

**Metal Organic Framework (MOF) Materials: Synthesis and Characterization
Study**

by

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Dissertation submitted in the partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirements for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Chew Thiam Leng)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

May 2015

CERTIFICATION OF ORIGINALITY

This to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SYARIFAH NURDIATUL RAHIDAH BINTI WAN MALIKI

ABSTRACT

Metal Organic Frameworks (MOFs) are microporous materials with crystalline structure composed of organic and inorganic species. MOF materials have gained popularity among researchers due to their potential for gas capture, separation, catalysis and other applications. $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ is one of the MOFs with characteristic such as high hydrophobicity and large channels properties. The current project emphasizes on synthesis and characterization of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$. Thus, the effect of synthesis conditions on the formation of the MOFs was studied. The MOFs were synthesized at different temperature (ranged from 120°C to 150°C) and synthesis time (ranged from 24 hr to 48 hr). The synthesized MOFs were characterized using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, Thermogravimetric Analysis (TGA) and tested for its gas adsorption capacity using Brunaur-Emmett-Teller (BET). All SEM images show polydispersity in size and shape of the MOF synthesized. X-ray Diffraction (XRD) pattern obtained shows similarity to the XRD pattern of MOF-2 as reported by Chen et al. (2009). Thus, the synthesized MOF is indeed MOF-2 with some unknown phase. The change of the crystalline structure of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ to MOF-2 was due to the exposure to the air longer than 36 hours. The FTIR spectrum of the synthesized MOF shows the presence of aromatics C-H bond, alkoxy C-O bond, aromatic ring C=C bond, carboxylic acids O-H bond, amine N-H bond and alcohols or phenols O-H bond. The TGA plots diagrams shows three steps of weight losses where the first step was the loss of water molecules, second step was the loss of N,N-Dimethylformamide (DMF) molecules and the last step was the decomposition of the MOF-2. The total weight loss for all synthesized MOF at 120°C and 150°C samples were in the range of 73 wt% to 84 wt%. The BET surface area and total pore volume for CO_2 and N_2 adsorption are 2.19 m^2/g and 14.8 m^2/g and 1.1633 cm^3/g and 0.0199 cm^3/g respectively.

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LIST OF ABBREVIATIONS

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
4,4-BPE	4,4-trans-bis(4-pyridyl)ethylene
BDC	1,4-Benzenedicarboxylic Acid
BDPB	1,4-bis[(3,5-dimethyl)pyrazol-4-yl]benzene
BET	Brunaur-Emmett-Teller
BIm	Benzimidazolate
bipy	4,4'-bipyridine
BPE	trans-1,2-bis(4-pyridyl)ethylene
BTB	1,3,5-Benzenetribenzoate
BTC	1,3,5-Benzenetricarboxylate
BTEC	1,2,4,5-Benzenetetracarboxylate
CHA	Zeolite Chabazite
CPT	4-(4-carboxyphenyl)-1,2,4-triazole
DABCO	1,4-diazabicyclo[2.2.2]octane
DEF	N,N-Diethylformamide
DMF	N,N-Dimethylformamide
EIA	Energy Information Administration
FTIR	Fourier Transform Infrared
HKUST	Hong Kong University of Science and Technology
IRMOF	Isorecticular Metal Organic Framework
Ln	Lanthanide
MIL	Material of Institute Lavoisier
MOF	Metal Organic Framework
NDC	2,6-Naphthalenedicarboxylate
NMP	N-methyl-2-pyrrolidone
PZC	Pyrazine-2-carboxylate
RHO	Zeolite rho
SBU	Secondary Building Unit
SEM	Scanning Electron Microscope
SOD	Zeolite Sodalite

STA	Simultaneous Thermal Analyzer
TBA	4-(1H-tetrazol-5-yl)-benzoic acid
TED	Triethylenediamine
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
ZIF	Zeolitic Imidazolate Framework
ZTF	Zeolitic Tetrazolate Framework

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Nowadays, global warming and environmental pressures have attracted the attention of the researchers and environmental scientists around the world due to the rapid increase of energy consumption and population. According to the Energy Information Administration (EIA), it is expected that the energy consumption will increase by 57% in year 2030. Carbon dioxide emission from industrial processes, fossil-fueled power plants, transportation and de-carbonization (production of hydrogen from carbon-rich feedstock) contributes to approximately 60% of the global warming effects and a huge quantity of CO₂ emits to the atmosphere every day. Therefore, it is essential to capture carbon dioxide using efficient and cheap technology in reducing the environmental pressures. Several methods have been reported for CO₂ capture such as adsorption onto zeolites and porous membranes (i.e. activated carbon, etc.). However, such methods require high energy input and high cost. Thus, MOFs which exhibit excellent performance in gas adsorption (i.e. CO₂, H₂, CH₄, etc.) from a gas mixture become the new alternative methods for CO₂ capture (Sabouni, 2013).

Metal-Organic Frameworks (MOFs) have attracted considerable attention due to their diverse fascinating topologies, pore size tunability, high surface area and pore volume, and the extensive uses in lots of fields such as adsorption (Peng et al., 2014; Vakiti, 2012). MOF is a relatively new crystalline structure composed of organic and inorganic species that can assemble into one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) structure. The structures of MOF are composed of metals as nodes and ligands as linkers which form extended networks via coordinate bonds (Lee, 2007; Vakiti, 2012).

Stock & Biswas (2011) stated that the most important goal in the synthesis of MOF is to establish the synthesis conditions that lead to defined inorganic building blocks without decomposition of the organic linker with appropriate kinetics of crystallization. There are various approaches for MOF preparation such as solvothermal or hydrothermal synthesis, microwave synthesis, sonochemical synthesis, electrochemical synthesis, mechanochemical synthesis and slow evaporation method. FIGURE 1.1 shows the synthesis methods to produce MOF (i.e. sonochemistry, electrochemistry, etc.), reaction temperature of MOF synthesis ranging from room temperature (25 °C) to solvothermal conditions (80 °C – 180 °C) and the final reaction products of MOF synthesis with various morphology and size (1 nm – 1 mm). Different synthesis methods of the same reaction mixtures can lead to different MOFs formation (Stock & Biswas, 2011). The most common synthesis method used for preparation of MOF is solvothermal synthesis where the heating of a mixture contains metal salt and organic linkers in a solvent system (Dey et al., 2013; Tranchemontagne et al., 2008). The synthesis of MOFs can be influenced by factors such as the nature of metal ions and organic ligands, solvent system and molecular interaction. MOF materials have been widely studied due to their application potential for gas capture, separation, catalysis, drug delivery, sensing devices, ion exchange, negative thermal expansion, optoelectronics and other emerging applications (Chen et al., 2010; Huang et al., 2014; Lee, 2007; Tranchemontagne et al., 2008; Chun et al., 2005; D'Alessandro et al., 2010; Zhao et al., 2009; Shimomura et al., 2009; Liu et al., 2001; Vakiti, 2012; Wang, 2015; Xu, 2015; Ke, 2015). For the past decades, MOFs have gained popularity as the new technology for gas storage application due to the nature of the frameworks which allow the molecules to access the space within the structure.

The MOF's characteristics such as pore size, stability and adsorption affinity have to be considered carefully for its various aim of application (Huang et al., 2014). These characteristics can be measured using analytical techniques such as X-ray diffraction methods (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and Thermogravimetric Analysis (TGA). It is important to develop proper synthesis method for preparing the MOFs with derived characteristic for the selected application. In recent years, there have been several researches

studying one type MOF named $\text{Zn(BDC)(TED)}_{0.5}$ (BDC=benzenedicarboxylate, TED=triethylenediamine) due to its high hydrophobicity, high thermal stability and high porosity with large channels ($7.5\text{\AA} \times 7.5\text{\AA}$ along *c*-axis and $4.8\text{\AA} \times 3.2\text{\AA}$ along *a*-axis and *b*-axis) (Chen et al., 2010; Huang et al., 2014; Liu et al., 2014). This material is very potential to be applied in the gas separation and gas capture due to its hydrophobicity properties which enable gas separation even at relatively humid condition. Several studies have been reported on this material for gas sorption capacity. However, there is no detailed studies reported on this material for the effect of synthesis conditions to the mechanism of $\text{Zn(BDC)(TED)}_{0.5}$. Therefore, it is worthwhile to investigate the effect of synthesis conditions on preparation of $\text{Zn(BDC)(TED)}_{0.5}$ and its gas adsorption capacity.

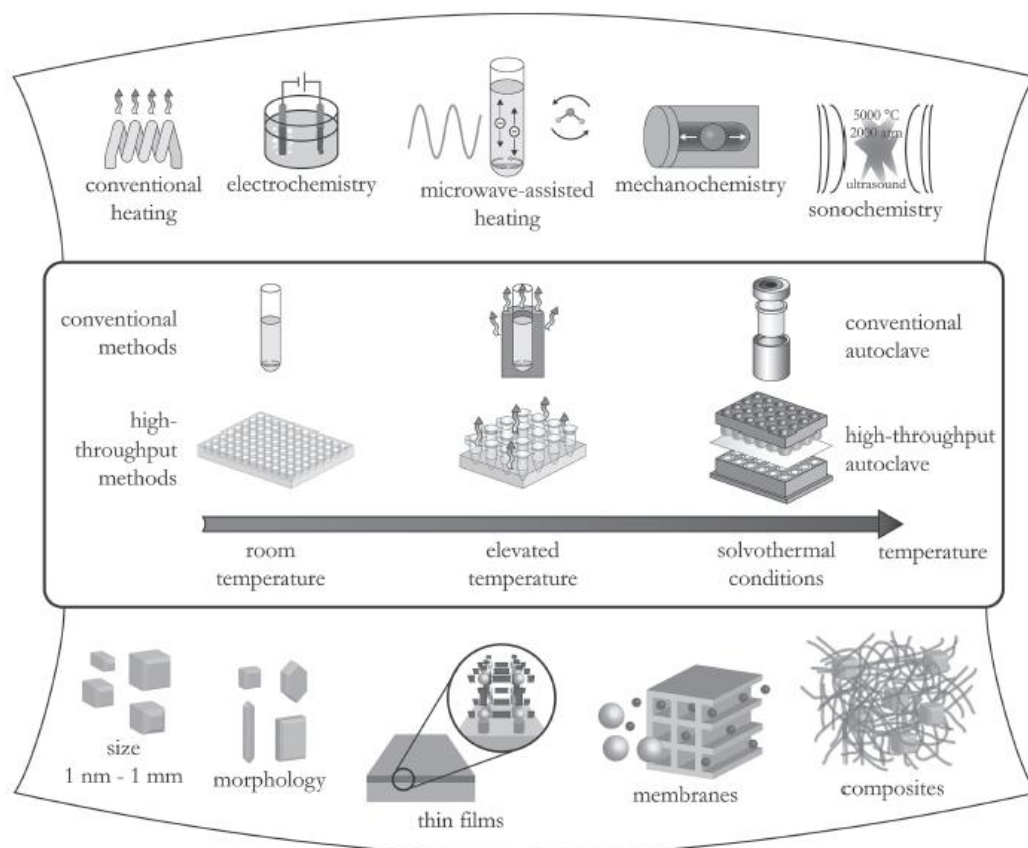


FIGURE 1.1 Overview of synthesis methods, reaction temperatures and final products in MOF synthesis (Stock & Biswas, 2011)

