Synthesis of Pillar-layered Metal Organic Frameworks for Carbon dioxide Adsorption applications

By

Ijlal Aamer

205586

Session 2017-19

Supervised by

Dr. Naseem Iqbal

A Thesis Submitted to the US-Pakistan Center for Advanced Studies in Energy in partial fulfillment of the requirements for the degree of

MASTERS of SCIENCE in

THERMAL ENERGY ENGINEERING

US-Pakistan Center for Advanced Studies in Energy (USPCAS-E)
National University of Sciences and Technology (NUST)
H-12, Islamabad 44000, Pakistan
October 2020

Synthesis of Pillar-layered Metal Organic Frameworks for Carbon dioxide Adsorption applications

By

Ijlal Aamer

205586

Session 2017-19

Supervised by

Dr. Naseem Iqbal

A Thesis Submitted to the US-Pakistan Center for Advanced Studies in Energy in partial fulfillment of the requirements for the degree of

MASTERS of SCIENCE in

THERMAL ENERGY ENGINEERING

US-Pakistan Center for Advanced Studies in Energy (USPCAS-E)

National University of Sciences and Technology (NUST)

H-12, Islamabad 44000, Pakistan

October 2020

Thesis Acceptance Certificate

Certified that final copy of MS thesis written by Mr. Ijlal Aamer, (Registration No. 205586), of U.S Pakistan Center for Advanced Studies in Energy has been vetted by undersigned, found complete in all respects as per NUST Statues/Regulations, is within the similarity indices limit and is accepted as partial fulfillment for the award of MS degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have also been incorporated in the said thesis.

Signature: ______________________________

Name of Supervisor: Dr. Naseem Iqbal

Date: _________________________

Signature (HoD): _________________________

Date: ______________________________

Signature (Dean/Principal): ___________________

Date: _____________________________________

Certificate

This is to certify that work in this thesis has been carried out by **Mr. Ijlal Aamer** and completed under my supervision in Energy Synthesis laboratory, US-Pakistan Center for Advanced Studies in Energy (USPCAS-E), National University of Sciences and Technology, H-12, Islamabad, Pakistan.

Supervisor:

Dr. Naseem Iqbal
USPCAS-E
NUST, Islamabad

GEC member # 1:

Dr. Majid Ali
USPCAS-E
NUST, Islamabad

GEC member # 2:

Dr. Rabia Liaquat
USPCAS-E
NUST, Islamabad

GEC member # 3:

Dr. Nadia Shahzad
USPCAS-E
NUST, Islamabad

HoD- (TEE)

Dr. Adeel Javaid

USPCAS-E
NUST, Islamabad

Principal/ Dean

Dr. Adeel Waqas
USPCAS-E
NUST, Islamabad

Dedication

I dedicated this work to my parents, siblings and all my well-wishers for their unwavering support and for believing in me.

Acknowledgment

All praise belongs to Allah Almighty, the Most Benevolent, the Most Merciful, who has granted me the strength, courage and willpower to complete my work. I consider myself, highly fortunate to be able to complete this work in the time allotted to me.

I would like to deeply express my gratitude to my supervisor, Dr. Naseem Iqbal, for his invaluable guidance and support throughout my postgraduate study.

I would also like to thank my Guidance and Examination Committee (GEC) members, Dr. Majid Ali, Dr. Nadia Shahzad and Dr. Rabia Liaquat, for their advice in easing the difficulties and removing the problems in my project. I am also thankful to them for their moral as well as material assistance.

I would also like to thank the lab staff for their help in carrying out the required testing and characterization techniques. Finally, I am immensely gratified to my family and friends, who have been the source of endless support and encouragement for me.

Abstract

Over the past century, the dependency of humans on fossil fuels has increased dramatically. Fossil Fuels have become the main source of energy production because of their low cost and easy availability but they have their own drawbacks. The biggest disadvantage of using Fossil Fuels is that they produce gasses that are harmful for the environment. The gasses that harm the environment are called Green House Gasses (GHGs) and Carbon dioxide is the biggest contributor of all GHGs present in the environment. For the past two decades a lot of work has been done to study GHGs and methods have been developed to capture, store or convert environmental and/or exhaust CO_2. One of the more advanced method for CO_2 capture is physical adsorption which has been accomplished using different materials by different researchers. Recently, Metal Organic Frameworks (MOFs) have come up as one of the more efficient adsorption materials for CO_2 capture or as catalysts to enhance CO_2 capture. MOFs are materials that contain a 2-D lattice that contains a network of Metal ions and Organic Linkers combining to produce a structure that can trap gaseous molecules. These MOFs are functionalized to produce enhanced adsorption results and better properties like improved surface area or affinity to CO2 molecules. There are two types of functionalization used in MOFs i) Pre synthetic Functionalization ii) Post synthetic Functionalization. In this research the method of Pre-synthetic Functionalization is used to turn the 2-D structure of the MOF into a 3-D structure to enhance its surface area and pore volume. These types of MOFs are called Pillared-Layer MOFs as they have a pillar material that combines multiple layers of the 2-D lattice and results in producing a 3-D MOF. In this study, we synthesize, characterize and test two Pilared-Layer MOFs for CO_2 capture. The MOFs are Zn-BDC-Dabco and Co-BDC-Dabco in which Zinc and Cobalt are the metal ions, BDC or Terephthalic Acid acts as the organic linker and Dabco acts as the pillar. These samples showed improved CO_2 adsorption compared to the same MOFs without Dabco and showed better results than a lot of other similar MOFs. The Cobalt and the Zinc based MOFs showed a CO_2 adsorption capacity of 4.4 mol/kg and 6.3 mol/kg respectively and showed good thermal stability up to 300 degrees Celsius.

Abbreviations

GHGs	Green House Gasses
MOFs	Metal Organic Frameworks
XRD	X-Ray Diffraction
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
FTIR	Fourier-transform infrared spectroscopy
SBUs	Secondary Building Units
REMs	Rare Earth Metals
OMSs	Open Metal Mites
LBs	Lewis Base sites
PSF	Post synthetic functionalization
PSM	Post synthetic modification
SALI	Solvent Assisted Ligand Incorporation
AIM	Atomic Layer Deposition
SALE	Solvent-Assisted Linker Exchange
PSE	Post-Synthetic Exchange

Table of Contents

Acknowledgment vi

Abstract vii

Abbreviations viii

List of Figures xi

List of Tables xii

Chapter 1: Introduction 2

1.1. Climate Change 2

1.2. Methods to reduce Carbon dioxide emission. 4

1.3. Metal Organic Frameworks (MOFs) 5

1.3.1. Use of Metal Organic Frameworks 5

1.3.2. Capture of CO2 in Metal Organic Frameworks 6

1.4. Problem Statement 6

1.5. Scope and Objectives of the Thesis 6

1.6. Thesis Layout 7

1.7. Summary 7

1.8. References 9

Chapter 2: Literature Review 12

2.1. Background 12

2.1.1. Carbon Capture Techniques 12

2.1.2. Metal Organic Frameworks 13

2.2. MOF synthesis with specific selected properties 16

2.2.1. Functional modification and structural spaces 16

2.2.2. Surface area and pore volume 16

2.2.3. Unsaturated open metal sites 17

2.3. Functionalization of metal-organic framework 17

2.3.1. Pre-synthesis functionalization 18

2.3.2. Post-synthetic functionalization 19

2.4. Selection of Metal Organic Framework 19

2.5. Summary 20

2.6. References 22

Chapter 3: Experiment and Methodology 34

3.1. Materials 34

3.2. Synthesis Methods ... 34
  3.2.1. Synthesis of Pillared Layer Metal Organic Frameworks. ... 34
  3.2.2. Synthesis of Metal Organic Frameworks without DABCO. ... 34
3.3. Characterization ... 35
  3.3.1. X-Ray Diffraction ... 35
  3.3.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy ... 36
  3.3.3. TGA ... 38
  3.3.4. FTIR ... 39
  3.3.5. Sorption Analyzer ... 40
3.4. Summary ... 40
3.5. References ... 42
Chapter 4: Results and Discussion ... 43
4.1. Characterization ... 43
  4.1.1. X-Ray Diffraction ... 43
  4.1.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy ... 44
  4.1.3. Thermogravimetric Analysis ... 46
  4.1.4. Fourier-transform infrared spectroscopy ... 47
  4.1.5. Surface area testing (BET) ... 48
4.2. Testing ... 48
  4.2.1. Sorption Analysis ... 48
4.3. Comparison of Results ... 49
4.4. Summary ... 50
4.5. References ... 51
Chapter 5: Conclusion and Recommendations ... 52
4.6. Conclusions ... 52
4.7. Challenges ... 52
4.8. Future recommendations ... 53
4.9. References ... 54

List of Figures

Figure 1: Annual Greenhouse Gas emissions (Globally) [1] 2
Figure 2: GHG Composition in percentage [1] 3
Figure 3: GHG emissions: Contribution from each sector in percentages [1] 3
Figure 4: Techniques used for MOF Synthesis and their respective operating conditions. 14
Figure 5: Proposed Model of the MOF [106] 18
Figure 6: Instrumentation Diagram of XRD Equipment 35
Figure 7: Diagram of SEM Equipment with Labelled components 37
Figure 8: Diagram explaining the image formation process in SEM 38
Figure 9: XRD Pattern of the synthesized MOF and the Simulated pattern from the Literature [1] 43
Figure 10: Structure Diagram of the Synthesized MOF showing C (red), O (orange), N (grey) and Metal (blue) atoms 44
Figure 11: SEM Images of the two MOFs 45
Figure 12: EDS of Cobalt based MOF 45
Figure 13: TGA Analysis of the two MOFs 46
Figure 14: FTIR Analysis graph of the two MOFs 47
Figure 15: Pore volume curve of the two MOFs 48
Figure 16: Sorption Analysis curves of All four synthesized MOF 49

List of Tables

Table 1: List of Pillared-Layer MOFs studied in the literature review..20

Table 2: Comparison of results with Literature...49

Chapter 1: Introduction

1.1. Climate Change

Over the past century, the human dependency on fossil fuel as the main source of energy has increased which has resulted in improved quality of life and a high level of industrialization, resulting in enhanced emission of Greenhouse Gasses (GHG). This effect has also been enhanced by the increase in deforestation. According to most researches it is expected that this relationship will continue in a similar way at least for the next few decades till the effects of the recent work on reducing the impact of GHG starts to show. The increased load up of GHGs in the atmosphere can potentially have a great impact on the world climate in the near future [1]. The emission of GHGs have dramatically increased over the period starting from 1970 to 2004 as shown in Figure 1 [1].

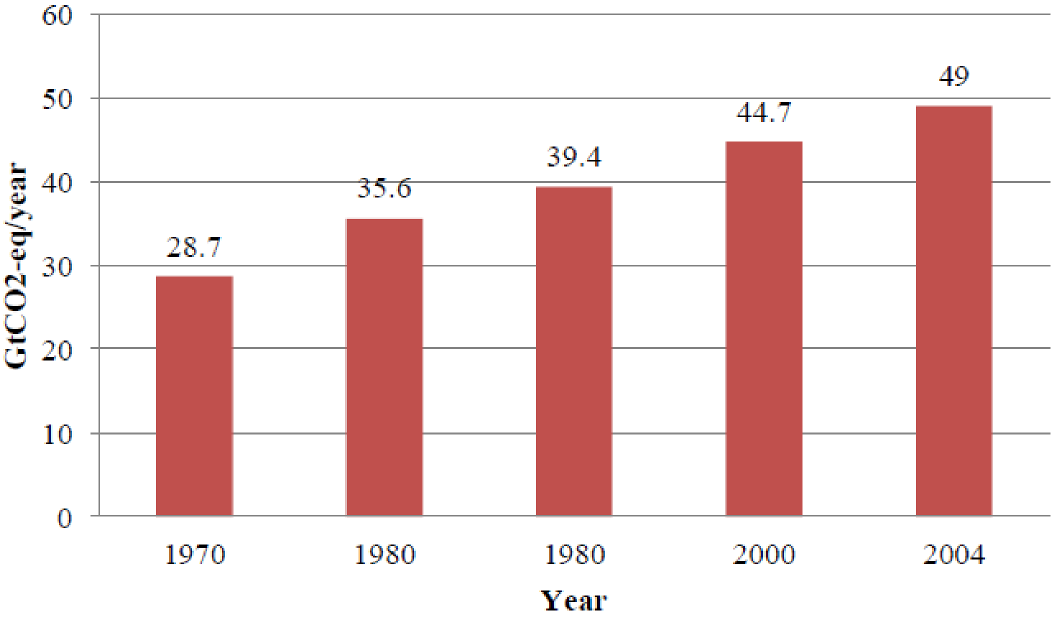


Figure 1: Annual Greenhouse Gas emissions (Globally) [1]

GHGs comprise of various different gasses but the biggest contributor is Carbon dioxide (CO_2) as can be seen in Figure 2, which contributes to about 80% of all GHGs [1]. The biggest source of CO_2 emission is fossil fuel combustion which has become the biggest source of energy over the past century and contributes to about 57% of the total GHG emissions. Deforestation and the decay of biomass are the second biggest contributors to the increased emissions. Different sectors and their contribution to the total GHG emission can be seen in Figure 3.

