, to use larger molecules as primary linkers to increase the pore size within the layer itself. This may contribute to the distance of the metal sites from each other and hence distance between the points where pillarig ligands would attach. The high pore volume would allow for easier escape of the solvent molecules and hence increased surface area.

Another test that could be performed is replacement of 1,6-hexanediamine in CoBDC-HD with an organic ligand with additional amine groups or even just N atoms in the middle of the chain. This would allow for highest CO$_2$ capture as amines participate in chemical adsorption of CO$_2$. Therefore, more adsorption sites would be introduced into the framework.
### 7.0 Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDC</td>
<td>1,4-benzene dicarboxylic acid</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller (BET) theory</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda (BJH) theory</td>
</tr>
<tr>
<td>DD</td>
<td>4,4-dimethylphenylamine</td>
</tr>
<tr>
<td>ED</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy (EDS)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HD</td>
<td>1,6-hexanediamae</td>
</tr>
<tr>
<td>NEU-1</td>
<td>CoBDC-ED</td>
</tr>
<tr>
<td>NEU-3</td>
<td>CoBDC-HD</td>
</tr>
<tr>
<td>NEU-5</td>
<td>CoBDC-DD</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal organic framework</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
8.0 References


inherited from metal organic frameworks and further application in CO oxidation, 