1.2 Problem Statement

Gas separation plays important role in reducing greenhouse gas (especially CO₂) emitted from industries. Conventional methods for CO₂ separation are generally chemical absorption, solid physical adsorption (i.e. pressure swing adsorption and temperature swing adsorption) and cryogenic distillation. However, technologies like chemical absorption and cryogenic distillation bring about drawbacks such as high energy consumption and high liquid losses due to evaporation of solvent. Adsorption is another promising method for CO₂ adsorption due to its advantages such as the simplicity in operation and the high energy efficiency.

There have been extensive researches reported on studying various adsorbents such as silicas, carbons, zeolites and metal-organic frameworks (MOFs). Carbons have large surface area but broad pore size distribution (Menéndez & Martín-Gullón, 2006; Shimomura et al., 2009). Zeolites have narrow and uniform pore size distribution but the cost to synthesize zeolites is generally high (Vakiti, 2012). In recent years, MOFs have attracted considerable interest due to their large surface area, well-defined pore, high adsorption capacity, high volume and adjustable chemical functionalities (Vakiti, 2012; Hu, 2011; Zhang, 2015). They have been tested and regarded as promising candidates for gas adsorption, Among the microporous metal organic frameworks, a MOF named Zn(BDC)(TED)_{0.5} (BDC=benzenedicarboxylate, TED=triethylenediamine) is selected for this project due to its highly hydrophobic properties and large channels structure (7.5Å × 7.5Å along *c*-axis and 4.8Å × 3.2Å along *a*-axis and *b*-axis) (Chen et al., 2010; Huang et al., 2014). So far, to the best knowledge, there was no detailed study reported on studying the effect of synthesis conditions on the preparation of Zn(BDC)(TED)_{0.5}. Exploration of the effect of synthesis conditions on the preparation of Zn(BDC)(TED)_{0.5} is important to optimize the synthesis of Zn(BDC)(TED)_{0.5} and hence its gas adsorption capacity. Therefore, current proposed project focused on exploration on the effect of synthesis conditions on the preparation of Zn(BDC)(TED)_{0.5} and its gas adsorption capacity.

1.3 Objectives of Study

The objectives of this project are:

1. To study the effect of synthesis conditions on preparation of MOFs.
2. To characterize synthesized MOFs by using different analytical techniques such as Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.
3. To study the CO₂ and N₂ gas adsorption properties of Zn(BDC)(TED)_{0.5}.

1.4 Scope of Study

The scopes of study of this project are:

1. Studying the preparation of Zn(BDC)(TED)_{0.5} under different synthesis conditions (i.e. temperature, time).
2. Characterization of Zn(BDC)(TED)_{0.5} using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy.
3. Performing gas adsorption studies for the synthesized Zn(BDC)(TED)_{0.5} using BET machine.

CHAPTER 2

LITERATURE REVIEW

2.1 Structures of Metal Organic Framework (MOF)

MOF is the metal organic structures of one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) built by linking linear or nonlinear organic linkers and metal clusters which often lead to open voids that can hold molecules so called “*guest molecule*”. In the structural formula, guest molecules are denoted outside of the bracket in the structural formula. Examples of MOFs with different structures are MOF-5, HKUST-1 and Cr-MIL-101 as shown in FIGURE 2.1. FIGURE 2.1 shows the MOFs with different structures by combining different type of metal ions or ligands as well as the addition of the secondary building units (SBU). Combination of $Zn_4O(CO_2)_6$ and $Cr_3OF(CO_2)_6$ with organic linkers, BDC produced MOF-5 and Cr-MIL-101 respectively. The framework of $[Zn(BDC)(TED)_{0.5}] \cdot 2DMF \cdot 0.2H_2O$ which is the MOF of interest in current project, holds two DMF molecules and 0.2 water molecule as guest molecules within its pores. FIGURE 2.2 shows the structure of $[Zn(BDC)(TED)_{0.5}]$ and its pore. Most MOFs are said to be micropores because of their pore diameters less than 2 nm. The advantages of these materials are well-characterized pores, high micropore volume, high surface area and small pore diameter. Other than that, the pore structure can be modified to adjust pore sizes and/or shapes and enhance sorbate-sorbent interactions (Lee, 2007). The MOFs also have the ability to tune their physical and chemical properties during their synthesis by changing the combination of metal and organic linkers group (Erucar & Keskin, 2011; Lee et al., 2007). The differences in synthesis, drying, filtration, activation and shaping can result in a wide variation of pore volume, surface area and crystalline size (Ming et al., 2014; Stock & Biswas, 2011).

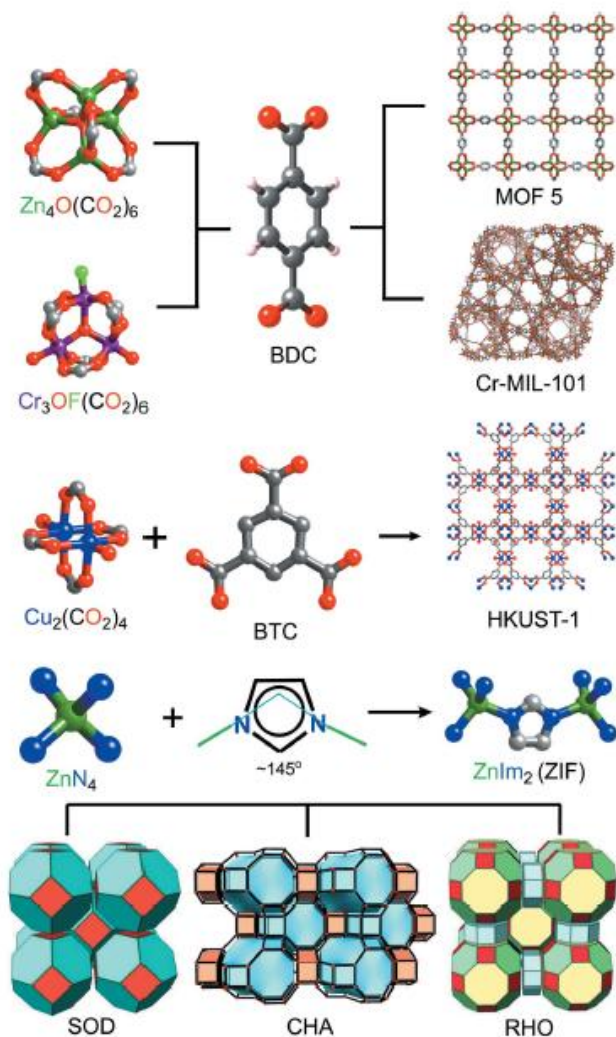


FIGURE 2.1 Examples of MOFs and ZIFs with different topologies as well as examples of secondary building units (SBU) (Dey et al., 2013)

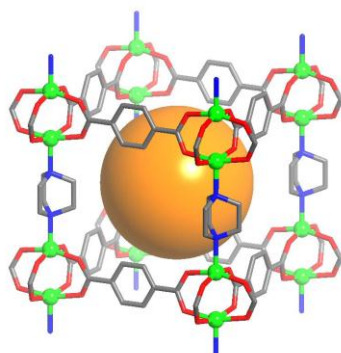


FIGURE 2.2 Metal organic framework structure of $[Zn(BDC)(TED)_{0.5}]$ and its pore (orange ball). In the figure, green denote Zn metal, red represents O, C is gray and N is blue (Lee, 2007)

2.2 Synthesis of MOFs

Generally, there are various approaches for MOF preparation including solvothermal or hydrothermal synthesis, microwave, slow evaporation, sonochemical, mechanochemical and electrochemical as shown in FIGURE 2.3. FIGURE 2.3 shows the type of energy required, the range temperature and time taken by each synthesis methods. The synthesis parameters (i.e. pH, time, temperature, etc.) need to be taken into consideration properly in order to produce the MOFs with derived characteristic. Most of the dicarboxylic acids used in MOF synthesis need to be deprotonated by dissolved in a suitable solvent before they can form bonds with metal cations. This results in a decrease in pH and the solution becomes acidic after the reaction. A new structure with different connectivity and properties occur by changing the molar ratio of the reactants (Lee, 2007). TABLE 2.1 shows the example of MOFs prepared under different synthesis methods (i.e. solvothermal, hydrothermal, slow evaporation, microwave-assisted, electrochemical, sonochemical and mechanochemical).