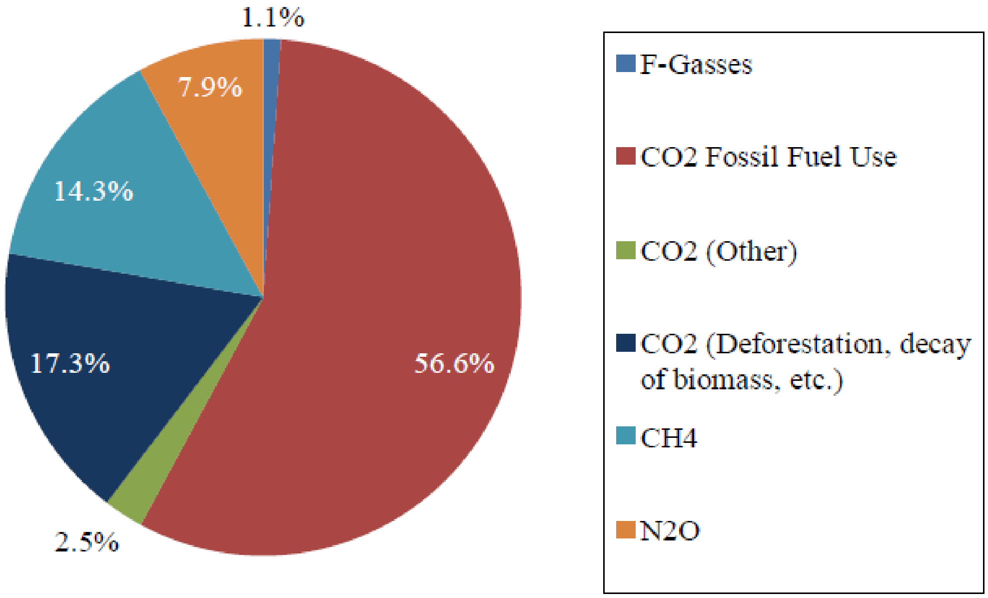


Figure 2: GHG Composition in percentage [1]

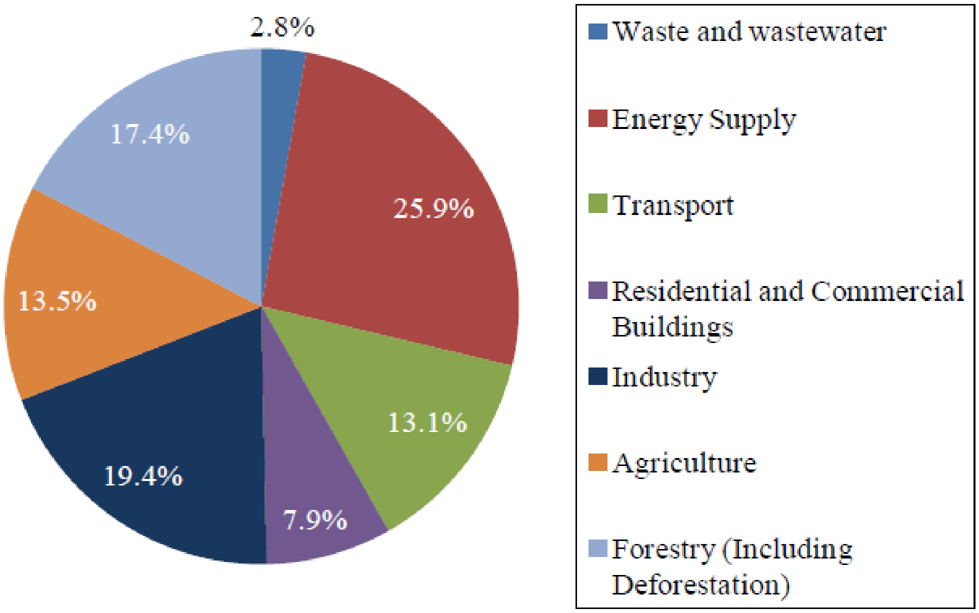


Figure 3: GHG emissions: Contribution from each sector in percentages [1]

It can be seen that larger sources that are specified as Energy Supply and Industries contribute to 45.3% of the total while Buildings, Transportation, Forestry, Agriculture, Commercial and Residential uses contribute to about 51.9% [1].

Over the past two decades, studies have been conducted to reduce CO_2 emissions and mitigate its effects on the atmosphere. Numerous studies and policies have been produced and a number of solutions have been studied. A list of some of these solutions is provided below:

a) Sustainable renewable energy sources.
b) Low carbon emission energy sources.
c) Improvement of Energy efficiency.
d) Enhancement of natural sinks.
e) Carbon dioxide capture and storage systems.

1.2. Methods to reduce Carbon dioxide emission.

A reduced growth of the economy is also a big effect of global warming and climate change [2]. Researchers have used various methods to separate carbon dioxide from gas mixtures that include other gasses like H2, N2, CO, CH4 etc. A lot of research is being carried out to remove CO2 using chemical solvents like activated carbon [3, 4] and zeolite adsorbents [5], and both these are very commonly used in different applications in the industrial world.

Generally, chemical solvents are considered feasible for use in the industry for CO2 adsorption. These chemicals base their strength on amine functionality which provides enhanced affinity to carbon dioxide molecules resulting in improved adsorption. but despite the enhanced adsorption [6], the cost of the solvents makes this technique not very financially applicable due to the high cost of the solvents and their regeneration [7].

Activated carbon has high surface area due to its high microporosity [8]. For enhanced sorption the surface of these pores is functionalized with an amine-based material [9]. Some other materials are more reliable for CO2 adsorption because they can be cheaper, and the adsorption capacity is not affected by humidity and moisture content.

The CO2/N2 selectivity is moderate at 1 atm but reduces with increase in pressure [10]. Generally, the adsorption capacity and selectivity of CO2 adsorbents gets reduced in post combustion applications and is therefore preferred for pre combustion applications [11]. A lot of CO2 is emitted from traditional power plants and that emission can be removed by the use of post-combustion CO2 removal processes [12]

A number of different zeolites like the natural zeolite [13], zeolite ZSM -5 [15], zeolite 13X [14], MCM-41 [16] and others [17, 18], are used for carbon capture applications. Zeolites when functionalized with amine functional groups enhance the capacity for CO2 adsorption [19] but the presence of moisture in the flue gasses reduces its effectiveness Moisture content creates blockages in the framework of the zeolite molecule due to the interaction of water with the hydrogen bonding of the framework [20]. This interaction can enhance the adsorption capacity in some cases and reduce the adsorption capacity in others based on the polarity of the adsorbates [21]. The water interaction, however, does reduce the strength of the framework [22] and due to the high energy requirements for the regeneration of zeolites, they lose their promise as effective adsorbents for CO2 capture [19, 23].

Most of the previously mentioned materials have shown promise due to their high capacity and thermal stability for CO2 capture [18, 24, 25] but Metal Organic frameworks (MOFs) [26, 27] are the center of interest for a lot of researchers as the best option for CO2 capture [28].

1.3. Metal Organic Frameworks (MOFs)

1.3.1. Use of Metal Organic Frameworks

Many different terminologies like organic framework, coordination polymers and hybrid inorganics is used to describe metal organic frameworks which are generally solid-state frameworks made by connecting organic ligands using metal ions [29]. Generally, these frameworks consist of multiple metal-organic units that combine together to form infinitely long chains of a 1-D, 2-D or 3-D structure [30]. A huge number of MOFs have been produced and studied for carbon capture and the number is continuously increasing, with each having different combination of functionalization and organic linkers resulting in varying adsorption capacity and cost based on the raw materials [31]. Originally there was a lot of interest in 3-D MOFs because of their high surface area and pore volume and the added benefit that they could’ve been functionalized differently for different applications [32] like gas separation, optoelectronics, purification, catalysts and gas storage etc. [33].

1.3.2. Capture of CO2 in Metal Organic Frameworks

Due to the high percentage of Carbon dioxide contribution to the GHGs, researchers and scientists have prioritized reduction of CO2 emissions as the biggest solution to fighting global warming. Due to the high energy requirements of the regeneration processes of the previously mentioned technologies used for separation, physical adsorption techniques are commonly used to capture carbon dioxide using highly porous materials because of the high capacity and low regeneration energy requirements. MOFs with their high porosity, functionalization ability and high surface area work as a preferred source of CO2 capture from a mixture of gases [34]. The activation of these materials is a very important part of the total process as it effects the amount of metal sites open for adsorption and interaction with CO2 and the gaseous mixtures [35]. Most studies of CO2 adsorption using MOFs are usually limited to adsorption at certain temperature and pressure which is a poor indicator for identifying the performance and effectiveness of these MOFs in industrial applications. Due to the quadripolar moment of the CO2 molecules, it has increased selectivity for MOFs when in a gaseous mixture [35]. Due to these interesting properties and qualities that enhance the separation and sorption of CO2, MOFs have caught the eye of many researchers for various different CO2 capture applications.

1.4. Problem Statement

Many different Metal organic frameworks have been tested and used for CO2 capture. Usually 2-D MOFs are combined with post synthesis amine-functionalization to enhance their CO2 adsorption capacity. Synthesis of Pillared Layer Metal Organic frameworks produces 3-d MOFs with higher surface area than 2-d MOFs which results in a higher adsorption capacity as well.

1.5. Scope and Objectives of the Thesis

The objective of this dissertation is to study the synthesis of two pillared-layer Metal Organic Frameworks and analyze their adsorption capacities for Carbon Dioxide capture and the improvement in capacity caused by the addition of the pillar. The aims are:

1. Synthesis of 2 Dabco based pillared layer Metal Organic Frameworks, Zn-BDC-Dabco and Co-BDC-Dabco
2. Characterization of the synthesized materials using X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM) & Energy Dispersive Spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR).

To test the synthesized materials for enhanced surface area and carbon dioxide adsorption capacities.

1.6. Thesis Layout

This is a brief layout of this thesis providing a little detail about each chapter present.

- Chapter 1 provides a short introduction to the background, problems and objectives of this research.
- Chapter 2 talks about the Literature Review, the papers that were studied to help find the solution to the problem and details on all the methods and materials that were studied through the literature.
- Chapter 3 is about the Experimentation and the methodology carried out to solve the problem. The synthesis method, characterization and the testing is all included in this chapter.
- Chapter 4 discusses the results obtained in this research in detail with each section in the chapter corresponding to a different analytical technique or test.
- Chapter 5 is the final chapter, and this is where the conclusions are discussed. It also contains details about the challenges faced in this research as well as the future recommendations.

1.7. Summary

The recent studies on global warming and climate change point out Greenhouse Gasses (GHGs) as its main source.   The biggest contribution to the total GHGs in the atmosphere comes from Carbon dioxide which is more than 50% of the total and since it is emitted at every industry and even every household it’s the most important and easier to counter emission compared to the rest. Carbon dioxide absorption and adsorption are both methods to capture the gas and either store it or convert it through different processes into various other different useful products. Various different methods are used to achieve this capture of CO_2, but pressure swing adsorption remains one of the more common methods used for this purpose. Metal Organic Frameworks have caught attention around the world because of their high porosity, surface area and flexibility which helps achieve high adsorption capacities for CO_2 capture. Not only that but MOFs can also work as catalysts for capture processes which makes them valuable tools for these methods.

1.8. References

1. IPCC, 2007, "IPCC Fourth Assessment Report - Climate Change 2007: Synthesis Report," IPCC, AR4, Geneva, Switzerland.
2. Tol RSJ. How much damage will climate change do? Recent estimates. World economics. 2000;1(4):179.
3. Kikkinides ES. Concentration and recovery of carbon dioxide from flue gas by pressure swing adsorption. Industrial & Engineering Chemistry Research. 1993;32(11):2714.
4. Heuchel M. Adsorption of carbon dioxide and methane and their mixtures on an activated carbon: simulation and experiment. Langmuir. 1999;15(25):8695.
5. Golden TC, Sircar S. Gas Adsorption on Silicalite. Journal of Colloid and Interface Science. 1994;162(1):182-8.
6. Maliz C. Carbon dioxide recovery: large scale design trends Proceedings of Technical Meeting / Petroleum Conference of The South Saskatchewan Section1995.
7. Wolsky AM, Daniels EJ, Jody BJ. CO2 Capture from the flue gas of conventional fossil-fuel-fired power plants. Environmental Progress. 1994;13(3):214-9.
8. Guo B, Chang L, Xie K. Adsorption of Carbon Dioxide on Activated Carbon. Journal of Natural Gas Chemistry. 2006;15(3):223-9.
9. Dantas TLP, Amorim SlM, Luna FMT, Silva IJ, de Azevedo DCS, Rodrigues ArE, et al. Adsorption of Carbon Dioxide onto Activated Carbon and Nitrogen-Enriched Activated Carbon: Surface Changes, Equilibrium, and Modeling of Fixed-Bed Adsorption. Separation Science and Technology. 2009 2011/12/09;45(1):73-84.
10. Radosz M, Hu X, Krutkramelis K, Shen Y. Flue-Gas Carbon Capture on Carbonaceous Sorbents: Toward a Low-Cost Multifunctional Carbon Filter for “Green” Energy Producers. Industrial & Engineering Chemistry Research. 2008 2011/12/09;47(10):3783-94.
11. D'Alessandro DM, Smit B, Long JR. Carbon Dioxide Capture: Prospects for New Materials. Angewandte Chemie International Edition. 2010;49(35):6058-82.
12. Klara SM, Srivastava RD. U.S. DOE integrated collaborative technology development program for CO2 separation and capture. Environmental Progress. 2002;21(4):247-53.

13. Siriwardane RV, Shen M-S, Fisher EP. Adsorption of CO2, N2, and O2 on Natural Zeolites. Energy & Fuels. 2003 2011/12/09;17(3):571-6.
14. Mérel J, Clausse M, Meunier F. Carbon dioxide capture by indirect thermal swing adsorption using 13X zeolite. Environmental Progress. 2006;25(4):327-33.
15. Armandi M, Garrone E, Areán CO, Bonelli B. Thermodynamics of Carbon Dioxide Adsorption on the Protonic Zeolite H-ZSM-5. ChemPhysChem. 2009;10(18):3316-9.
16. Kim JM, Kwak JH, Jun S, Ryoo R. Ion Exchange and Thermal Stability of MCM-41. The Journal of Physical Chemistry. 1995 2011/12/09;99(45):16742-7.
17. Delgado JA, Uguina MaA, Sotelo JL, Ru أz B, Ros، أrio M. Carbon Dioxide/Methane Separation by Adsorption on Sepiolite. Journal of Natural Gas Chemistry. 2007;16(3):235-43.
18. Lee J-S, Kim J-H, Kim J-T, Suh J-K, Lee J-M, Lee C-H. Adsorption Equilibria of CO2 on Zeolite 13X and Zeolite X/Activated Carbon Composite. Journal of Chemical & Engineering Data. 2002 2011/12/09;47(5):1237-42.
19. Zhao H, Hu J, Wang J, Zhou L, Liu H. CO2 Capture by the Amine-modified Mesoporous Materials. Acta Physico-Chimica Sinica. 2007;23(6):801-6.
20. Hutson ND, Zajic SC, Yang RT. Influence of Residual Water on the Adsorption of Atmospheric Gases in Li- X Zeolite: Experiment and Simulation. Industrial & Engineering Chemistry Research. 2000 2011/12/09;39(6):1775-80.
21. Moïse J-C, Bellat J-P. Effect of Preadsorbed Water on the Adsorption of pxylene and m-xylene Mixtures on BaX and BaY Zeolites. The Journal of Physical Chemistry B. 2005 2011/12/09;109(36):17239-44.
22. Brandani F, Ruthven DM. The Effect of Water on the Adsorption of CO2 and C3H8 on Type X Zeolites. Industrial & Engineering Chemistry Research. 2004 2011/12/09;43(26):8339-44.
23. Harlick PJE, Tezel FH. An experimental adsorbent screening study for CO2 removal from N2. Microporous and Mesoporous Materials. 2004;76(1-3):71-9.
24. Kokotailo GT, Kokotailo. Structure of synthetic zeolite ZSM-5. Nature. 1978;272(5652):437.