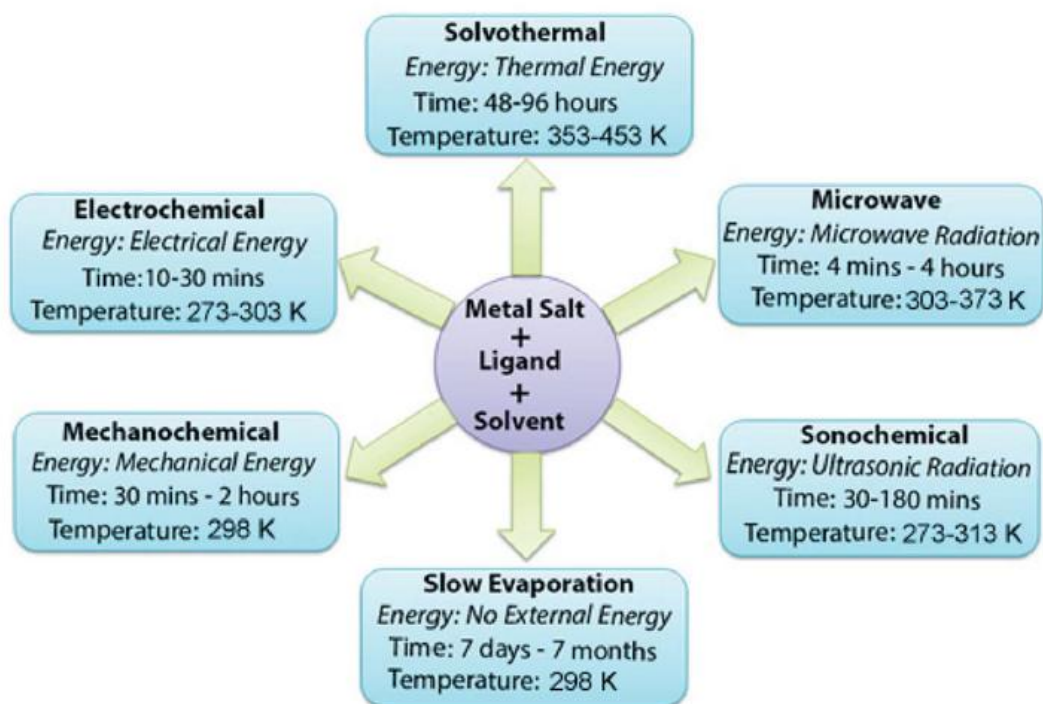


FIGURE 2.3 Synthesis conditions commonly used for MOF preparation (Dey et al., 2013)

TABLE 2.1 Example of MOFs prepared under different synthesis methods

Synthesis Methods	MOFs	Applications	Reference
Solvothermal Reactions	M(BDC)(TED) _{0.5} (M= Ni, Zn, Cu)	Selective gas separation (CO ₂ , CH ₄ , H ₂) and gas sorption (H ₂ , CO ₂ , CH ₄)	(Tan et al., 2012; Erucar & Keskin, 2011; Lee et al., 2007)
	[Zn ₄ O(BDC) ₃].7DEF.3H ₂ O or MOF-5 or IRMOF-1	Gas adsorption (N ₂ , CO ₂ , CO), H ₂ storage at high pressures	(McKinstry et al., 2013; Vakiti, 2012; Panella et al., 2006)
	Zn(NDC)(4,4-BPE) _{0.5} .2.25DMF.0.5H ₂ O	H ₂ storage	(Chen et al., 2006)
	MIL-53 or Al(OH)(BDC)	H ₂ adsorption	(Roswell & Yaghi, 2005)
	Cu ₃ (BTC) ₂ (H ₂ O) ₃ or Cu-BTC	H ₂ storage at low pressures	(Panella et al., 2006)
	Cd ₂ (TBA) ₂ (bipy)(DMA) ₂	Luminescent sensing materials	(Wang et al., 2015)
	{[(Cu ₄ Cl)(CPT) ₄ (H ₂ O) ₄].3NO ₃ .5NMP.3.5H ₂ O} _n	Adsorbing and separating dye molecules	(Chen et al., 2015)
Slow Evaporation (Room Temperature synthesis)	Eu(BTC)	Sensing of small molecules	(Chen et al., 2007)
	[Zn ₄ O(BDC) ₃].7DEF.3H ₂ O or MOF-5 or IRMOF-1	Gas adsorption (N ₂ , CO ₂ , CO), H ₂ storage	(Tranchemontagne et al., 2008; Vakiti, 2012)
	[Zn ₄ O(BTB) ₂] or MOF-177	H ₂ adsorption	(Tranchemontagne et al., 2008; Stock & Biswas, 2011; Roswell & Yaghi, 2005)
	M-MIL-100 (M = Cr, Fe)	Benzene sorption, imaging and drug delivery	(Stock & Biswas, 2011)
Electrochemical synthesis	[Zn ₄ O(BDC) ₃].7DEF.3H ₂ O or MOF-5 or IRMOF-1	Gas adsorption (N ₂ , CO ₂ , CO), H ₂ storage	(Stock & Biswas, 2011; Zhao et al., 2009; Vakiti, 2012; Panella et al., 2006)
	HKUST-1	Gas separation, storage and purification	(Stock & Biswas, 2011)
	Cu-EMOF	Gas purification, gas separation	(Vakiti, 2012)
Mechanochemical synthesis	Cu ₃ (BTC) ₂ (H ₂ O) ₃ or Cu-BTC	H ₂ storage at low pressures	(Panella et al., 2006)
	HKUST-1	Gas separation, storage and purification	(Stock & Biswas, 2011)
	Zn ₂ (BDC) ₂ (DABCO)	H ₂ adsorption	(Stock & Biswas, 2011; Roswell & Yaghi, 2005)

Synthesis Methods	MOFs	Applications	Reference
Sonochemical synthesis	$[\text{Zn}_4\text{O}(\text{BDC})_3] \cdot 7\text{DEF} \cdot 3\text{H}_2\text{O}$ or MOF-5 or IRMOF-1	Gas adsorption (N_2 , CO_2 , CO), H_2 storage at high pressures	(Stock & Biswas, 2011; Zhao et al., 2009; Panella et al., 2006)
	$[\text{Zn}_4\text{O}(\text{BTB})_2]$ or MOF-177	H_2 adsorption	(Stock & Biswas, 2011; Roswell & Yaghi, 2005)
	IRMOF-9	CO_2 adsorption	(Stock & Biswas, 2011)

2.2.1 Solvothermal or Hydrothermal Reactions

The synthesis of the MOFs can be generally carried out via solvothermal reaction or hydrothermal reaction. In solvothermal reaction, a solvent (organic or inorganic) is used at elevated temperatures and pressures in a closed system, often in the vicinity of its critical point. The reactions are referred to as hydrothermal when water is used as a solvent. Certain properties of the solvent such as density, viscosity and diffusion coefficient may change dramatically under solvothermal or hydrothermal conditions. The selection of the solvent is depending on the metal sources and organic linkers used because some of them have very low solubility. Two or three solvents can be mixed to increase the solubility. Reactants are dissolved or partially dissolved in the beaker by adding more fresh solvent and assisted by ultrasonic treatment in a warm water bath before transferring the mixture into reaction vessels (Lee, 2007). Hydrothermal methods often yield crystals that are suitable for single crystal X-ray diffraction analysis. However, this method is unsuitable starting materials which are thermally sensitive, energy demanding and relatively slow in synthesis process (Tranchemontagne et al., 2008). The selection of synthesis conditions (i.e. pH, temperature, time, etc.) is very essential in ensuring the successful preparation of the derived MOFs.

The effect of synthesis conditions on the MOF-5 preparation was studied by McKinstry et al. (2013). They reported that at specific temperature which is 140°C, it allows the starting materials to follow the simplest pathway among all conditions investigated with an intermediate phase formed first before gradual conversion to MOF-5 at a longer times. Reducing the synthesis temperature below 140°C resulted in the formation of MOF-5 following far more complex reaction pathways with multiple intermediate solid phases present during the process. Isolation and subsequent characterization was not possible due to the metastable nature of these transient, short-lived phases present during the process. The overall synthesis conditions on the MOF-5 formation are shown in the FIGURE 2.4. FIGURE 2.4 shows the pathway in the formation of MOF-5 under temperature ranged from 110 °C to 140 °C, time ranged from 1 hr to 6 hr and stirred or unstirred condition.

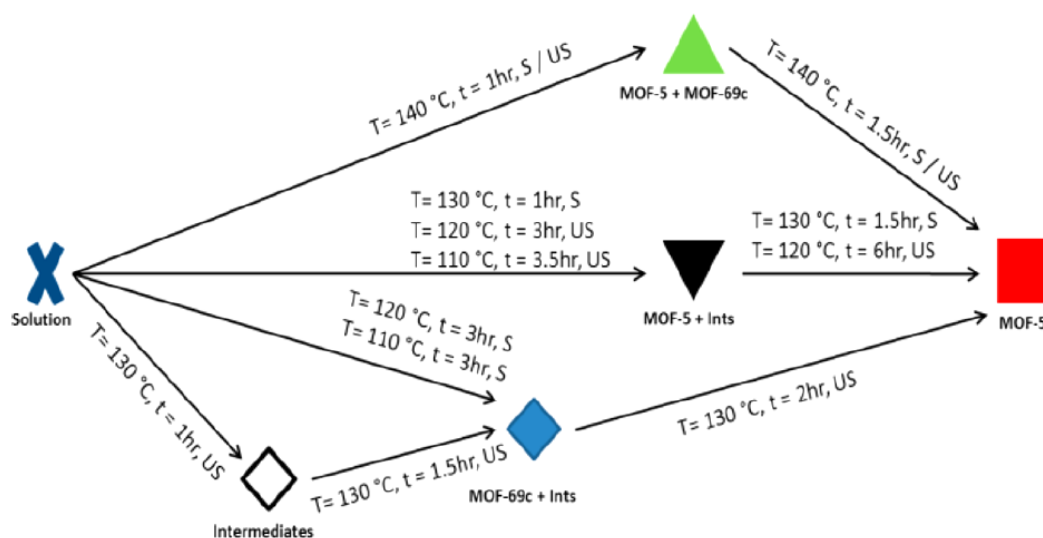


FIGURE 2.4 MOF-5 formation pathways (McKinstry et al., 2013)

2.2.1.1 Synthesis of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$

There have been limited studies reported on preparation of single crystals of $[\text{Zn}(\text{BDC})(\text{TED})_{0.5}]\cdot 2\text{DMF}\cdot 0.2\text{H}_2\text{O}$ using solvothermal reaction. Basically, the preparation of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ was carried out by subjecting the precursor solution of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ to heating at 150°C in a closed digestion bombs. Single crystal of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ was obtained after a series of purification on the solution after heating (Chen et al., 2010; Lee, 2007). So far, $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ was synthesized only at temperature 120°C or 150°C for one day or two days as reported by Lee et al., 2007; Huang et al., 2014; Tan et al., 2013; Liu et al., 2014; Tan et al., 2012; and Chen et al., 2010. However, optimization of the solvothermal synthesis to shorten reaction time or reduce reaction temperature was not tested by the literature.