25. Jadhav PD, Chatti RV, Biniwale RB, Labhsetwar NK, Devotta S, Rayalu SS. Monoethanol Amine Modified Zeolite 13X for CO2 Adsorption at Different Temperatures. Energy & Fuels. 2007 2011/12/09;21(6):3555-9.
26. Férey G. Crystallized frameworks with giant pores: Are there limits to the possible? Accounts of Chemical Research. 2005;38(4):217.
27. Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. Reticular synthesis and the design of new materials. Nature. 2003;423(6941):705-14.
28. Bourrelly S, Llewellyn PL, Serre C, Millange F, Loiseau T, Ferey Gr. Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47. Journal of the American Chemical Society. 2005 2011/12/09;127(39):13519-21.
29. Biradha K, Ramanan A, Vittal JJ. Coordination Polymers Versus Metal- Organic Frameworks. Crystal Growth & Design. 2009 2011/12/28;9(7):2969-70.
30. Janiak C. Engineering coordination polymers towards applications. Dalton Transactions. 2003(14):2781-804.
31. Ferey G. Hybrid porous solids: past, present, future. Chemical Society Reviews. 2008;37(1):191-214.
32. Ma S. Gas adsorption applications of porous metal–organic frameworks. Pure and applied chemistry. 2009;81(12):2235.
33. Fischer RA, Wöll C. Functionalized Coordination Space in Metal–Organic Frameworks. Angewandte Chemie International Edition. 2008;47(43):8164-8.
34. Simmons JM, Wu H, Zhou W, Yildirim T. Carbon capture in metal-organic frameworks-a comparative study. Energy & Environmental Science. 2011;4(6):2177-85.
35. Dietzel PDC, Besikiotis V, Blom R. Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide. Journal of Materials Chemistry. 2009;19(39):7362-70.

Chapter 2: Literature Review

2.1. Background

2.1.1. Carbon Capture Techniques

There are various different technologies used to reduce CO_2 emissions like capture and compression from combustion exhausts, transportation to oceans or geological reservoirs for storage and utilization by converting the exhaust CO_2 into useful products [1, 2]. But all these technologies come with their own risks like acidification of the ocean in deep ocean storage and environmental issues due to other types of sequestration. Due to this reason, techniques in which carbon dioxide is first captured and then converted to valuable products, also known as Carbon Capture and Utilization (CCU) [3] is considered one of the best techniques for CO_2 capture. Due to the easy process and the easy regeneration by multiple methods, adsorption seems like the most competitive method for CO_2 capture of all the other options like membrane technology, cryogenic, absorption, and micro algal bio-fixation [4,5].

Adsorption has shown promise as a low energy and cost consuming process for post combustion carbon capture compared to other methods when the durability and the ability to regenerate the solvent can be guaranteed [4,6-8]. The conversion of CO_2, captured from exhausts and other emission sources, into useful products provides not only reduces net CO_2 emissions but also generates high value fuels and chemicals [4,6-9] with the added advantage of providing better health conditions and environment to humans as well as improve climatic issues. Despite these advantages, the aggressive nature of the high temperature and high-pressure conditions required to break down the highly thermal stable and chemically inert CO_2 for the adsorption process is a big concern as it requires high energy input which is not good for the environment. Therefore, the carbon dioxide is activated first using MOFs as catalysts to allow it to convert under comparatively milder conditions. MOFs have recently been used as effective adsorbents for carbon capture as well as [10-13] efficient catalyst [14-19] to help other materials be able to adsorb CO_2 because of their high surface area, stability, porosity and open channels. MOFs also provide high porosity and crystallinity as well as the ability to be synthesized with various different functionalized organic linkers based on the use. This gives MOFs a major advantage over other adsorbents for carbon capture, due to the enhanced efficiency in CO_2 capture as well as the ability to work as a catalyst to convert CO_2.

2.1.2. Metal Organic Frameworks

Synthesis of Metal Organic Frameworks (MOFs) is easy, it is achieved by the application of modular synthesis in which a metal salt is mixed with an organic linker that results in a crystal structure with a fine network of pores that possess exceptional porosity, stability, and a high pore size and surface area. Over the past few years, various different techniques and methods have been used for the synthesis of MOFs, these techniques contain both continuous and discontinuous phase MOFs and the synthesis conditions vary with each method as well. However only cautious MOFs are commonly used for adsorption applications and there are very few examples of discontinuous MOFs being used for CO_2 adsorption. All the common techniques used for MOF synthesis are usually either solid phase synthesis methods or liquid phase synthesis methods. Solvothermal methods [20] are the most commonly used method for MOF synthesis, but other methods like electrochemical synthesis [22], microwave-assisted synthesis [21], sonochemical synthesis [24-29], mechanochemical synthesis [23], spray-drying synthesis [30-32] and flow chemistry [33-36] are also commonly used for the synthesis of MOFs. The various methods used for the synthesis of MOFs and their respective operating conditions are shown in Figure 4. The structure of the MOF is based on the three basic components of the MOFs during synthesis, i) inorganic secondary building units (SBUs) ii) the organic linkers [37-39] and iii) the solvent used during the synthesis process as both the other two components are usually solids at room temperature and pressure. The different types of approaches used for MOF synthesis that have been developed over the past two decades are shown in Fig [30].

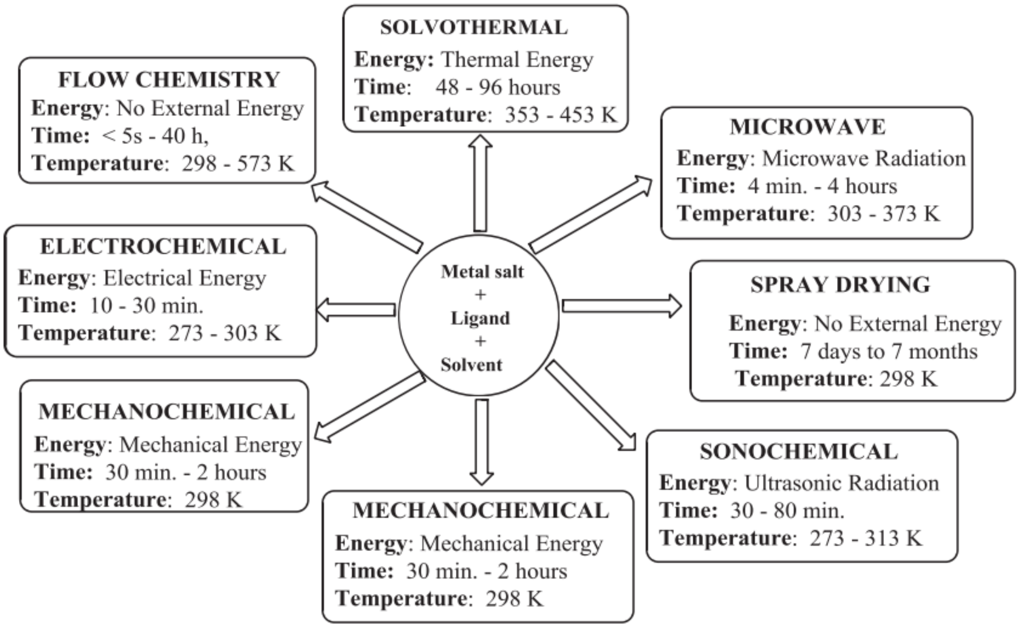


Figure 4: Techniques used for MOF Synthesis and their respective operating conditions [20-36].

An advanced explanation of all the main parts of Metal Organic Frameworks is provided below:

Linkers: Linkers are neutral molecules or ions that bond to the metal ions and donate electron pairs (act as Lewis bases). They are also called bridging ligands or Organic Linkers and they can consist of heterocyclic compounds, anions such as phosphonate or sulfonate and carboxylic acids. For the synthesis of MOFs, usually multidentate ligands are used, these ligands have two or more donor atoms. Nitriles, carboxylates and azoles are some of the more commonly used ligands in MOF synthesis [37,41]. Multivariate MOFs in which a single framework consists of multi organic functionalities that provide a more complex design for the pores of a MOF have also been reported [42,43].

Metal precursors: The metal part of MOFs is usually contributed mostly by divalent or trivalent Rare Earth metals and Transition metals, for example Zn2+, Zn3+, Cu2+, Co2+, Ni2+, Fe2+, Fe3+, Ru2+, Al3+ etc. [44-48]. Over the past few years, Lithium [49,50],Magnesium [51-56],Boron [57],Carbon [56,58,59] and other light weight metals have also been studied for use as metal precursors in MOFs mainly due to their good gravimetric properties which is essential in gas separation applications. Lanthanide series (e.g. Pm, Gd, La, Dy, Er, Tm, Sm) have received a lot of attention from researchers for use as SBUs in MOF synthesis because of their peculiar chemical characteristics and strong coordination features [60-62]. These properties give the lanthanide series strong affinity for ligands and donor atoms that contain oxygen and nitrogen and their hybrids. The problem faced by researchers is that the lack of control in the synthesis of lanthanide complexes because of their coordination flexibility and high coordination number; which results in their use in MOF synthesis being low compared to transition metals [63-65]. MOFs have become very popular in the past two decades and new materials are being studied every day, recent studies have also included the use of mix metals, alkaline earth metals like, p-block elements and even actinides as SBUs in the synthesis of MOF materials [66-71].

Solvents: These are mainly used because usually both the metal precursor and ligand material are usually solids, so solvents help them dissolve together. Many different solvents are used for different types of MOF synthesis, the most common ones are water and some organic solvents like acetone, ethanol, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), etc. Solvent molecules are responsible for defining the dimensions and connectivity properties of the MOFs [72,74-76] because they influence the coordination and interaction of and between metal ions [72,73]. The total organic part of the MOFs contributes to three major roles in the total process of synthesis of the material. This includes:

1. Use as an organic solvent and as a source of defining the coordination of the linkers which is reported to be based on the basicity of the organic solvent [77].
2. The solvent also plays an important role in dictating the formation of the MOF structure
3. The ligand is also organic, and it contributes by coordinating with the metal ion to form the structure [78].

MOFs can also be synthesized with the use of a mixture of solvents and mixtures of water and organic solvents or mixtures of different organic solvents in varying ratios have also been reported for MOF synthesis [79]. In all these mixtures, it is important to keep the polarity of the MOFs close to allow the different solvents to mix with each other seamlessly.

2.2. MOF synthesis with specific selected properties

A rational design of the MOFs systematically enhances its performance for specific applications [80-85].Adsorbate-Adsorbent interactions are one of the most important factors when it comes to CO2 capture as it controls the amount of CO2 captured in a MOF, and these interactions depend on other properties such as the metal ions that have open sites and interact with the Carbon dioxide molecules[86,87]. Thanks to the high structural and chemical tunability of MOFs, they can be modified differently for different applications.

2.2.1. Functional modification and structural spaces

Organic ligands and Metal precursors have exceptional flexibility which allows them to adapt to functional and structural modifications. The metal part of the MOFs includes all series of transition and lanthanide metals, p-elements and rare earth metals (REMs) but the most commonly used ones are Cu, Zn, Co, Ni, and Fe. Amine based carboxylate and heterocyclic ligands are widely used as organic ligands for MOF synthesis, with the carboxylates being the favorite choice due to their stability. This allows researchers to synthesize MOFs for different applications using different combination of carboxylic acid ligands and metal centers and a proper selection can produce enhanced results.

2.2.2. Surface area and pore volume

For MOFs, the pore size is also a key parameter when testing MOFs and it has great importance for Carbon dioxide capture and conversion applications. When synthesizing a MOF, the metal ions and organic ligands are arranged evenly to form a regular lattice structure, and the solvent guest molecules help in the formation and growth of the framework structure. After the guest molecules are removed, that is when the porous structure of the MOFs is produced. When preparing samples, if the compound is made to trap guest molecules into the channels, narrow pores (nps) are formed which are very small in size and have high selectivity which helps in selective uptake of CO2 over other gasses in humid conditions [88-90]. Another very important parameter is BET surface area which defines the adsorption capacity and the performance as a catalyst of the selected MOF. A general trend is that with the increase of specific surface area, the adsorption and catalytic properties of a MOF increase as well up to a certain limit. Therefore, it is important to select both the organic ligands and metal precursors in a way that results in an enhanced surface area per unit mass. Ideally, the use of longer organic linkers provides optimum results for CO2 capture in MOFs as they produce MOFs with narrow pore (np) and high specific surface area [91].

2.2.3. Unsaturated open metal sites

These open metal sites are what make MOFs so effective in adsorption. These unsaturated sites are saturated with the presence of guest molecules such as DMF, ethanol, water, methanol and other organic solvents which can be removed to expose the unsaturated sites by using some activation methods. The Lewis acidity of these metal sites results in them carrying a partial positive charge ($\delta+$) on them. Metal Organic Frameworks that contain these sites show comparatively higher heats of adsorption for CO2 (Qst) at lower pressures which results in higher selectivity of CO2 over N2 in flue gasses. This is because of the greater polarizability and quadruple moment of the CO2 in comparison with the N2which results in a stronger force of attraction for the CO2 and a better interaction with the molecules [92]. The adsorption capacity of the MOFs can also be enhanced by proper evacuation of guest molecules which results in increased density of open metal sites and allows efficient binding and access to CO2 molecules.

2.3. Functionalization of metal-organic framework

The isorecticular chemistry of the MOFs allows them to be functionalized which is achieved using two main approaches. The first one involves the incorporation of a functionalized organic linker which adds to the already built structure of the MOF, this is called pre-synthetic functionalization. The second approach is post synthetic functionalization in which a linker or additional functional group is added after the initial synthesis of the MOF has been completed. [94-99]. The application of MOFs is limited by the vacancy in the metal sites after evacuation as they usually have only one available slot and applications like use as a catalyst require at least two coordination vacancies [100]. This has led to isorecticular chemistry becoming an important feature in recent studies to tailor the organic linkers as it assists in the design of functional MOFs that are specifically designed to address a specific application. The use of organic solvents such as DMF or even water in the synthesis process results in the production of open metal sites (OMSs) and the heating of the MOF after synthesis results in the removal of these solvent molecules [101-105]. CO2 and N2 interact strongly with these metal sites that have a high density of charges due to the high polarizability of N2 compared to Co2 and their greater quadrupole moment [92]. Introducing Lewis Base sites (LBs) into MOFs that are usually nitrogen containing organic groups is also another approach used for functionalizing MOFs and enhancing their CO2 adsorption capacities [101-105].

2.3.1. Pre-synthesis functionalization

Yaghi first used this approach in which a functionalized MOF was produced using the originally used SBU by functionalized organic linkers that had similar connectivity (MOF-46) [106] (Figure 5 below). In the IRMOF series, Yaghi and coworkers mixed Rbdc and Zinc nitrate tetrahydrate in DEF using the solvothermal method [107]. The IRMOFs had a cubic MOF-5 like structure and when functional groups such as NH2, C2h4 and Br etc. were introduced, the pore diameter was reported to go from 12.8 Å all the way up to 28.8 Å. Many researchers have used the concept of isorecticular chemistry to produce different MOFs with enhanced crystal structure and stability. NH2-BDC, fumarate, BPDC and 2,6-napthalene were used to replace the BDC linker to produce (MIL-88: [Fe3O(bdc)6]n) by Ferey et al. [93,108] while Li et. al. [109] used h2bdc linkers and titanium metal material to synthesized NH2-MIL-125, [110] to produce a MOF with a quasi-cubic tetragonal structure. Pillared-Layer MOFs are also a type of pre-synthetically functionalized MOFs that produce a three-dimensional structure, in these MOFs a material is introduced that connects the 2D lattices of the traditional MOFs and turns them into a 3D structure which results in an enhanced surface area and adsorption capacity.

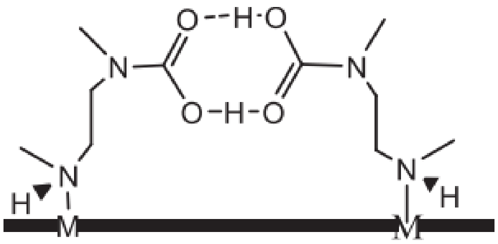


Figure 5: Proposed Model of the MOF [106]

2.3.2. Post-synthetic functionalization

Post synthetic modification (PSM) or Post synthetic functionalization (PSF) is the name given to the process in which the modification of an already synthesized MOF is done to produce a new MOF with its own structure and chemical properties. Amino, aldehyde, halogen, alkyne and a lot of other different types of functional groups are used for this purpose [112]. This approach is also very commonly used to dedicate the open metal sites and active centers of a MOF for a specific task or application. It involves reaction of pendant aldehyde [114], azides [111,116], and pendant amine [113-115] and it cannot be used by the usual solvothermal or hydrothermal processes used for the production of MOFs. The functional group can be introduced either to the organic linker or the metallic cluster in which case it is referred to as post-synthetic metalation (PSMet). For the former, three different strategies are reported, which include

I. The replacement of the nonstructural labile inorganic linkers with nonstructural functional organic linkers called the solvent assisted ligand incorporation (SALI).
II. The addition of metal clusters or complexes on the nodes for support called the atomic layer deposition (AIM).
III. Replacing the structural linkers with alternative linkers called the solvent-assisted linker exchange (SALE) or the post-synthetic exchange (PSE). [118].

These strategies have the same aim i.e. incorporation of functional groups into the MOFs but are still very different [118]. For example, in SALE changes the physical and chemical properties but does not change the topology of the MOF by allowing to decorate the pores and sites of the MOF with organic linkers while AIM and SALI make use of the available, reactive and labile ligands present in the nodes of the MOFs [118].

2.4. Selection of Metal Organic Framework

Following the Pre-synthesis functionalization technique, a number of MOFs were shortlisted and studied from the literature. All these metal organic frameworks were Pillared-layer three dimensional MOFs which resulted in them having high surface area and pore size. Table below provides a list of Metal Organic frameworks that were studied from the literature. [119-126]

Table 1: List of Pillared-Layer MOFs studied in the literature review.

S.No	Metal Organic Framework	Reference
1	WOFOUR-1-Ni or Co	119
2	SIFSIX-3-Cu	120
3	SIFSIX-3-Co	121
4	Zn2(BDC)2(Dabco) Ni2(BDC)2(Dabco)	122
5	TIFSIX-1-Cu SNIFSIX-1-Cu	123
6	Co(Imda)(4,4'-bpy)	124
7	[Zn4(TRZ)4(TTBDC)2]n [Zn2(TRZ)2(DOBDC)]n	125
8	UTSA-15a	126

2.5. Summary

This chapter begins by discussing various different technologies used for Carbon dioxide capture and their advantages and disadvantages. There are different methods used for this including compression, capture and storage but they all come with their own risks which resulted in giving birth to the idea of Carbon Capture and Utilization in which CO_2 is captured but instead of storing it in a reservoir it is used in different processes or converted into useful products. For CCU, adsorption has shown a lot of promise as it is not a very energy or cost intensive process. MOFs offer high CO_2 capture capacities and also act as catalysts to help other materials capture CO_2 which makes them ideal for this process. This chapter talks about MOFs in detailed. MOFs are synthesized using 3 main components i.e. metal precursor, organic linker and a solvent. There are various different methods used for MOF synthesis but the most commonly used method is Solvothermal Synthesis which uses a solvent in the presence of high heat to allow the metal and the linker to react and form a MOF. MOFs for CO_2 capture are specially designed in a different way than normal methods to enhance their affinity for CO_2 capture and increase their surface area and for this MOFs are functionalized. There are two different methods for MOF functionalization:

1. Pre synthesis functionalization in which an additional material is added to the MOF for the reaction of the synthesis that causes the resultant MOF to possess high affinity for CO_2 or result in an increased surface area and 2. Post synthesis functionalization in which already synthesized MOFs are reacted with other materials to enhance the properties of the MOF. At the end, the chapter contains a list of MOFs that were studied before the final selection of the MOF to be synthesized was made.

2.6. References

1. DOE. Report of the Interagency Task Force on Carbon Capture and Storage, The U. S. Department of Energy and the Environmental Protection Agency; 2010.
2. Haszeldine RS. Carbon capture and storage: how green can black be? Science 2009;325:1647–52.
3. Markewitz P, Kuckshinrichs W, Leitner W, Linssen J, Zapp P, Bongartz R, Schreibera A, Muller TE. Worldwide innovations in the development of carbon capture technologies and the utilization of CO2. Energy Environ Sci 2012;5:7281–305.
4. Thiruvenkatachari R, Su S, An H, Yu XX. Post combustion CO2 capture by carbon fibre monolithic adsorbents. Progress Energy Combust Sci 2009;35(5):438–55.
5. Pellerano M, Pré P, Kacem M, Delebarre A. CO2 capture by adsorption on activated carbons using pressure modulation. Energy Procedia 2009;1(1):647–53.
6. Zangeneh FT, Sahebdelfar S, Ravanchi MT. Conversion of carbon dioxide to valuable petrochemicals: an approach to clean development mechanism. J Natl Gas Chem 2011;20(3):219–31.
7. Li JR, Kuppler RJ, Zhou HC. Selective gas adsorption and separation in metal–organic frameworks. Chem Soc Rev 2009;38:1477–504.
8. Dantas TLP, Luna FMT, Silva Jr IJ, Torres AEB, Azevedo DCS, Rodrigues AE, Moreira RFPM. Carbon dioxide–nitrogen separation through pressure swing adsorption. Chem Eng J 2011;172(2–3):698–704.
9. Dechamps P. CO2 capture and storage projects, E. 22574, Editor; 2007.
10. Choi S, Drese JH, Jones CW. Adsorbent materials for carbon dioxide capture from large anthropogenic point sources. ChemSusChem 2009;2(9):796–854.
11. Li J-R, Ma Y, McCarthy MC, Sculley J, Yu J, Jeong H-K, Balbuena PB, Zhou H-C. Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks. Coord Chem Rev 2011;255(15–16):1791–823.
12. Anbia M, Hoseini V. Development of MWCNT@MIL-101 hybrid composite with enhanced adsorption capacity for carbon dioxide. Chem Eng J 2012;191(10):326–30.
13. Abid HR, Pham GH, Ang H-M, Tade MO, Wang S. Adsorption of CH4 and CO2 on Zr-metal organic frameworks. J Colloid Interface Sci 2012;366(1):120–4.

14. Ma LQ, Falkowski JM, Abney C, Lin WB. A series of isoreticular chiral metal-organic frameworks as a tunable platform for asymmetric catalysis. Nat Chem 2010;2:838–46.
15. Jiang HL, Xu Q. Porous metal-organic frameworks as platforms for functional applications. Chem Commun 2011;47:3351–70.
16. Dhakshinamoorthy A, Garcia H. Catalysis by metal nanoparticles embedded on metal–organic frameworks. Chem Soc Rev 2012;41:5262–84.
17. Yoon M, Srirambalaji R, Kim K. Homochiral metal-organic frameworks for asymmetric heterogeneous catalysis. Chem Rev 2012;112:1196–231.
18. Gu Z-Y, Park J, Raiff A, Wei ZW, Zhou HC. Metal-organic frameworks as biomimetic catalysts. ChemCatChem 2014;6:67–75.
19. Zhao M, Ou S, Wu C-D. Porous metal-organic frameworks for heterogeneous biomimetic catalysis. Acc Chem Res 2014;47:1199–207.
20. Wang C, Ying JY. Sol−Gel Synthesis and hydrothermal processing of Anatase and Rutile titania nanocrystals. Chem Mater 1999;11:3113–20.
21. Lagashetty A, Havanoor V, Basavaraja S, Balaji SD, Venkataraman A. Microwave-assisted route for synthesis of nanosized metal oxides. Sci Technol Adv Mater 2007;8:484–93.
22. Martinez Joaristi A, Juan-Alcan ˜iz J, Serra-Crespo P, Kapteijn F, Gascon J. Electrochemical synthesis of some archetypical Zn2+,Cu2+ and Al3+ metal-or- ganic frameworks. Cryst Growth Des 2012;12:3489–98.
23. Beldon PJ, Fabian L, Stein RS, Thirumurugan A, Cheetham AK, Friscic T. Rapid room-temperature synthesis of zeolitic imidazolate frameworks by using mechanochemistry. Angew Chem Int Ed 2010;49:9640–3.
24. Carson CG, Brown AJ, Sholl DS, Nair S. Sonochemical synthesis and characterization of submicrometer crystals of the metal-organic framework Cu (hfipbb) (H2hfipbb)0.5. Cryst Growth Des 2011;11:4505–10.
25. Dharmarathna S, King’ondu CK, Pedrick W, Pahalagedara L, Suib SL. Direct sonochemical synthesis of manganese octahedral molecular sieve (OMS-2) nanomaterials using cosolvent systems, their characterization, and catalytic applica- tions. Chem Mater 2012;24:705–12.

26. Jung DW, Yang DA, Kim J, Kim J, Ahn WS. Facile synthesis of MOF-177 by a sonochemical method using 1-methyl-2-pyrrolidinone as a solvent. Dalton Trans 2010;39:2883–7.
27. Kim J, Yang S, Choi SB, Sim J, Kim J, Ahn W. Control of catenation in CuTATB-n metal–organic frameworks by sonochemical synthesis and its effect on CO2 adsorption. J Mater Chem 2011;21:3070–6.
28. Mohanty P, Khine Linn NM, Landskron K. Ultrafast sonochemical synthesis of methane and ethane bridged periodic mesoporous organosilicas. Langmuir 2009;26:1147–51.
29. Son W-J, Kim J, Kim J, Ahn W-S. Sonochemical synthesis of MOF-5. Chem Commun 2008:6336–8.
30. Garzo ́n-Tovar L, Cano-Sarabia M, Carné-Sánchez A, Carbonell C, Imaz I, Maspoch D. A spray-drying continuous-flow method for simultaneous synthesis and shaping of microspherical high nuclearity MOF beads, React. Chem Eng 2016;1:533–9.
31. Garzo ́n-Tovar L, Rodrı ́guez-Hermida S, Imaz I, Maspoch D. Spray drying for making covalent chemistry: postsynthetic modification of metal–organic frameworks. J Am Chem Soc 2017;139:897–903.
32. Guillerm V, Garzon-Tover L, Yazdi A, Imaz I, Juanhuix J, Maspoch D. Continuous one- step synthesis of porous M-XF6-based metal–organic and hydrogen-bonded frameworks. Chem – Eur J 2017. http://dx.doi.org/10.1002/chem.201605507.
33. Polyzoidis A, Altenburg T, Schwarzer M, Loebbecke S, Kaskel S. Continuous microreactor synthesis of ZIF-8 with high space–time-yield and tunable particle size. Chem Eng J 2016;283:971–7.
34. Tai S, Zhang W, Zhang J, Luo G, Jia Y, Deng M, Ling Y. Facile preparation of UiO-66 nanoparticles with tunable sizes in a continuous flow microreactor and its application in drug delivery. Microporous Mesoporous Mater 2016;220:148–54.
35. McKinstry C, Cathcart RJ, Cussen EJ, Fletcher AJ, Patwardhan SV, Sefcik J. Scalable continuous solvothermal synthesis of metal organic framework (MOF-5) crystals. Chem Eng J 2016;285:718–25.

36. Taddei M, Steitz DA, van Bokhoven JA, Ranocchiari M. Continuous-flow microwave synthesis of metal–organic frameworks: a highly efficient method for large-scale production. Chem – Eur J 2016;22:3245–9.

37. Kitagawa S, Kitaura R, Noro S-I. Functional porous coordination polymers. Angew Chem Int Ed 2004;43(18):2334–75.

38. Rowsell J, Yaghi OM. Metal–organic frameworks: a new class of porous materials. Microporous Mesoporous Mater 2004;73:3–14.

39. Rosseinsky MJ. Recent developments in metal–organic framework chemistry: design, discovery, permanent porosity and flexibility. Microporous Mesoporous Mater 2004;73:15–30.

40. Furukawa H, Cordova KE, O'Keeffe, Yaghi OM. The chemistry and applications of Metal Organic Frameworks. J Sci 2013;341:974–83.

41. Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. Reticular synthesis and the design of new materials. Nature 2003;423(6941):705–14.

42. Deng H, Doonan CJ, Furukawa H, Ferreira RB, Towne J, Knobler CB, Wang B, Yaghi OM. Multiple functional groups of varying ratios in metal-organic frame- works. Science 2010;327:846–50.

43. Furukawa H, Ko N, Go YB, Aratani N, Choi SB, Choi E, Yazaydin AÖ, Snurr RQ, O'Keeffe M, Kim J, Yaghi OM. Ultrahigh porosity in metal-organic frameworks. Science 2010;329(5990):424–8.

44. Millward AR, Yaghi OM. Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. J Am Chem Soc 2005;127(51):17998–9.

45. Wang JQ, Kong DL, Chen JY, Cai F, He LN. Synthesis of cyclic carbonates from epoxides and carbon dioxide over silica-supported quaternary ammonium salts under supercritical conditions. J Mol Catal A Chem 2006;249:143–8.

46. Ma S, Zhou H-C. A metal-organic framework with entatic metal centers exhibiting high gas adsorption affinity. J Am Chem Soc 2006;128(36):11734–5.

47. Hou L, Shi WJ, Wang YY, Guo Y, Jin C, Shi QZ. A rod packing microporous metal-organic framework: unprecedented UKV topology, high sorption selectivity and affinity for CO2. Chem Commun 2011;47(19):5464–6.

48. Garibay SJ, Cohen SM. Isoreticular synthesis and modification of frameworks with the UiO-66 topology. Chem Commun 2010;46(41):7700–2.
49. Banerjee D, Kim SJ, Borkowski LA, Xu W, Parise JB. Solvothermal synthesis and structural characterization of ultralight metal coordination networks. Cryst Growth Des 2009;10(2):709–15.
50. Banerjee D, Kim SJ, Li W, Wu H, Li J, Borkowski LA, Philips BL, Parise JB. Synthesis and structural characterization of a 3-D lithium based metal-organic framework showing dynamic structural behavior. Cryst Growth Des 2010;10(6):2801–5.
51. Banerjee D, Finkelstein J, Smirnov A, Forster PM, Borkowski LA, Teat SJ, Parise JB. Synthesis and structural characterization of magnesium based coordination networks in different solvents. Cryst Growth Des 2011;11(6):2572–9.
52. Mallick A, Saha S, Pachfule P, Roy S, Banerjee R. Selective CO2 and H2 adsorption in a chiral magnesium-based metal organic framework (Mg-MOF) with open metal sites. J Mater Chem 2010;20(41):9073–80.
53. Volkringer C, Loiseau T, Marrot J, Ferey G, MOF-type A. magnesium benzene- 1,3,5-tribenzoate with two-fold interpenetrated ReO3 nets. CrystEngComm 2009;11(1):58–60.
54. Caskey SR, Wong-Foy AG, Matzger AJ. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. J Am Chem Soc 2008;130(33):10870–1.
55. McDonald TM, Lee WR, Mason JA, Wiers BM, Hong CS, Long JR. Capture of carbon dioxide from air and flue gas in the alkylamine-appended metal-organic framework mmen- Mg2(dobpdc). J Am Chem Soc 2012;134:7056–65.
56. Noro S, Mizutani J, Hijikata Y, Matsuda R, Sato H, Kitagawa S, Sugimoto K, Inubushi Y, Kubo K, Nakamura T. Porous coordination polymers with ubiquitous and biocompatible metals and a neutral bridging ligand. Nat Comm 2015;6:5851–9.
57. Côté AP, El-Kaderi HM, Furukawa H, Hunt JR, Yaghi OM. Reticular synthesis of microporous and mesoporous 2D covalent organic frameworks. J Am Chem Soc 2007;129(43):12914–5.