2.2.2 Slow Evaporation/Room Temperature Synthesis

It is not necessary to heat the reaction in order to produce highly crystalline MOFs. Several MOFs can be synthesized through room temperature synthesis such as MOF-2, MOF-5, MOF-74, MOF-177 and MOF-199. The slow evaporation method does not need any external energy supply but it requires more time compared to other conventional methods (Dey et al., 2013). In room temperature synthesis, the starting materials are mixed at ambient temperature. Subsequently, addition of solvent causes deprotonation of the organic linker to precipitate. Base addition can

either be done slowly by diffusion or rapidly as an aliquot. Base addition by diffusion yields MOF single crystal mixtures which must be mechanically separated, whereas base addition as an aliquot yields MOFs as microcrystalline powders (Getachew et al., 2014; Tranchemontagne et al., 2008).

2.2.3 Microwave-assisted Synthesis

Microwave assisted method provide a very rapid technique for MOFs preparation. This method used extensively in the production of nanosize metal oxides. Such processes involve heating a solution with microwave for about an hour to obtain nanosized crystals. Generally, the quality of the crystal obtained through this synthesis method is the same as those produced by the regular solvothermal method but with lesser time (Dey et al., 2013).

2.2.4 Electrochemical Synthesis

Electrochemical synthesis is a fast process which offers continuous production of MOFs crystals. The basic principle of electrochemical synthesis relies on providing the metal ion by anodic dissolution into synthesis mixtures that include organic linkers and electrolytes (Dey et al., 2013).

2.2.5 Mechanochemical Synthesis

Mechanochemical synthesis is a solvent-free synthesis method for MOFs preparation by applying mechanical force to perform a chemical reaction (Dey et al., 2013). This methods focus on the use of grinding to initiate reaction between solid reactants. Usually, the two reactants are grind using pestle and mortar or ball mills (shaker and planetary mills) (Garay et al., 2007). Some zeolistic imidazolate frameworks are synthesized by using mechanochemical method (Dey et al., 2013). Pichon et al. (2006) reported that mechanochemical synthesis is a convenient and effective method for synthesizing a three-dimensional microporous metal organic framework. In terms of materials, energy and time, Pichon and co-workers state mechanochemical synthesis can present higher efficiency compared to solvothermal synthesis.

2.2.6 Sonochemical Synthesis

A phenomenon by which molecules undergo chemical change due to the application of intensive ultrasonic radiation (20 kHz – 10 MHz) is called sonochemistry. Ultrasound induces chemical or physical changes due to a cavitation process (i.e. formation, growth and instantaneous collapse of bubbles in a liquid) which creates local hot spots of a short lifetime with high temperature and pressure. A chemical reaction can be promoted under extreme conditions by immediate formation of a surplus crystallization nucleus. Sonochemical method can generate homogeneous nucleation centres and reduce a considerable crystallization time when compared with conventional hydrothermal synthesis (Dey et al., 2013).

2.3 Characterization of MOFs

MOF properties such as pore volume, particle size distribution, surface area and crystalline structure can be affected through the differences in synthesis, filtration, drying, activation, and shaping. Therefore, characterization of MOFs is needed to analyze the MOF properties. The data on the MOFs properties is needed for industry applications including gas separations, gas capture and storage, and catalysis. An extensive set of techniques are usually used to characterize several properties of MOFs (i.e. crystallinity, pore volume, surface area, particle size distribution, thermal stability, density, heat capacity, gas adsorption properties, etc.). The properties of MOF that are commonly measured are the crystalline structure, pore volume, surface area and thermal stability using equipment such as X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Thermogravimetric Analysis (TGA) and others.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter describes the series of steps and procedures used in order to successfully complete the project. The research project activities can be divided into three parts which is illustrated in FIGURE 3.1.



FIGURE 3.1 Research project activities

The first part deals with synthesis of metal organic framework (MOF) named $\text{Zn(BDC)(TED)}_{0.5}$ by varying the synthesis temperature and synthesis time. In the second part, the synthesized $\text{Zn(BDC)(TED)}_{0.5}$ was characterized using the selected characterization techniques such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy, X-ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). For the last part, gas adsorption capacity of $\text{Zn(BDC)(TED)}_{0.5}$ was investigated.

FIGURE 3.2 illustrates the project flow of the study. The project flow involves the identification of problem statement and objectives of the project followed by literature review, experimental design, data analysis and interpretation, and documentation and reporting.

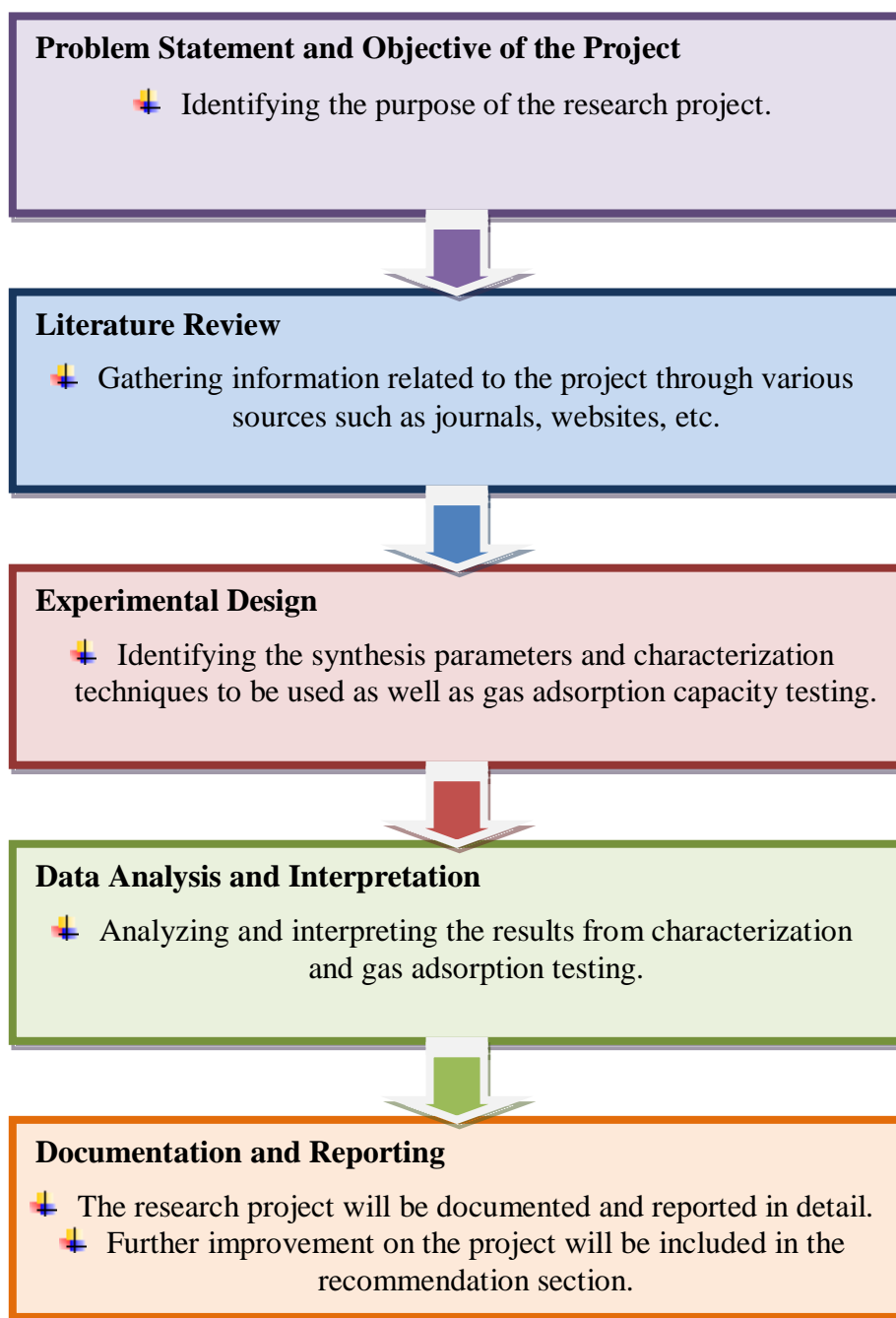


FIGURE 3.2 Project flow of the study

3.2 Chemicals and Equipment

The list of chemicals and equipment used to synthesize and characterize $\text{Zn(BDC)(TED)}_{0.5}$ is shown in the TABLE 3.1 and TABLE 3.2.

TABLE 3.1 List of Chemicals for preparation of Zn(BDC)(TED)_{0.5}

Chemical
Zinc (II) Nitrate Hexahydrate
1,4-Benzenedicarboxylic acid (BDC)
Triethylenediamine (TED)
N,N-Dimethylformamide (DMF)
Nitric acid

TABLE 1.2 List of equipment for preparation and characterization of Zn(BDC)(TED)_{0.5}

Preparation Equipment	Analytical Equipment
Stainless steel pressure reactor	Scanning Electron Microscope (SEM)
Ultrasonic bath	X-ray Diffraction (XRD)
Centrifuge	Fourier Transform Infrared (FTIR) spectroscopy
Oven	Thermogravimetric Analysis (TGA)
Vacuum oven	BET

3.3 Preparation of Zn(BDC)(TED)_{0.5}

The procedures for the synthesis of Zn(BDC)(TED)_{0.5} are explained as below:

1. Zinc (II) Nitrate Hexahydrate, 1,4-Benzenedicarboxylic acid (BDC), Triethylenediamine (TED) and N,N-Dimethylformamide (DMF) were mixed in a beaker under room temperature at stirring rate of 325 rpm.
2. Nitric acid was added to the mixture at an approximate ratio of one drop per 10 mL of DMF to dissolve the solid chemicals.
3. The resultant mixture was subjected to ultrasonic treatment in a warm water bath at 50°C for at least 2 hours until a clear solution was formed.
4. The solution was then transferred into the stainless-steel pressure vessel and heated in the oven according to the conditions shown in TABLE 3.3.

TABLE 3.3 Synthesis condition for the reaction

Sample	Temperature (°C)	Time (hr)
1	120	24
2	120	36
3	120	48
4	150	24
5	150	36
6	150	48

5. After synthesis, the solution was filtered and washed with 10 mL DMF for three times and dried under vacuum at 50°C for at least 2 hours to remove DMF and water.
6. The synthesized MOFs under different synthesis conditions was characterized and tested for gas adsorption capacity.

3.4 Characterization of Zn(BDC)(TED)_{0.5}

The synthesized Zn(BDC)(TED)_{0.5} was then characterized to study its properties using Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy and Thermogravimetric Analysis (TGA).

3.4.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) allows the examination of the physical structures of the sample as well as their elemental composition. SEM images were taken with Phenom Pro X with an acceleration voltage of 10 kV and acceleration voltage of 15 kV for elemental analysis with EDS.

Model Name: Phenom Pro X

Manufacturer: Phenom-World

3.4.2 X-ray Diffraction (XRD)

The phase purity and crystal structure of Zn(BDC)(TED)_{0.5} was measured by X-ray Diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with a Bruker D8 Advance X-ray Diffractometer with CuK α radiation between 2° and 80° (2-Theta) with a step width of 0.02°. The X-ray diffraction patterns were obtained in between 15 min to 90 min.

Model Name: D8 Advance

Manufacturer: Bruker AXS Inc.

3.4.3 Fourier Transform Infrared (FTIR) spectroscopy

Infrared spectroscopy uses the infrared (IR) portion of the electromagnetic spectrum to characterize materials as molecules absorb specific IR frequencies that match the vibrational frequency of chemical bonds present in the molecular structures. Fourier Transform (data processing technique) turns the raw data into the FTIR spectrum. The functions of the FTIR are to determine molecular structure, identify functional group, type of chemical bonds and in-situ surface studies. The IR absorption spectra were recorded under room temperature with frequency ranging from 3200 cm⁻¹ to 800 cm⁻¹.

Model Name: Spectrum One

Manufacturer: Perkin Elmer Inc.

3.4.4 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was used to measure materials thermal stability and composition. TGA is a technique to measure the change in weight of a sample as a function of temperature or time in a controlled atmosphere. The operating temperature was from 15 °C to 800 °C and heating rate from 1 °C/min to 3 °C/min. The thermogravimetric analysis was recorded with STA 6000.

Model Name: Simultaneous Thermal Analyzer (STA) 6000

Manufacturer: Perkin Elmer Inc.

3.5 Gas Adsorption Studies of Zn(BDC)(TED)_{0.5}

BELSORP-mini is a sorption measuring instrument that can analyze specific BET surface area of $> 0.01 \text{ m}^2/\text{g}$ and pore size distribution in the range 0.35 nm to 200 nm of solids (i.e. adsorbents, powder, pellets, etc.). Zn(BDC)(TED)_{0.5} was tested for CO₂/N₂ adsorption selectivity based on the ratio of adsorption capacity between CO₂ and N₂.

Model Name: BELSORP-mini

Manufacturer: BEL JAPAN, INC.

3.6 Gantt Chart

TABLE 3.4 shows the activities involve during FYPI and TABLE 3.5 shows the activities throughout FYPII.

TABLE 3.4 Project Gantt Chart for FYPI

ACTIVITIES	PROJECT DURATION (WEEK)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Title Selection	■	■													
Literature Review			■	■	■	■	■								
Requisition of Laboratory Workstation and Apparatus				■	■	■	■								
Synthesis of Zn(BDC)(TED) _{0.5}							■	■	■	■	■	■	■	■	■
Preparation of Extended Proposal			■	■	■	■	■								
Submission of Extended Proposal							■	■							
Research Proposal Defense										■					
Preparation of Interim Report							■	■	■	■	■	■			
Submission of Draft Interim Report												■			
Submission of Final Interim Report													■		
Characterization of Zn(BDC)(TED) _{0.5}													■	■	■

TABLE 3.5 Project Gantt Chart for FYPII

ACTIVITIES	PROJECT DURATION (WEEK)														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Synthesis of Zn(BDC)(TED) _{0.5}	█	█	█	█	█	█	█								
Characterization of Zn(BDC)(TED) _{0.5}	█	█	█	█	█	█	█								
Gas Adsorption Capacity Test	█	█	█	█	█	█	█								
Submission of Progress Report							█								
Preparation of Final Report							█	█	█	█	█				
Pre-SEDEX										█					
Submission of Draft Final Report											█				
Submission of Dissrertation (soft-bound)												█			
Submission of Technical Paper												█			
Viva													█		
Submission of Project Dissertation (hard-bound)															█

3.7 Key Milestone

TABLE 3.6 and TABLE 3.7 show the key milestone of the project for FYPI and FYPII respectively.

TABLE 3.6 Key Milestone for FYPI

WEEK	ACTIVITIES
1-2	<ul style="list-style-type: none">• Received project title from coordinator• Understand the general idea of the project• Identify the objectives and scope of study of the project
3-4	<ul style="list-style-type: none">• Find the literature review of the project• Meet with supervisor for further understanding of the project
5-6	<ul style="list-style-type: none">• Select the method for the synthesis of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ based on previous research paper• Determination of synthesis condition parameters for preparation of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$
7-8	<ul style="list-style-type: none">• Preparation of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ samples• Submission of extended proposal
9-12	<ul style="list-style-type: none">• Research proposal defense presentation
13	<ul style="list-style-type: none">• Submission of final interim report (softcopy and hardcopy)• Characterization of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ using FTIR
14	<ul style="list-style-type: none">• Characterization of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ using SEM
15	<ul style="list-style-type: none">• Characterization of $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ using XRD

TABLE 3.7 Key Milestone for FYPII

WEEK	ACTIVITIES
1-6	<ul style="list-style-type: none"> Continuation of synthesis and characterization of Zn(BDC)(TED)_{0.5} Testing for gas adsorption capacity of Zn(BDC)(TED)_{0.5}
7	<ul style="list-style-type: none"> Submission of progress report
8-9	<ul style="list-style-type: none"> Preparation of final report
10	<ul style="list-style-type: none"> Poster presentation (Pre-SEDEX)
11	<ul style="list-style-type: none"> Submission of draft final report
12	<ul style="list-style-type: none"> Submission of dissertation (soft-bound) Submission of technical paper
13	<ul style="list-style-type: none"> Viva
15	<ul style="list-style-type: none"> Submission of project dissertation (hard-bound)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The purpose of synthesizing of MOF, named Zn(BDC)(TED)_{0.5} by varying the temperature and time in the current project, is to develop understanding of the affect of the synthesis parameters on the formation of Zn(BDC)(TED)_{0.5}. This chapter presents the results of the Zn(BDC)(TED)_{0.5} characterization and gas adsorption capacity.

4.2 Yield of Solidification

TABLE 4.1 shows the yield of the nine samples prepared under different temperature and time in the current project. It can be observed that the yield increased from 38.27% to 82.32% when time was increased from 24 to 48 hours at 120 °C. At constant 24 hours and 36 hours, the yield increased from 38.27% to 84.67% and 46.23% to 96.71% respectively across temperature from 120 °C to 150 °C.

TABLE 4.1 Percentage yield of solidification

SAMPLE	TEMPERATURE	TIME	MASS	YIELD
S1	120 °C	24 hrs	0.9253 g	38.27 %
S2	120 °C	36 hrs	1.1201 g	46.32 %
S3	120 °C	48 hrs	1.9906 g	82.32 %
S4	135 °C	24 hrs	1.9520 g	80.73 %
S5	135 °C	36 hrs	1.9250 g	79.61 %
S6	135 °C	48 hrs	1.9014 g	78.63 %
S7	150 °C	24 hrs	2.0474 g	84.67 %
S8	150 °C	36 hrs	2.3385 g	96.71 %
S9	150 °C	48 hrs	1.7919 g	74.11 %

4.3 Characterization of Zn(BDC)(TED)_{0.5}

4.3.1 Scanning Electron Microscope (SEM)

FIGURE 4.1 – 4.3 shows the SEM images of the MOF synthesized taken with Phenom Pro X. The growth of MOF is not uniform and there is polydispersity in size and shape as indicate in the SEM images. The MOF shows amorphous phase in all SEM images except for MOF synthesized at 120 °C for 48 hours.

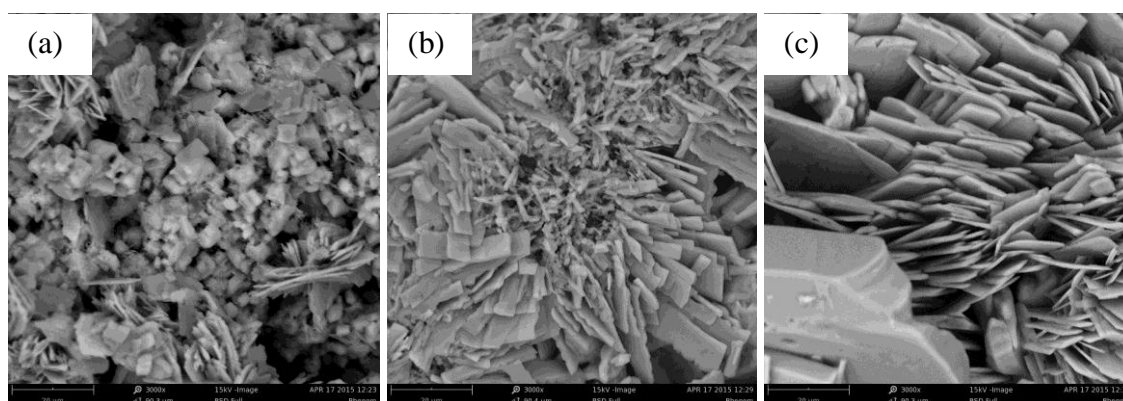


FIGURE 4.1 SEM images of the synthesized MOF at 120 °C for (a) 24 hours, (b) 36 hours and (c) 48 hours

It was observed that from FIGURE 4.1, the size increased with increasing time from 24 to 48 hours at 120 °C.