58. Banerjee D, Zhang Z, Plonka AM, Li J, Parise JB. A calcium coordination framework having permanent porosity and high CO2/N2 selectivity. Cryst Growth Des 2012;12:2162–5.

59. Miller SR, Alvarez E, Fradcourt L, Devic T, Wuttke S, Wheatley PS, Steunou N, Bonhomme C, Gervais C, Laurencin D, Morris RE, Vimont A, Daturi M, Horcajada P, Serre C. A rare example of a porous Ca-MOF for the controlled release of biologically active NO. Chem Commun 2013;49:7773–5.

60. Serre C, Stock N, Bein T, Férey G. Synthesis and characterization of a new three-dimensional lanthanide carboxyphosphonate: Ln4(H2O)7[O2C−C5H10N−CH2-PO3]4(H2O)5. Inorg Chem 2004;43(10):3159–63.

61. Mancino G, Ferguson AJ, Beeby A, Long NJ, Jones TS. Dramatic increases in the lifetime of the Er3+ ion in a molecular complex using a perfluorinated imidodiphosphinate sensitizing ligand. J Am Chem Soc 2004;127(2):524–5.

62. Guo X, Zhu G, Fang Q, Xue M, Tian G, Sun J, Li X, Qiu S. Synthesis, structure and luminescent properties of rare earth coordination polymers constructed from paddle-wheel building blocks. Inorg Chem 2005;44(11):3850–5.

63. Long D-L, Blake AJ, Champness NR, Wilson C, Schröder M. Lanthanum coordination networks based on unusual five-connected topologies. J Am Chem Soc 2001;123(14):3401–2.

64. Long D-L, Blake AJ, Champness NR, Schroder M. Lanthanide co-ordination frameworks of 4,4[prime or minute]bipyridine-N,N[prime or minute]-dioxide. Chem Commun 2000;15:1369–70.

65. Wang Z, Jin C-M, Shao T, Li Y-Z, Zhang K-L, Zhang H-T, You X-Z. Syntheses, structures, and luminescence properties of a new family of three-dimensional open-framework lanthanide coordination polymers. Inorg Chem Commun 2002;5(9):642–8.

66. Cui Y, Xu H, Yue Y, Guo Z, Yu J, Chen Z, Gao J, Yang Y, Qian G, Chen B. A luminescent mixed-lanthanide metal-organic framework thermometer. J Am Chem Soc 2012;134:3979–82.

67. Kong X, Scott E, Ding W, Mason JA, Long JR, Reimer JA. CO2 dynamics in a metal-organic framework with open metal sites. J Am Chem Soc 2012;134:14341–4.

68. Shultz AM, Farha OK, Hupp JT, Nguyen ST. A catalytically active, permanently microporous MOF with metalloporphyrin struts. J Am Chem Soc 2009;131:4204–5.

69. Stavila V, Bhakta RK, Alam TM, Majzoub EH, Allendorf MD. Reversible hydrogen storage by NaAlH4 confined within a titanium-functionalized MOF-74 (Mg) nanoreactor. ACS Nano 2012;6:9807–17.

70. Dey C, Kundu T, Banerjee R. Correlation between coordinated water content and proton conductivity in Ca-BTC-based metal–organic frameworks. Chem Commun 2012;48:266–8.

71. Kim J-Y, Norquist AJ, O'Hare D. [(Th2F5)(NC7H5O4)2(H2O)][NO3], an actinide-organic open-framework. J Am Chem Soc 2003;125:12688–9.

72. Chen S-C, Zhang Z-H, Huang K-L, Chen Q, He M-Y, Cui A-J, Li C, Liu Q, Du M. Solvent-controlled assembly of manganese(II) tetrachloroterephthalates with 1D chain, 2D Layer, and 3D coordination architectures. Cryst Growth Des 2008;8(9):3437–45.

73. Huang X-C, Li D, Chen X-M. Solvent-induced supramolecular isomerism in silver(I) 2- methylimidazolate. CrystEngComm 2006;8(4):351–5.

74. Pedireddi VR, Varughese S. Solvent-dependent coordination polymers: cobalt complexes of 3,5-Dinitrobenzoic acid and 3,5-dinitro-4-methylbenzoic acid with 4,4'-bipyrdine. Inorg Chem 2003;43(2):450–7.

75. Wang F-K, Yang S-Y, Huang R-B, Zheng L-S, Batten SR. Control of the topologies and packing modes of three 2D coordination polymers through variation of the solvent ratio of a binary solvent mixture. CrystEngComm 2008;10(9):1211–5.

76. Ma L-F, Wang L-Y, Lu D-H, Batten SR, Wang J-G. Structural variation from 1D to 3D: effects of temperature and pH values on the construction of Co(II)-H2tbip/bpp mixed ligands system. Cryst Growth Des 2009;9(4):1741–9.

77. Pan L, Frydel T, Sander MB, Huang X, Li J. The effect of pH on the dimensionality of coordination polymers. Inorg Chem 2001;40(6):1271–83.

78. Fang Q, Zhu G, Xue M, Sun J, Tian G, Wu G, Qiu S. Influence of organic bases on constructing 3D photoluminescent open metal-organic polymeric frameworks. Dalton Trans 2004;14:2202–7.

79. Chowdhury P, Bikkina C, Meister D, Dreisbach F, Gumma S. Comparison of adsorption isotherms on Cu-BTC metal organic frameworks synthesized from dif- ferent routes. Microporous Mesoporous Mater 2009;117(1–2):406–13.
80. Xiang S-C, Zhang Z, Zhao C-G, Hong K, Zhao X, Ding D-R, Xie M-H, Wu C-D, Das MC, Gill R, et al. Rationally tuned micropores within enantiopure metal-organic frameworks for highly selective separation of acetylene and ethylene. Nat Commun 2011;2:204–10.
81. Dawson R, Adams DJ, Cooper AI. Chemical tuning of CO2 sorption in robust nanoporous organic polymers. Chem Sci 2011;2:1173–7.
82. Das MC, Guo Q, He Y, Kim J, Zhao CG, Hong K, Xiang S, Zhang Z, Thomas KM, Krishna R, et al. Interplay of metalloligand and organic ligand to tune micropores within isostructural mixed-metal organic frameworks (M'MOFs) for their highly selective separation of chiral and achiral small Mol. J Am Chem Soc 2012;134:8703–10.
83. Böhme U, Barth B, Paula C, Kuhnt A, Schwieger W, Mundstock A, Caro J, Hartmann M. Ethene/ethane and propene/ propane separation via the olefin and paraffin selective metal-organic framework adsorbents CPO-27 and ZIF-8. Langmuir 2013;29:8592–600.
84. Mason JA, Oktawiec J, Taylor MK, Hudson MR, Rodriguez J, Bachman JE, Gonzalez MI, Cervellino A, Guagliardi A, Brown CM, et al. Methane storage in flexible metal-organic frameworks with intrinsic thermal management. Nature 2015;527:357–61.
85. Cui X, Chen K, Xing H, Yang Q, Krishna R, Bao Z, Wu H, Zhou W, Dong X, Han Y, et al. Pore Chemistry and size control in hybrid porous materials for acetylene capture from ethylene. Science 2016;353:141–4.
86. Caskey SR, Wong-Foy AG, Matzger AJ. Dramatic tuning of carbon dioxide uptake via metal substitution in a coordination polymer with cylindrical pores. J Am Chem Soc 2008;130:10870–1.
87. Mason JA, Sumida K, Herm ZR, Krishna R, Long JR. Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption. Energy Environ Sci 2011;4:3030–40.

88. Ren H-Y, Zhang X –M. Enhanced selective CO2 capture upon incorporation of dimethylformamide in the cobalt metal–organic framework [Co3(OH)2(btca)2]. Energy Fuels 2016;30(1):526–30.

89. Suh BL, Lee S, Kim J. Size-Matching Ligand Insertion in MOF-74 for Enhanced CO2 capture under humid conditions. J Phys Chem C 2017;121(44):24444–51.

90. Alhamami A, Doan H, Cheng C-H. A review on breathing behaviors of metal-organic- frameworks (MOFs) for gas adsorption. Materials 2014;7:3198–250.

91. Deng H, Grunder S, Cordova KE, Valente C, Furukawa H, Hmadeh M, Gandara F, Whalley AC, Liu Z, Asahina S, et al. Large-pore apertures in a series of metal- organic frameworks. Science 2012;336:1018–23.

92. Sumida K, Rogow DL, Mason JA, McDonald TM, Bloch ED, Herm ZR, Bae T-H, Long JR. Carbon dioxide capture in metal–organic frameworks. Chem Rev 2012;112:724–81.

93. Bauer S, Serre C, Devic T, Horcajada P, Marrot J, Férey G, Stock N. High- throughput assisted rationalization of the formation of metal organic frameworks in the iron(III) aminoterephthalate solvothermal system. Inorg Chem 2008;47:7568–76.

94. Szeto KC, Lillerud KP, Tilset M, Bjùrgen M, Prestipino C, Zecchina A, Lamberti C, Bordiga S. A Thermally stable Pt/Y-based metal-organic framework: exploring the accessibility of the metal centers with spectroscopic methods using H2O, CH3OH, and CH3CN as probes. J Phys Chem B 2006;110:21509–20.

95. Szeto KC, Prestipino C, Lamberti C, Zecchina A, Bordiga S, Bjùrgen M, Tilset M, Lillerud KP. Characterization of a new porous Pt-containing metal-organic framework containing potentially catalytically active sites: local electronic structure at the metal centers. Chem Mater 2007;19:211–20.

96. Szeto KC, Kongshaug KO, Jakobsen S, Tilset M, Lillerud KP. Design, synthesis and characterization of a Pt-Gd metal-organic framework containing potentially catalytically active sites. Dalton Trans 2008:2054–60.

97. Kandiah M, Nilsen MH, Usseglio S, Jakobsen S, Olsbye U, Tilset M, Larabi C, Quadrelli EA, Bonino F, Lillerud KP. Synthesis and stability of tagged UiO-66 Zr-MOFs. Chem Mater 2010;22:6632–40.

98. Silva CG, Corma A, Garcia H. Metal–organic frameworks as semiconductors. J Mater Chem 2010;20:3141–56.

99. Øéien S, Agostini G, Svelle S, Borfecchia E, Lomachenko KA, Mino L, Gallo E, Bordiga S, Olsbye U, Lillerud KP, Lamberti C. Probing reactive platinum sites in UiO-67 zirconium metal-organic frameworks. Chem Mater 2015;27:1042–56.

100. Butova VV, Soldatov MA, Guda AA, Lomachenko KA, Lamberti C. Metal-organic frameworks: structure, properties, methods of synthesis and characterization; Russian. Chem Rev 2016;85(3):280–307.

101. Lin X, Telepeni I, Blake AJ, Dailly A, Brown CM, Simmons JM, Zopp M, Walker GS, Thomas KM, Mays TJ, Hubberstey P, Champness NR, Schröder M. High capacity hydrogen adsorption in Cu(II) tetracarboxylate framework materials: the role of pore size, ligand functionalization, and exposed metal sites. J Am Chem Soc 2009;131:2159–71.

102. Wu H, Zhou W, Yildirim T. High-capacity methane storage in metal– organic frameworks M2(dhtp): the important role of open metal sites. J Am Chem Soc 2009;131:4995–5000.

103. Queen WL, Brown CM, Britt DK, Zajdel P, Hudson MR, Yaghi OM. Site-specificCO2 adsorption and zero thermal expansion in an anisotropic pore network. J Phys Chem 2011;C115:24915–9.

104. Bloch ED, Queen WL, Krishna R, Zadrozny JM, Brown CM, Long JR. Hydrocarbon separations in a metal-organic framework with open iron(II) coordination sites. Science 2012;335:1606–10.

105. Pang J, Jiang F, Wu M, Liu C, Su K, Lu W, Yuan D, Hong M. A porous metal-organic framework with ultrahigh acetylene uptake capacity under ambient conditions. Nat Commun 2015;6:7575. http://dx.doi.org/10.1038/ncomms8575.

106. Braun ME, Steffek CD, Kim J, Rasmussen PG, Yaghi OM. 1,4- Benzenedicarboxylate derivatives as links in the design of paddle-wheel units and metal–organic frameworks. Chem Commun 2001:2532–3.

107. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M, Yaghi OM. Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. Science 2002;295:469–72.

108. Surblé S, Serre C, Mellot-Draznieks C, Millange F, Férey G. A new isoreticular class of metal-organic-frameworks with the MIL-88 topology. Chem Commun 2006:284–6.

109. Fu YH, Sun DR, Chen YJ, Huang RK, Ding ZX, Fu XZ, Li ZH. An amine-functionalized titanium metal-organic framework photocatalyst with visible-light-in- duced activity for CO2 reduction. Angew Chem Int Ed 2012;51:3364–7.

110. Dan-Hardi M, Serre C, Frot T, Rozes L, Maurin G, Sanchez C, Ferey G. A new photoactive crystalline highly porous titanium(IV) dicarboxylate. J Am Chem Soc 2009;131:10857–9.

111. Wang Z, Tanabe KK, Cohen SM. Accessing postsynthetic modification in a series of metal-organic frameworks and the influence of framework topology on reactivity. Inorg Chem 2009;48(1):296–306.

112. Morel FL, Xu X, Ranocchiari M, van Bokhoven JA. Functional metal-organic frameworks: synthesis and reactivity. Chem Organo 2015:200–32.

113. Song Y-F, Cronin L. Postsynthetic covalent modification of metal-organic framework (MOF) materials. Angew Chem Int Ed 2008;47:4635–7.

114. Wang Z, Cohen SM. Tandem modification of metal–organic frameworks by a postsynthetic approach. Angew Chem 2008;120:4777–80.

115. Costa JS, Gamez P, Black CA, Roubeau O, Teat SJ, Reedijk J. Chemical modification of a bridging ligand inside a metal-organic framework while maintaining the 3D structure. Eur J Inorg Chem 2008:1551–4.

116. Goto Y, Sato H, Shinkai S, Sada K. “Clickable” metal−organic framework. J Am Chem Soc 2008;130:14354–5.

117. Burrows AD, Frost CG, Mahon MF, Richardson C. Post-synthetic modification of tagged metal-organic frameworks. Angew Chem Int Ed 2008;47:8482–6.

118. Islamoglu T, Goswami S, Li Z, Howarth AJ, Farha OK, Hupp JT. Postsynthetic tuning of metal−organic frameworks for targeted applications. Acc Chem Res 2017;50(4):805–13

119. M. H. Mohamed, S. K. Elsaidi, L. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space and M. J. Zaworotko, J. Am. Chem. Soc., 2012, 134, 19556.

120. Shekhah O, Belmabkhout Y, Adil K, Bhatt PM, Cairns AJ, Eddaoudi M. A facile solvent-free synthesis route for the assembly of a highly CO2 selective and H2S tolerant NiSIFSIX metal–organic framework. Chem Commun 2015;51:13595–8.
121. Elsaidi SK, Mohamed MH, Schaef HT, Kumar A, Lusi M, Pham T, Forrest KA, Space B, Xu W, Halder GJ, Liu J, Zaworotko MJ, Thallapally PK. Hydrophobic pillared square grids for selective removal of CO2 from simulated flue gas. Chem Commun 2015;51:15530–3.
122. S. Mahdian, M. Naimi-Jamal and L. Panahi, "Activity of M2(BDC)2(DABCO) (M= Co, Ni, Cu and Zn) Metal-Organic Frameworks Prepared via Ball-Milling Solvent-Free Method in Acylation of Alcohols, Amines and Aldehydes", *ChemistrySelect*, vol. 3, no. 40, pp. 11223-11229, 2018.
123. C. Chen, M. Jia, G. Wang, X. Li and S. Li, "High and selective CO2 uptake in a nitrogen-rich pillar-layered metal organic framework", RSC Advances, vol. 5, no. 127, pp. 104932-104935, 2015. Available: 10.1039/c5ra22144g [Accessed 18 August 2020].
124. C. Chen, M. Jia, G. Wang, X. Li and S. Li, "High and selective CO2 uptake in a nitrogen-rich pillar-layered metal organic framework", RSC Advances, vol. 5, no. 127, pp. 104932-104935, 2015.
125. X. Yan, S. Li, Y. Jiang, M. Hu and Q. Zhai, "Synthesis, crystal structures and gas adsorption of two porous pillar-layered MOFs decorated with different functional groups", Inorganic Chemistry Communications, vol. 62, pp. 107-110, 2015.
126. Z. Chen et al., "Three-Dimensional Pillar-Layered Copper(II) Metal−Organic Framework with Immobilized Functional OH Groups on Pore Surfaces for Highly Selective CO2/CH4and C2H2/CH4Gas Sorption at Room Temperature", Inorganic Chemistry, vol. 50, no. 8, pp. 3442-3446, 2011. Available: 10.1021/ic102347b [Accessed 18 August 2020].

Chapter 3: Experiment and Methodology

3.1. Materials

Zinc Nitrate Hexahydrate $Zn(NO_3)_2.6H_2O$ and Cobaltous Nitrate Hexahydrate $Co(NO_3)_2.6H_2O$ were used as metal precursor, Terephthalic acid also known as Benzene-dicarboxylic acid, $C_6H_4(CO_2H)_2$, was used as the organic linker. DMF was used as the main solvent in this process. DABCO, $N_2(C_2H_4)_3$, was used as the pillar as all these MOFs were Pillared Layer MOFs. All these materials were obtained from Sigma-Aldrich. N-N, dimethylformamide or DMF was used as the main solvent for synthesis which was obtained from Merck

3.2. Synthesis Methods

4 main samples were produced. 2 of these samples were Pillared-layer and contained DABCO while the other 2 did not contain DABCO and were thus not Pillared-layer. The synthesis detail of the samples both with and without DABCO are given below.

3.2.1. Synthesis of Pillared Layer Metal Organic Frameworks.

The MOFs were produced by solvothermal method. For the Zinc based MOF, 1 mole of $Zn(NO_3)_2.6H_2O$ was mixed with 1 mole of Terephthalic acid in a beaker containing 40ml of DMF. The solution was mixed using a hot plate stirrer till a clear transparent solution was achieved. 0.5 moles of DABCO was then added into the solution. The stirring was continued till the solution again became clear, which was evidence that all 3 of the components had dissolved completely. The solution was poured into a Teflon lined steel autoclave and heated at 120°C for 48 hours in a heating oven. The solution was allowed to cool down and then the produced crystals were filtered and then washed 3 times using DMF after which the obtained crystals were put in a vacuum oven at 40 °C for 48 hours. The same process was repeated for the Cobalt based MOF with one change i.e. tr was used as the organic linker instead of $Zn(NO_3)_2.6H_2O$.

3.2.2. Synthesis of Metal Organic Frameworks without DABCO.

The same process with the same concentrations was repeated for these MOF. The only change was that no DABCO was added in the solution.

3.3. Characterization

3.3.1. X-Ray Diffraction

XRD provides an analysis of the crystallinity and phase purity of a material. XRD allows researchers to study material properties at atomic level. A detailed study provides atomic numbers, bond lengths, pore volume and other important details

3.3.1.1. Instrumentation

Figure 6 shows a schematic of X-ray Diffractometer (XRD) which have four main components:

- X-ray Source
- Monochromator
- Goniometer
- Detector

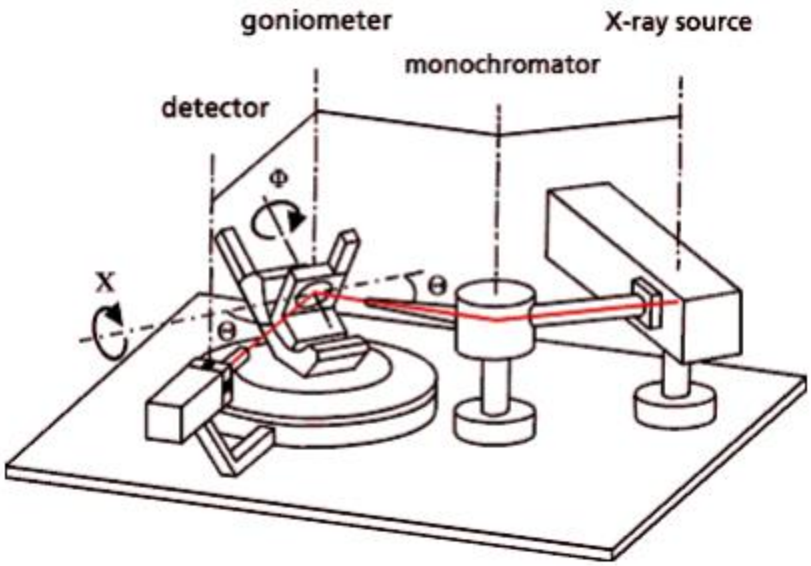


Figure 6: Instrumentation Diagram of XRD Equipment

3.3.1.2. Working Principle

In X Ray Diffraction the working principle is based on the interference of the monochromatic X-rays. X-Rays are incident on the material under study and each material has its own diffraction pattern that represents the crystal structure. On contact with the material, some of the X rays are refracted, some are transmitted, some of it is diffracted while the remaining portion is absorbed in the sample material. These percentages as well as the diffraction of light are specific for every single material based upon their chemical structure. as After XRD the distance between two atoms can be measure using Bragg's Law which is defined as:

$$n\lambda = 2d \sin\theta \tag{1}$$

n = order of diffracted beam

λ = wavelength of incident x-ray beam

d = distance between adjacent planes of atoms

Since every material has its own XRD pattern, the XRD patterns of all known materials are collected and stored in databases which allows materials to be easily identified by comparing the result with the patterns available in the literature/databases.

3.3.1.3. Applications

XRD is used to check the purity of the samples, to identify and compare unknown crystalline materials and to determine atomic level dimensions inside a material.

3.3.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy

SEM or Scanning electron microscopy is a process that produces images used to analyze the morphology and structure of a material. This process helps identify the surface and cross-sectional morphology of different materials and MOFs. Sputter coating is carried out to coat gold on the surface of the materials before it can be analyzed.

3.3.2.1. Components of SEM

SEM consists of following components (Figure 7):

- Electron column
- Scanning system
- Detector
- Display
- Vacuum system
- Electronic control

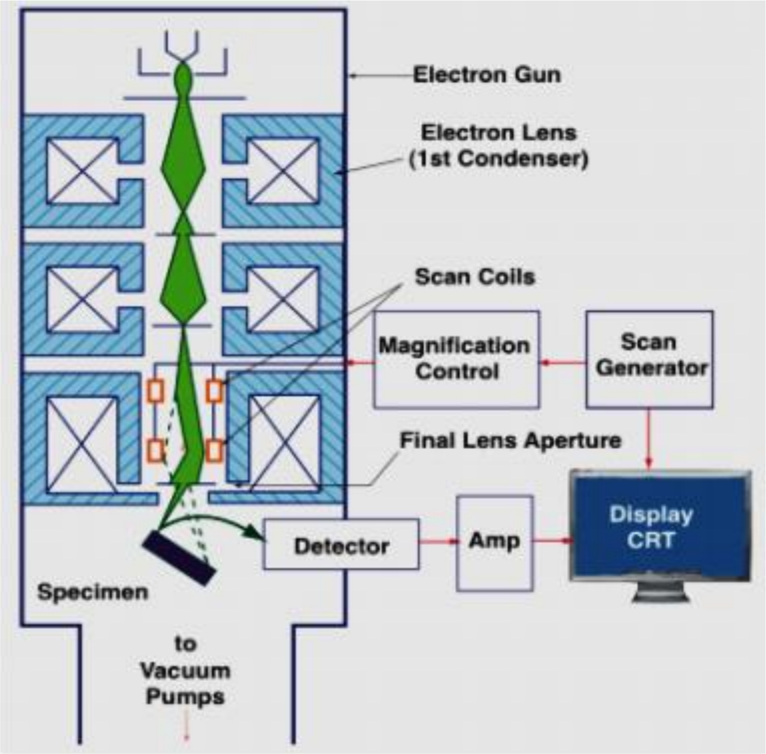


Figure 7: Diagram of SEM Equipment with Labelled components

3.3.2.2. Working Principle

High energy electrons which dissipate different kinds of signals are decelerated and focused on the surface of the target material. The secondary electrons explicate the topology and morphology of the material. The interactions between electrons does not damage the sample material therefore SEM is a non-destructive technique.

3.3.2.3. Magnification in SEM

Optical transformation or magnification is not used in SEM. The magnification and clarity of a sample in SEM is modified by varying the length of the scan (Lspec) This makes calibration of the SEM equipment very important. 27 length is the standard scan length of the monitor (Lmon) and by that the linear magnification (M) of the SEM can be obtained by:

$$M = Lmon/Lspec \qquad (2)$$

3.3.2.4. Image Formation

The image formed in the SEM is electronic, and not true as each pixel of the image represents the intensity of the signal at that point which combines to form a full image (Figure 8).

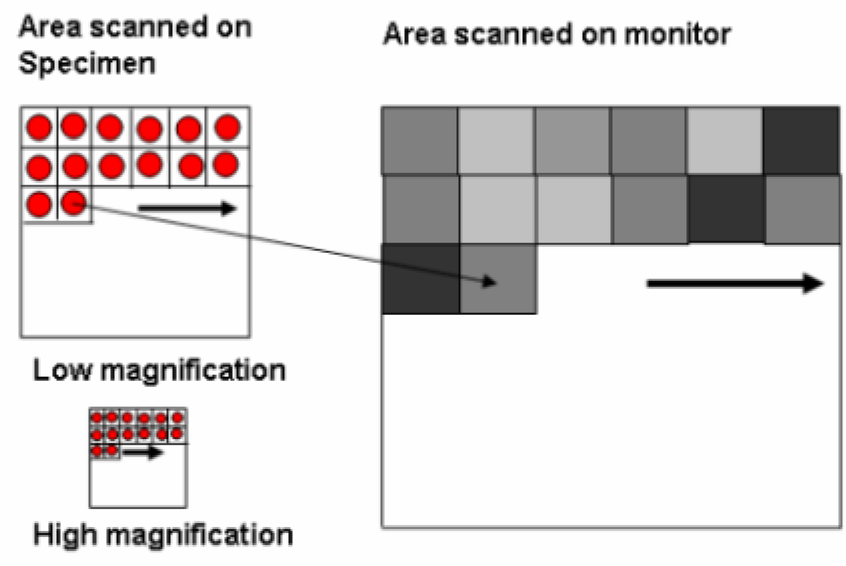
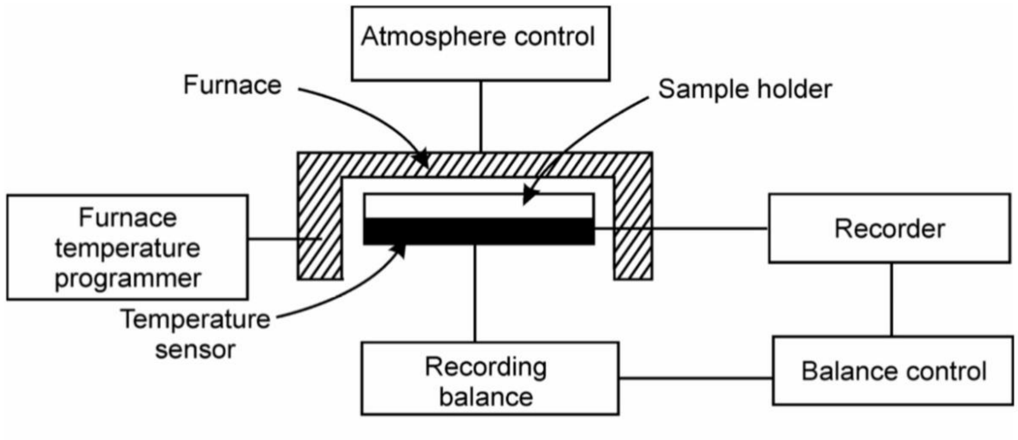


Figure 8: Diagram explaining the image formation process in SEM

Energy dispersive Spectroscopy or EDS is used to quantify and identify the composition of the target sample. The principle is similar to that of XRD as the target sample is bombarded with an electron beam which results in atoms from the sample emitting x rays of specific wavelength. The energy dispersive detector in the EDS equipment analyzes the rays and uses it to identify the elements and their weight percentage in the sample.

3.3.3. TGA

To understand and analyze the thermal stability of the material, Thermogravimetric analysis is used. The basic principle of TGA is that it measures the rate of change in mass of the sample as the temperature is increased within a certain pre-selected limit, in a controlled environment. The weight is initially measured and then as the temperature increases and weight loss starts to happen, the weight is constantly logged in the machine. The final output from TGA is a graph in which the X axis represents the temperature in ascending order and the y axis represents the change in mass or mass lost.



3.3.4. FTIR

Spectroscopy is the Interaction of radiation with matter. The spectrum provides information about the vibrations of different functional groups present in a molecule. It is a powerful tool used for the identification of the types of chemical bonds by producing an infrared absorption spectrum.