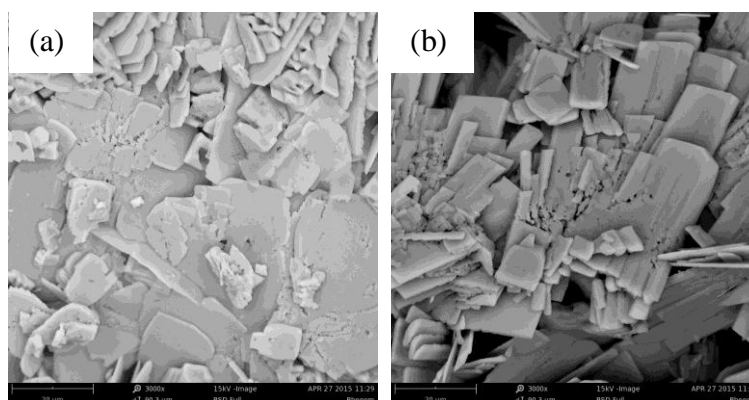


FIGURE 4.2 SEM images of the synthesized MOF at 135 °C for (a) 24 hours and (b) 36 hours

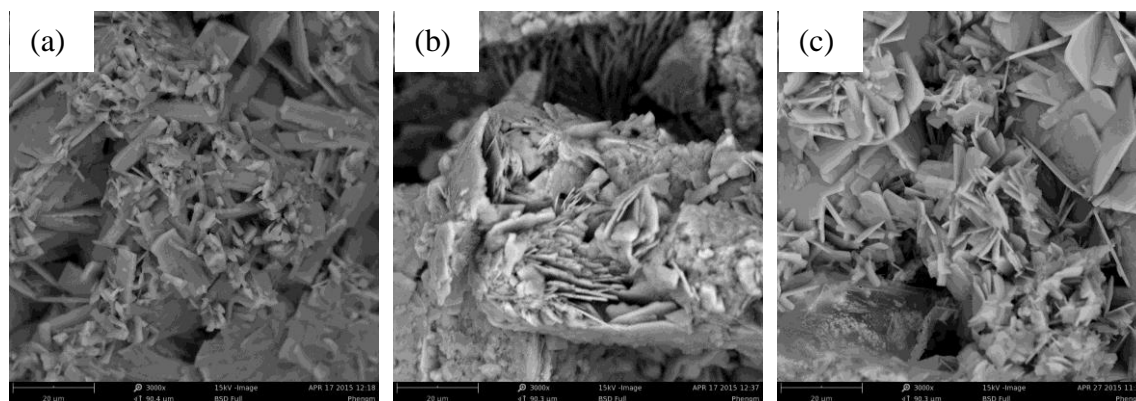


FIGURE 4.3 SEM images of the synthesized MOF at 150 °C for (a) 24 hours, (b) 36 hours and (c) 48 hours

4.3.2 X-ray Diffraction (XRD)

FIGURE 4.4 – 4.6 show the X-ray diffraction patterns of the synthesized MOF collected from the bottom of the autoclave at different temperature and time through solvothermal synthesis. The XRD pattern of synthesized MOF is similar from FIGURE 4.4 – 4.6. However, the XRD pattern obtained did not display the required XRD patterns for the intended MOF, $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ as reported by Lee et al. (2007). According to Chen et al. (2009), they noticed that $\text{Zn}(\text{BDC})(\text{TED})_{0.5}$ or $\text{Zn}_2(\text{BDC})_2(\text{Dabco})\cdot 4\text{DMF}\cdot 0.5\text{H}_2\text{O}$ that are three-dimensional (3D) structure can be transformed to two-dimensional (2D) structure MOF called MOF-2 or $\text{Zn}_2(\text{BDC})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})$ due to exposure to the environment for more than 36 hours. The XRD pattern in FIGURE 4.4 – 4.6 matched with XRD pattern for MOF-2 reported in the studies by Chen et al. (2009). Chen and his co-workers done a studies on the reversible two-dimensional to three-dimensional framework transformation. Chen et al. (2009) studies explained that in the presence of air, MOF-1 or $\text{Zn}_2(\text{BDC})_2(\text{H}_2\text{O})_2\cdot(\text{DMF})$ can be transformed into a two-dimensional structure which is MOF-2. MOF-2 also can transformed back to MOF-1 after the organic linker, Dabco or triethylenediamine (TED) was added to MOF-2 in DMF. In his research, Chen and co-workers reported that after exposing MOF-1 to the air for 36 hours, most of MOF-1 was transformed to MOF-2.

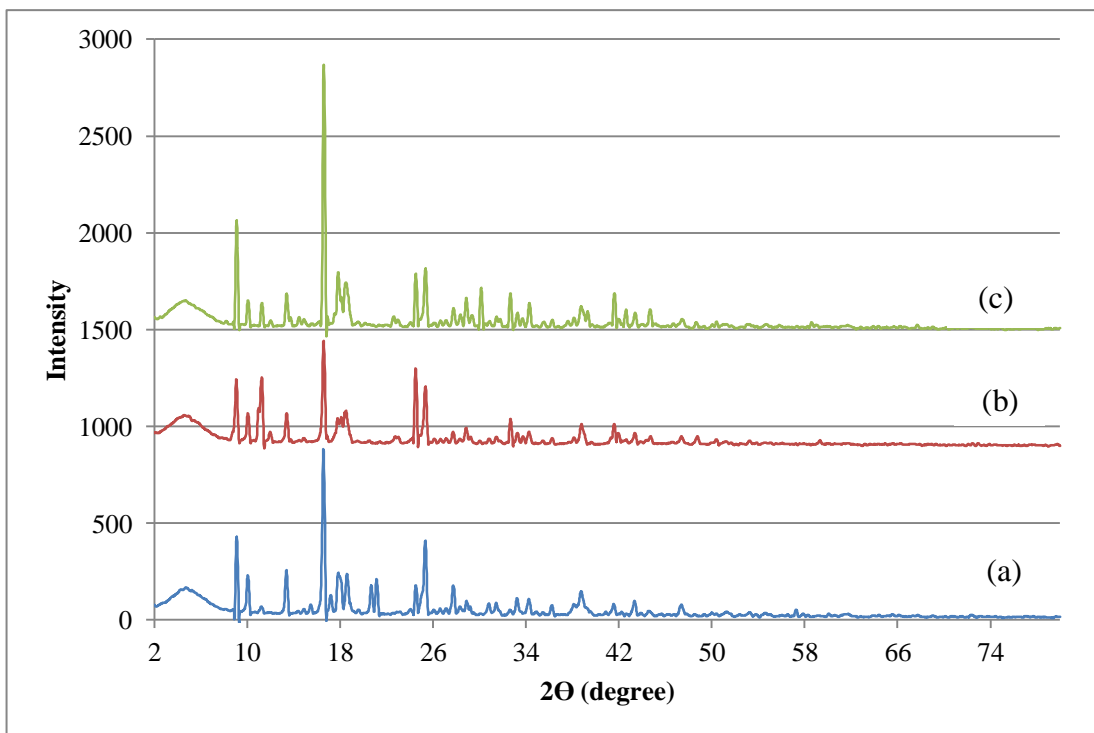


FIGURE 4.4 X-ray diffraction pattern of MOF synthesized at 120 °C for (a) 24 hours (b) 36 hours and (c) 48 hours

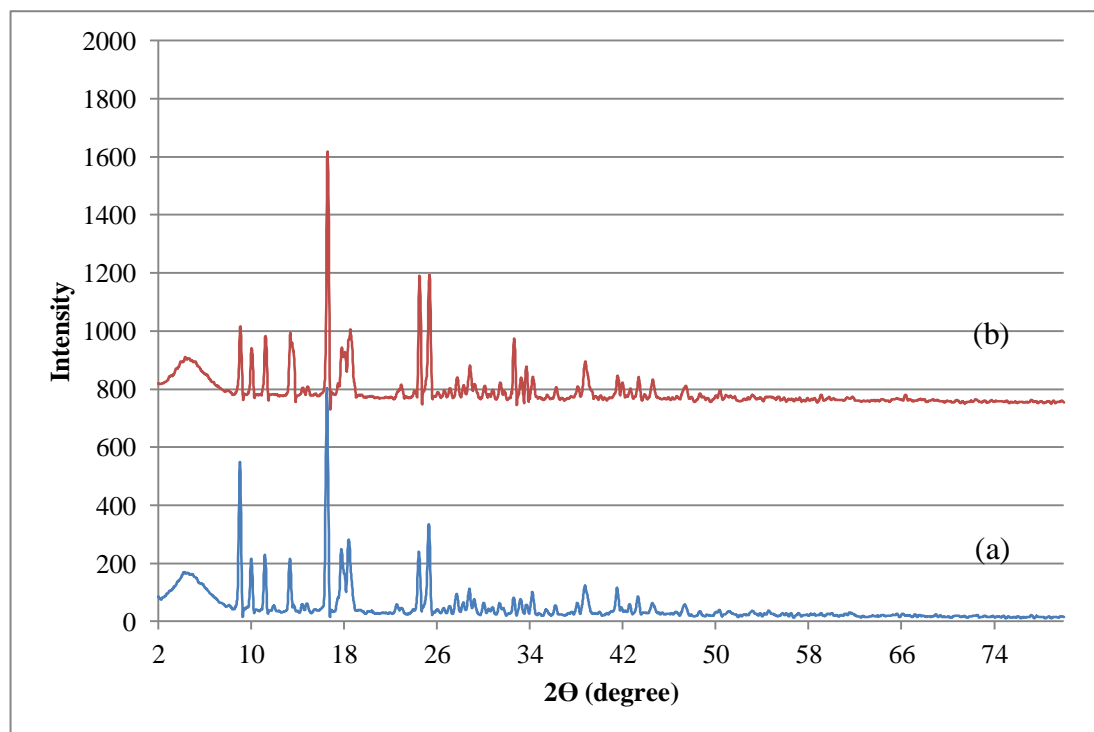


FIGURE 4.5 X-ray diffraction pattern of MOF synthesized at 135 °C for (a) 24 hours and (b) 48 hours