3.3.4.1. Infrared Region

Infrared region lies between the visible and microwave regions of the electromagnetic spectrum. IR waves have longer wavelengths than visible and shorter than microwaves. The frequency of IR waves is lower than visible and higher than microwaves. IR region is further divided into three spectra:

- The spectrum closer to the visible light- near infrared
- The spectrum closer to the microwave region- far infrared
- The region between near infrared and far infrared- mid infrared

3.3.4.2. Wavenumber

Usually, IR spectrum refers to the radiations lying in the mid IR region and is represented by wavenumber ῡ, cm -1.

3.3.4.3. FTIR Instrumentation

The principle components of the FTIR system are:

- IR source
- Interferometer

- Sample
- Detector
- Signal processor (computer)

3.3.4.4. Applications

- Detection of impurities during the reaction
- Qualitative analysis of a sample
- Chemical Bonding and functional groups
- Compositional analysis of organic, Inorganic and polymers

3.3.5. Sorption Analyzer

Once the characterization and identification process are complete, the next part is to test out the application of the materials. For CO_2 capture, MOFs are tested based on their physical adsorption capacity for CO2 under selected pressure and temperature conditions. Different types of raw materials used for the synthesis of MOF produced different kinds of pore sizes and surface area resulting in different kind of adsorption performance. For this testing, High Pressure iSorp HP volumetric sorption analyzer from Quantachrome was used. The sample was first outgassed at a selected temperature and pressure and the degassed sample is then allowed to adsorb CO2 from a stream of CO2 gas as the pressure of the gas is slowly increased. The temperature and mass of the sample can be varied too based on the type of analysis. The equipment provides analysis in terms of an adsorption isotherm (volume adsorbed as a function of relative pressure) which can be converted into required units and used to calculate the surface area as well [1]. The isotherm is produced by recording the amount of carbon dioxide adsorbed on every pressure point. The desorption isotherm is also produced.

3.4. Summary

This chapter discusses the methodology used in this research to achieve the objectives of the study. At the start of the chapter, the materials and the methods used for the synthesis of the selected MOFs are explained in detail. The second part of the chapter includes detailed explanation of all the methods used for characterization of the produced samples including SEM, EDS, XRD, TGA and FTIR. The availability of the equipment used in laboratories is also mentioned and the chapter ends with a detailed explanation of the equipment and method used for testing the sorption capacity of the synthesized MOF.

3.5. References

1. NPTEL, “Surface area, pore size, pore volume determination.” [Online]. Available: https://nptel.ac.in/courses/103103026/module2/lec10/2.html. [Accessed: 05-Jul-2019].

Chapter 4: Results and Discussion

4.1. Characterization

4.1.1. X-Ray Diffraction

D8 Advanced X-Ray diffraction system by Byrker was used to perform the XRD of the samples. The XRD pattern of both our Pillared layer MOFs are shown in Figure 9. The XRD pattern of both our Zinc and Cobalt based MOFs match the XRD pattern of the same Ni MOF present in the literature [1]. This tells us that the synthesized MOF was synthesized properly and also tells us that both our MOFs are similar in structure. These MOFs have a three-dimensional structure thanks to the DABCO which connects the two-dimensional lattice of the original metal-linker combination with each other by taking up the axial sites present in the metal atoms. For synthesis, DMF is used as the solvent and after the synthesis the crystals need to be heated at a certain temperature which causes the guest particles to leave the structure leaving large 3D spaces that enhances gas adsorption and provides a high surface area. Figure 10 shows the proposed structure of the respective MOFs.

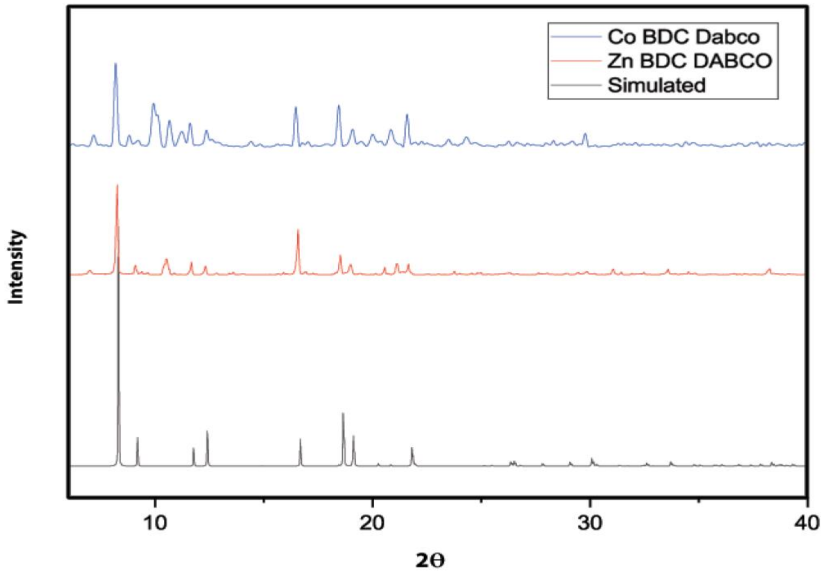


Figure 9: XRD Pattern of the synthesized MOF and the Simulated pattern from the Literature [1]

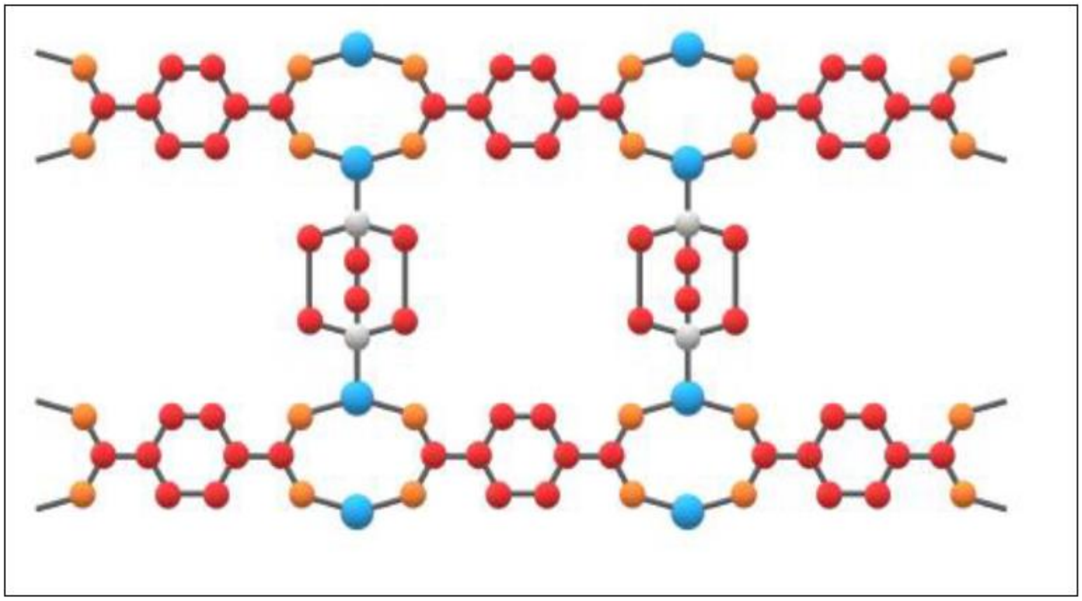


Figure 10: Structure Diagram of the Synthesized MOF showing C (red), O (orange), N (grey) and Metal (blue) atoms

4.1.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy

For the purpose of SEM, The TESCAN SEM VEGA3 was used. To avoid charging of the material, gold sputtering process was conducted to coat gold on the material after drying. As shown in the Figure 11, the SEM images show that this material has a morphology built up by a combination of large number of three-dimensional structures. This could be further zoomed to 1um which then shows that these crystals have a detailed sheet like structure. The tetragonal structure of the original MOF is responsible for the sheet like structure [2]. The EDS is shown in the Figure 12. For the MOF the C, O and Metal percentages are in the expected range, the gold coating mechanism results in the EDS showing some gold traces in the results.

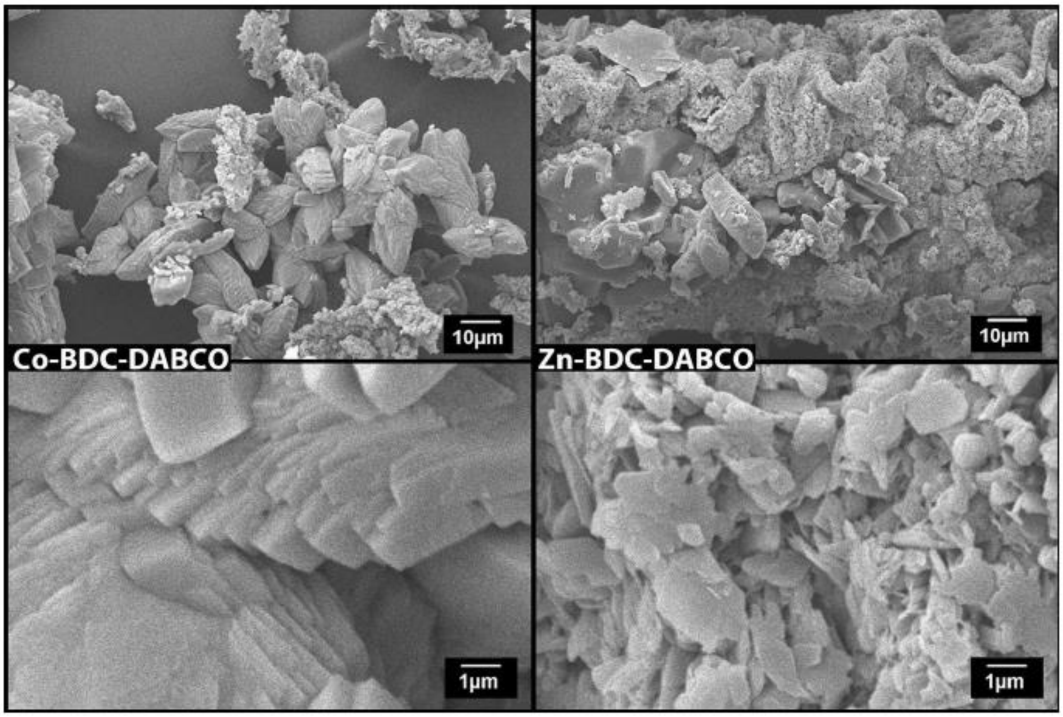


Figure 11: SEM Images of the two MOFs

Element	Weight%	Atomic%
Carbon	50.27	61.19
Oxygen	39.77	36.34
Cobalt	9.96	2.47
Totals	100.00	

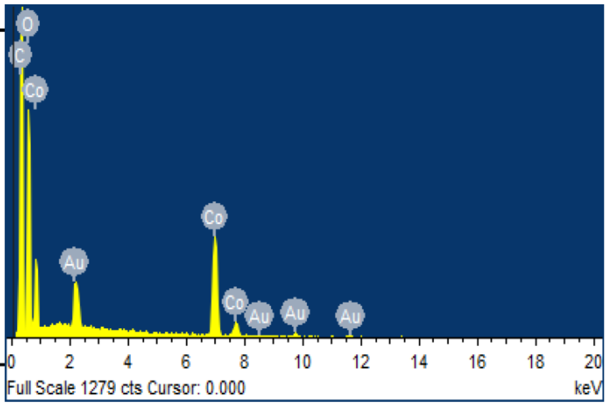


Figure 12: EDS of Cobalt based MOF

4.1.3. Thermogravimetric Analysis

DTG-60H Thermo Gravimetric Analyzer (TGA) was used for the TGA of the sample materials Figure 13 shows the TGA of both the MOFs. Both these MOFs show two major weight loss stages in the curves. Moisture content and DMF removal as well as the removal of other volatile compounds results in the first major weight loss stage which comes at around and below the 250°C temperature mark on the graph. The second major stage of decomposition is different in both the MOFs and it represents the final decomposition of the MOF. The Cobalt based MOF shows a higher thermal stability and decomposes at 380°C which is about 80°C more than the Zinc MOF and this could be because of the much higher surface to volume ratio present in that MOF compared to the Cobalt MOF, and as more heat is needed to decompose this material and as can be seen from the figure it takes longer to decompose the Zinc MOF as compared to the Cobalt MOF which decomposes instantly at soon as it reaches a certain temperature. These three steps are divided into three different sections. The first one is called the DMF degradation step because in this step the guest molecules of the solvent (DMF in our case) are removed from the material. The second step is called the linker degradation step as in this step the linker starts to deteriorate until a certain point where it stops to deteriorate anymore. This point is where Metal oxide starts to form.

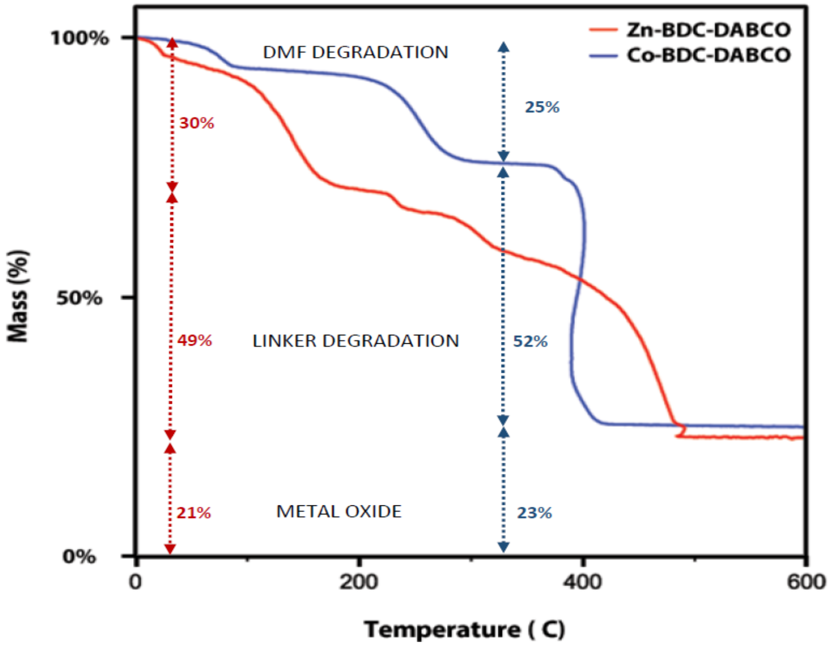


Figure 13: TGA Analysis of the two MOFs

4.1.4. Fourier-transform infrared spectroscopy

Agilent cary 630 was used to carry out the FTIR analysis of the materials the results that show the functional groups present in the materials in the 650-3750 cm^{-1} range for wavelength are shown in Figure 14. The first band in the 700-750 cm^{-1} region represents the Metal-Oxygen bond. The Carbon-Oxygen single bonds were represented by the second and third band in the 1050cm^{-1} and the 1360 cm^{-1} wavelength range respectively and the 1550-1600 cm^{-1} range represents the Carbon-Oxygen double bonds present in the framework. These double bonds appear because of the benzene structure of the Organic Linker from the BDC. The extra peaks represent the stretching of the COOH groups and the absence of hydrogen peaks shows that a framework has been produced. The Carbon Hydrogen bond causes the FTIR to show a final peak in the 2900-3400 cm^{-1} range. The metallic structure introduced in the structure causes the stretching of the C-H bond.

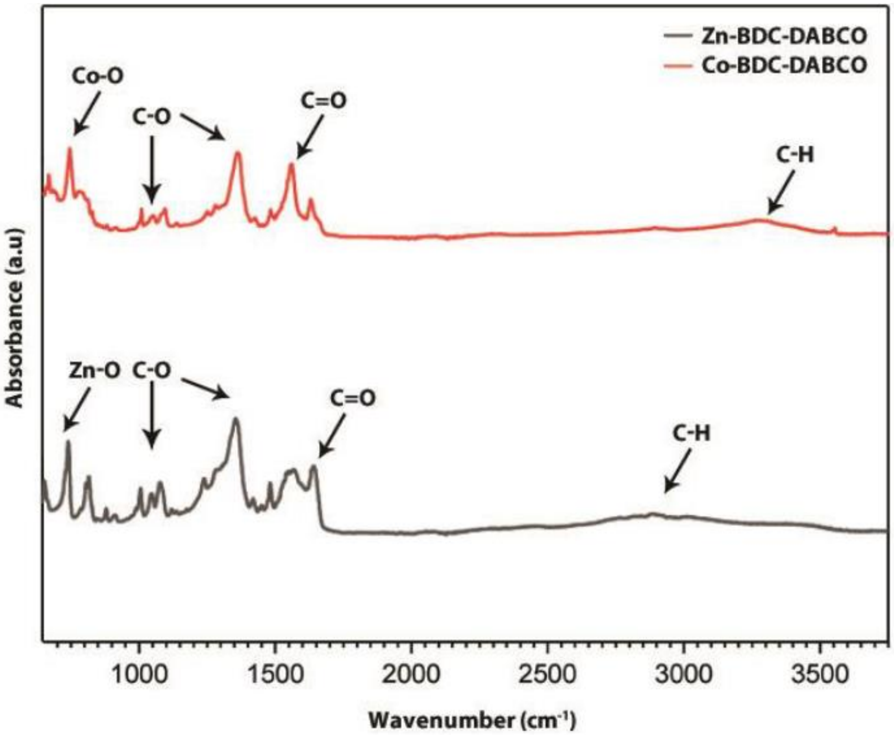


Figure 14: FTIR Analysis graph of the two MOFs

4.1.5. Surface area testing (BET)

The BET was done for both the Zinc and Cobalt based pillared MOFs. The pore volume curves are shown in the figure 15. The surface area was calculated to be 511.7 m^2/g for the Zinc based MOF and 98.2 m^2/g for the Cobalt based MOF.

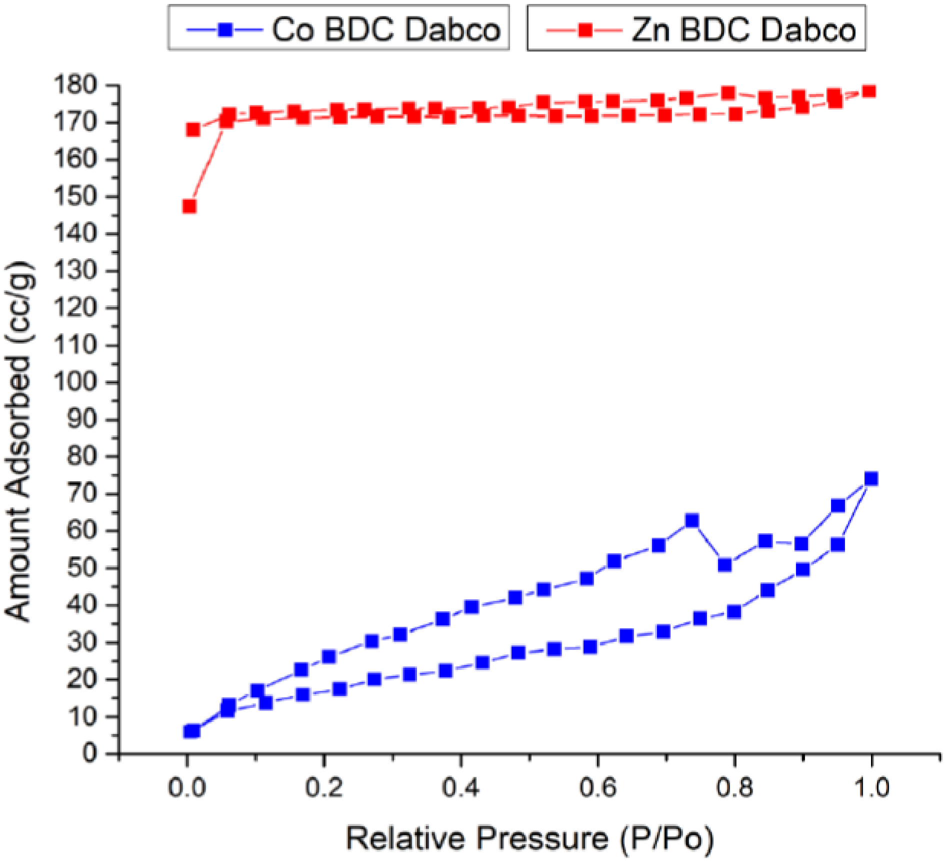


Figure 15: Pore volume curve of the two MOFs

4.2. Testing

4.2.1. Sorption Analysis

High Pressure Gas Sorption Analyzer (iSorp HP1) was used to test the adsorption capacity of the MOFs. In this part, both the MOFs with DABCO and without DABCO were tested, specifically to study the effect of addition of the pillar in the MOFs. All readings were taken at 25°C between pressures of 0-25 bar the adsorption isotherms are shown in Figure 16. The Cobalt based pillared MOF showed a CO_2 adsorption capacity of 4.4 mol/kg and the Zinc based pillared MOF showed an adsorption capacity of 6.3 mol/kg of CO_2 and the results of both these were significantly greater than their non-Dabco counterparts as can be seen in the figure which could be a result of the increase in surface area due to the addition of the pillar which turns the MOF into a 3D structure. The results are much higher than that of the Zeolite 13X which shows a reported value of 2.2 mol/kg at room temperature [3].

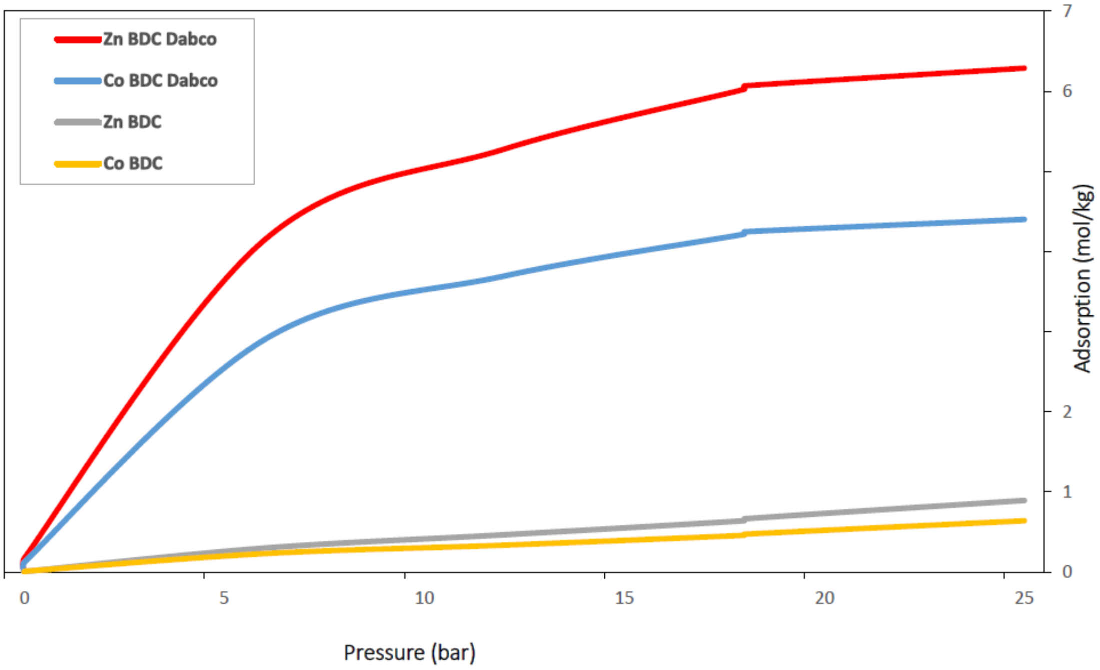


Figure 16: Sorption Analysis curves of all four synthesized MOF

4.3. Comparison of Results

Table 2 contains a list of MOFs similar to the synthesized MOF of this research. The adsorption capacities of these MOFs at 1 atm and 298 K are also mentioned in the table for comparison.

Table 2: Comparison of results with Literature

S. No	Name of MOF	Surface Area (m^2/g)	Adsorption Capacity (mol/kg)	Reference
1	Zn BDC Dabco	511.7	6.3	This research
	Co BDC Dabco	98.2	4.4	
2	M177-1000	1978	3.3	4

3	MOOFOUR-1-Ni	456	2.45	5
4	SNU-M11	505	2.09	6
5	$[Zn_4(TRZ)_4(TTBDC)_2]_n$	255.5	1.39	7
6	NDC	365.1	1.5	8

4.4. Summary

This chapter includes detailed discussion on the results obtained from the synthesis of the selected MOF and its characterization and testing. The crystals formed showed a 3D structure which confirmed the synthesis of a pillared MOF. The XRD further confirmed it as the results were very similar to the XRD present in the literature of similar MOFs. The TGA showed high thermal stability and the FTIR confirmed the presence of the required functional groups. The addition of the pillar material resulted in enhanced surface area of the MOF which in turn resulted in increased Carbon dioxide capture capacity. The results also confirmed that the performance MOFs with the pillar material were significantly better than that without the pillar material.

4.5. References

1. K. Seki and W. Mori. The Journal of Physical Chemistry B 2002 106 (6), 1380-1385D.N. Dybtsev, H. Chun, K. Kim, Angew Chem. Int. Ed. 43 (2004) 5033.
2. C. Chen, M. Jia, G. Wang, X. Li and S. Li, "High and selective CO2 uptake in a nitrogen-rich pillar-layered metal organic framework", RSC Advances, vol. 5, no. 127, pp. 104932-104935, 2015.
3. Zhai QG, Bai N, Li S, Bu X, Feng P. Design of Pore Size and Functionality in Pillar-Layered Zn-Triazolate-Dicarboxylate Frameworks and Their High CO2/CH4 and C2 Hydrocarbons/CH4 Selectivity. Inorg Chem. 2015;54(20):9862-9868.
4. H. Kim, T. Yoon, S. Kim, J. An, Y. Bae and C. Lee, "Beyond pristine MOFs: carbon dioxide capture by metal–organic frameworks (MOFs)-derived porous carbon materials", RSC Advances, vol. 7, no. 3, pp. 1266-1270, 2017. Available: 10.1039/c6ra26824b [Accessed 20 September 2020].
5. M. H. Mohamed, S. K. Elsaidi, L. Wojtas, T. Pham, K. A. Forrest, B. Tudor, B. Space and M. J. Zaworotko, J. Am. Chem. Soc., 2012, 134, 19556.
6. H. S. Choi and M. P. Suh, Angew. (2009). Highly Selective CO2 Capture in Flexible 3D Coordination Polymer Networks. Angewandte Chemie International Edition. 48. 6865 - 6869.
7. X. Yan, S. Li, Y. Jiang, M. Hu and Q. Zhai, "Synthesis, crystal structures and gas adsorption of two porous pillar-layered MOFs decorated with different functional groups", Inorganic Chemistry Communications, vol. 62, pp. 107-110, 2015.
8. Zhai QG, Bai N, Li S, Bu X, Feng P. Design of Pore Size and Functionality in Pillar-Layered Zn-Triazolate-Dicarboxylate Frameworks and Their High CO2/CH4 and C2 Hydrocarbons/CH4 Selectivity. Inorg Chem. 2015;54(20):9862-9868.

Chapter 5: Conclusion and Recommendations

This detailed research and study of the selected MOFs produced some really good results and a number of valuable findings in terms of both synthesis and application.

4.6. Conclusions

1. The Zinc and Cobalt pillared Layer MOFs provide high adsorption for CO_2. The results show that the Zinc MOF shows a CO_2 adsorption capacity of 6.3 mol/kg while the Cobalt MOF shows a CO_2 adsorption capacity of 4.4 mol/kg. Both these capacities are good and are much better compared to some of the other Pillared-Layer MOFs like NDC [171] and SNU-M11 [172] which show an adsorption capacity of 1.5 and 2.09 mol/kg respectively.
2. The MOFs show a high surface area which is because of the addition of the pillared-linker (DABCO). The enhanced surface area is the reason why the MOFs show good adsorption capacities as well. The pillar attaches itself to the two-dimensional structure of the Metal-BDC MOF and turns it into a three-dimensional system resulting in more space and pores to accommodate additional gas molecules. This is also proved by the fact that the non-pillared layer MOFs showed considerably lower surface area and adsorption capacities. Both the non-pillared layer MOFs showed an adsorption capacity of less than 1mol/kg which is very low.

4.7. Challenges

1. Synthesis of these MOFs using co-precipitation failed a number of times. The process of synthesis and all the temperatures were kept the same but the process still did not produce reasonable products.
2. Synthesis of the Pillared Layer MOFs was tougher than synthesis of normal MOFs. It took a lot of practice and hard work to get it right for the first time. Despite following the process mentioned in various different literatures.
3. Use of the Hydrothermal reactor failed. The reason for this is unknown but the MOFs produced, by following the same process as done for the synthesis of our final product, using Hydrothermal Reactor instead of a Teflon-lined steel autoclave produced poor

results and the XRD and FTIR analysis of those MOFs showed that the correct product was not produced

4.8. Future recommendations

The current study focused on the synthesis and effect of Pillared-Layer Metal Organic Frameworks. Other properties can be varied in the future to help understand the world of pillared MOFs better. These experiments can be:

1. The use of different solvents for the synthesis of the MOFs and a comparative study of their adsorption capacities.
2. Studying the effect of change of metal in Pillared-layer MOFs by using 4 to 5 or more different metals for the synthesis and comparing the adsorption and surface area results.

Furthermore, a financial study could be conducted to analyze similar MOFs available in the literature and to compare the price to performance ratio of all these MOFs.

4.9. References

9. Zhai QG, Bai N, Li S, Bu X, Feng P. Design of Pore Size and Functionality in Pillar-Layered Zn-Triazolate-Dicarboxylate Frameworks and Their High CO2/CH4 and C2 Hydrocarbons/CH4 Selectivity. Inorg Chem. 2015;54(20):9862-9868.
10. X. Yan, S. Li, Y. Jiang, M. Hu and Q. Zhai, "Synthesis, crystal structures and gas adsorption of two porous pillar-layered MOFs decorated with different functional groups", Inorganic Chemistry Communications, vol. 62, pp. 107-110, 2015.