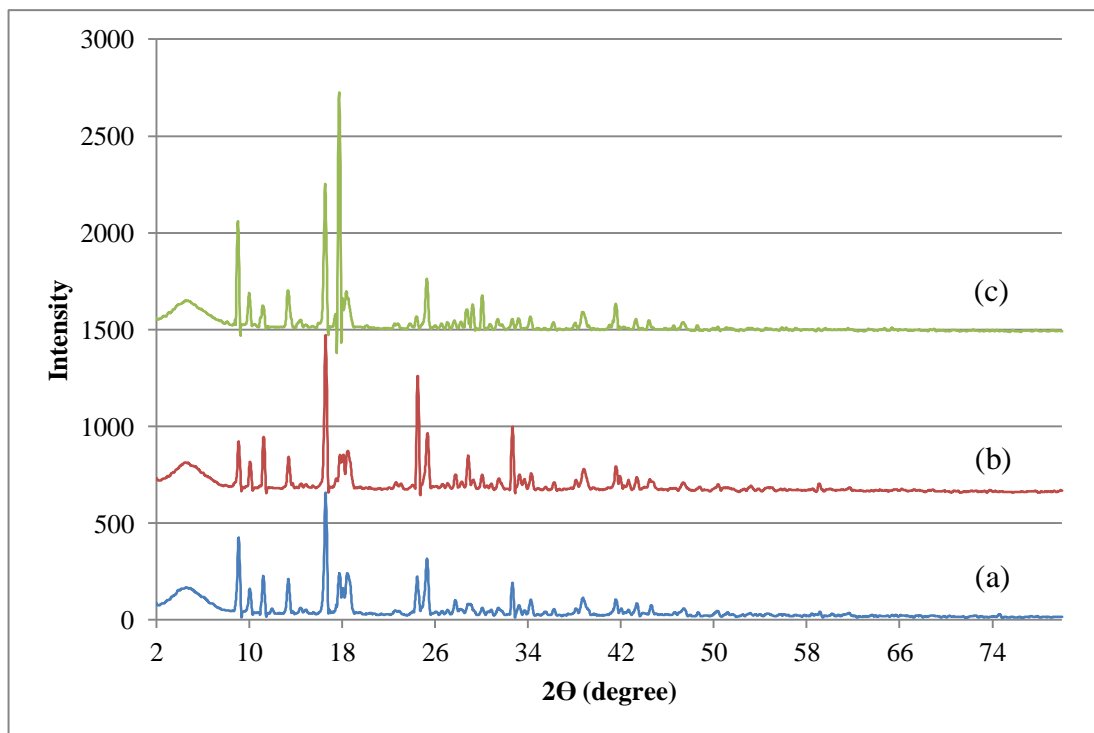


FIGURE 3.6 X-ray diffraction pattern of MOF synthesized at 150 °C for (a) 24 hours (b) 36 hours and (c) 48 hours

4.3.3 Fourier Transform Infrared (FTIR)

The Fourier Transform Infrared (FTIR) spectrum for the synthesized MOF is shown in the FIGURE 4.7 to FIGURE 4.9. The FTIR spectrum of the synthesized MOF shows similar pattern as the FTIR spectrum for MOF-2 reported by Li et al. (2011). The sharp peaks are observed at the range of wavenumber from 900 cm^{-1} to 675 cm^{-1} , 1052 cm^{-1} to 1054 cm^{-1} , 1373 cm^{-1} to 1411 cm^{-1} , 1556 cm^{-1} to 1567 cm^{-1} and a broad peak is observed 3412 cm^{-1} to 3435 cm^{-1} . TABLE 4.2 shows the list of type of bonding attributed by the peaks. All the bonds shows the existence of 1,4-benzenedicarboxylic acid and triethylenediamine in the MOF synthesized.

TABLE 4.2 Type of the bond shown in the FTIR spectrum

Wavenumber	Type of Bond
900 cm ⁻¹ to 675 cm ⁻¹	Aromatic C-H
1120 cm ⁻¹ to 995 cm ⁻¹	Alkoxy C-O
1700 cm ⁻¹ to 1500 cm ⁻¹	Aromatic ring C=C
3250 cm ⁻¹ to 2800 cm ⁻¹	Carboxylic acid O-H stretch
3500 cm ⁻¹ to 3200 cm ⁻¹	Alcohol/phenol O-H stretch, amine N-H stretch

Source: (1) orgchem.colorado.edu (2) www.cpp.edu

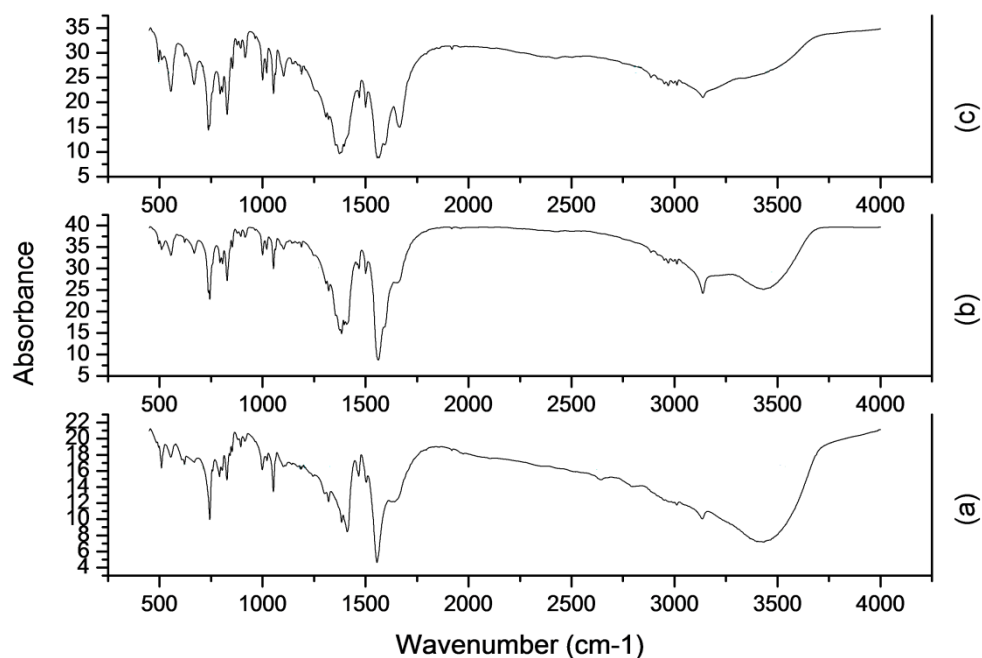


FIGURE 4.7 IR absorption spectra of Zn(BDC)(TED)_{0.5} at 120 °C for (a) 24 hours (b) 36 hours and (c) 48 hours

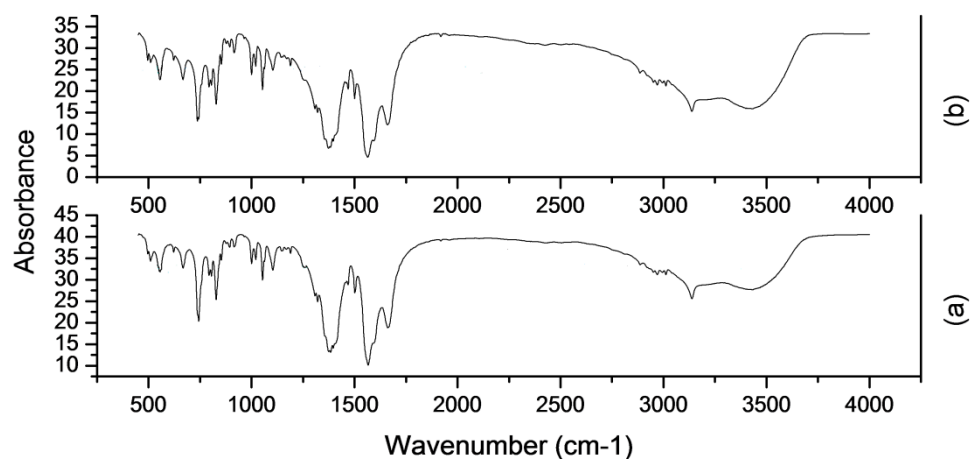


FIGURE 4.8 IR absorption spectra of Zn(BDC)(TED)_{0.5} at 135 °C for (a) 24 hours and (b) 36 hours

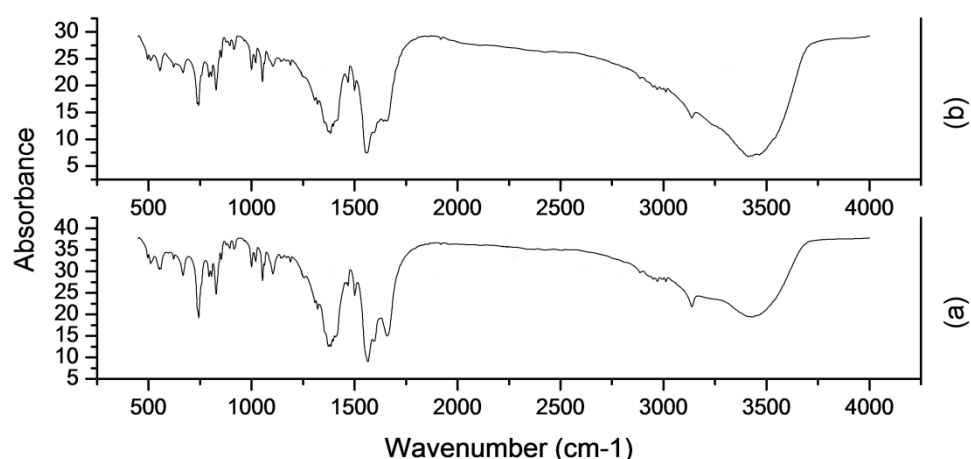


FIGURE 4.9 IR absorption spectra of Zn(BDC)(TED)_{0.5} at 150 °C for (a) 24 hours and (b) 36 hours

4.3.4 Thermogravimetric Analysis (TGA)

FIGURE 4.10 and FIGURE 4.11 display the TGA plots of the synthesized MOF prepared through solvothermal process under temperature from 120 °C to 150 °C and time from 24 hours to 36 hours. All TGA diagrams show the similar trend of change of percentage weight with time. The total weight loss ranged 73 wt% to 85 wt% for all the synthesized samples after heated up to 800 °C in the TGA studies as shown in TABLE 4.3. FIGURE 4.10 (c) display the graph of MOF synthesized at 120 °C for 48 hours. The first weight loss (10.8 wt%) is observed at

96 °C due to the water molecules loss and the second weight loss (6.0 wt%) is due to the DMF molecules loss in the framework at 160 °C. The third weight loss (55.3 wt%) is observed at 440 °C due to the decomposition of the organic species in the framework. The TGA results of MOF synthesized at 120°C and 150°C showed the framework was stable below 440 °C.

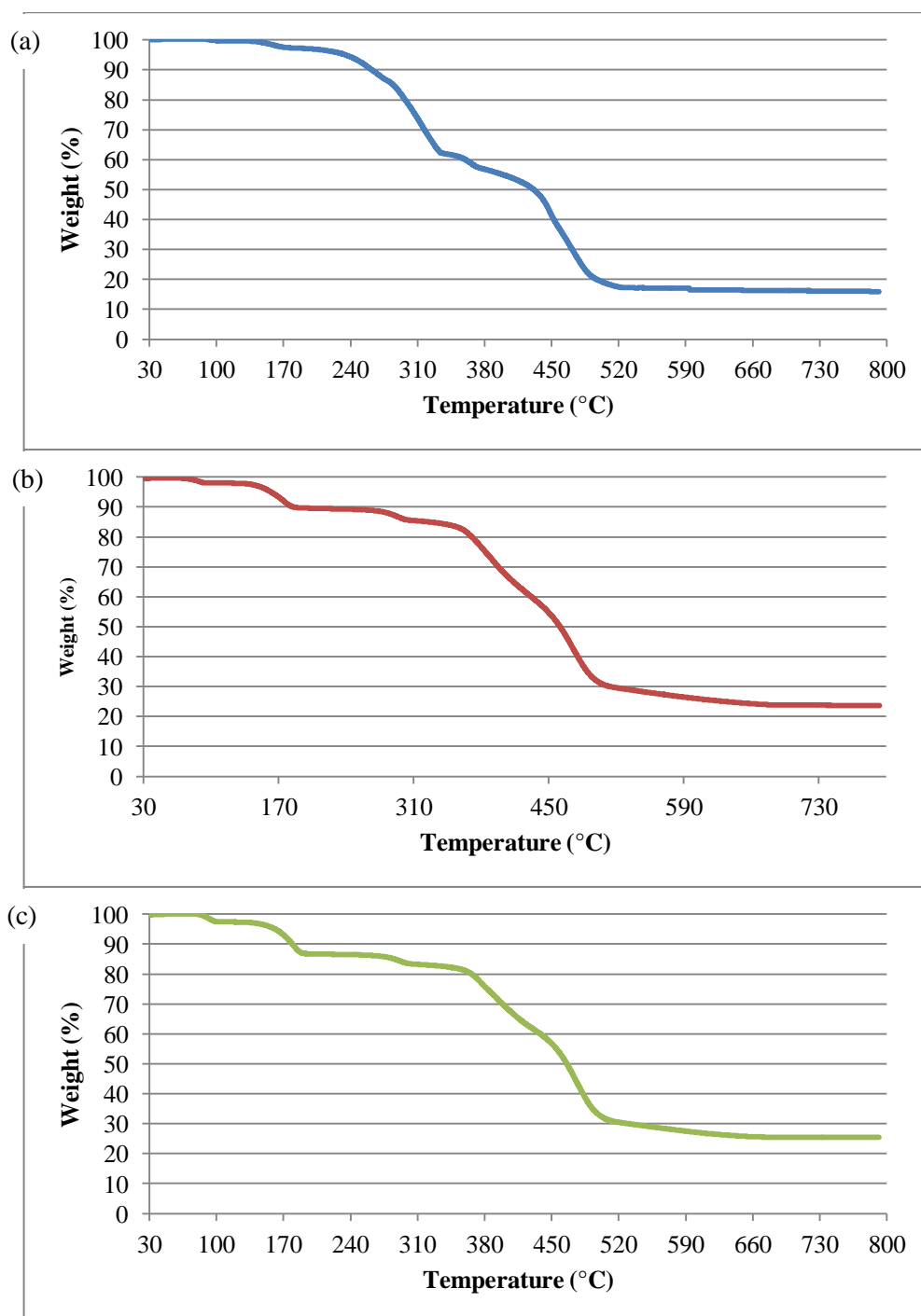


FIGURE 4.10 TGA plots of MOF synthesized at 120 °C for (a) 24 hours, (b) 36 hours and (c) 48 hours

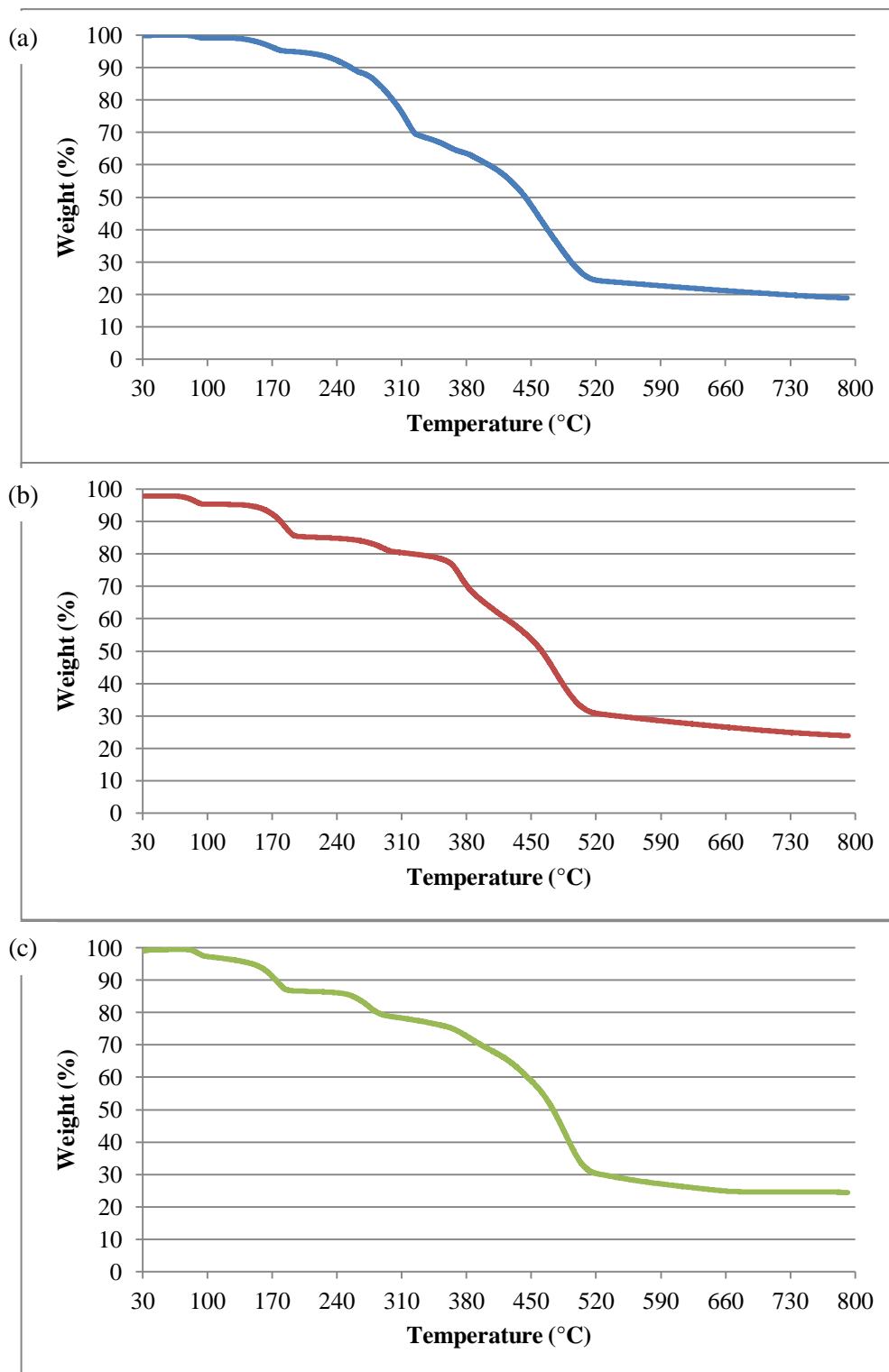


FIGURE 4.11 TGA plots of MOF synthesized at 150 °C for (a) 24 hours, (b) 36 hours and (c) 48 hours

TABLE 4.3 Total weight loss of the molecules

Temperature	Time	Total Weight Los (wt%)
120 °C	24 hrs	83.48
120 °C	36 hrs	75.97
120 °C	48 hrs	74.37
150 °C	24 hrs	81.08
150 °C	36 hrs	75.88
150 °C	48 hrs	73.71

4.4 Gas Adsorption Studies

FIGURE 4.12 shows the adsorption and desorption isotherm of CO₂ adsorption at 298K. From the adsorption isotherm shown in Figure 19, it can be observed that CO₂ adsorption increased as increasing relative pressure. This shown that, CO₂ adsorption was the highest at relatively high pressure. Adsorption of CO₂ was the highest at 1 atm which is 0.053 mmol/g. The BET surface area and total pore volume for CO₂ adsorption is 2.19 m²/g and 1.1633 cm³/g. Liu et al. (2012) stated that the BET surface area of CO₂ adsorption in MOF-2 is 345 m²/g. According to Saha et al. (2012) studies, they reported that the CO₂ uptake is 1.20 mmol/g as the pressure approaches 1 atm.

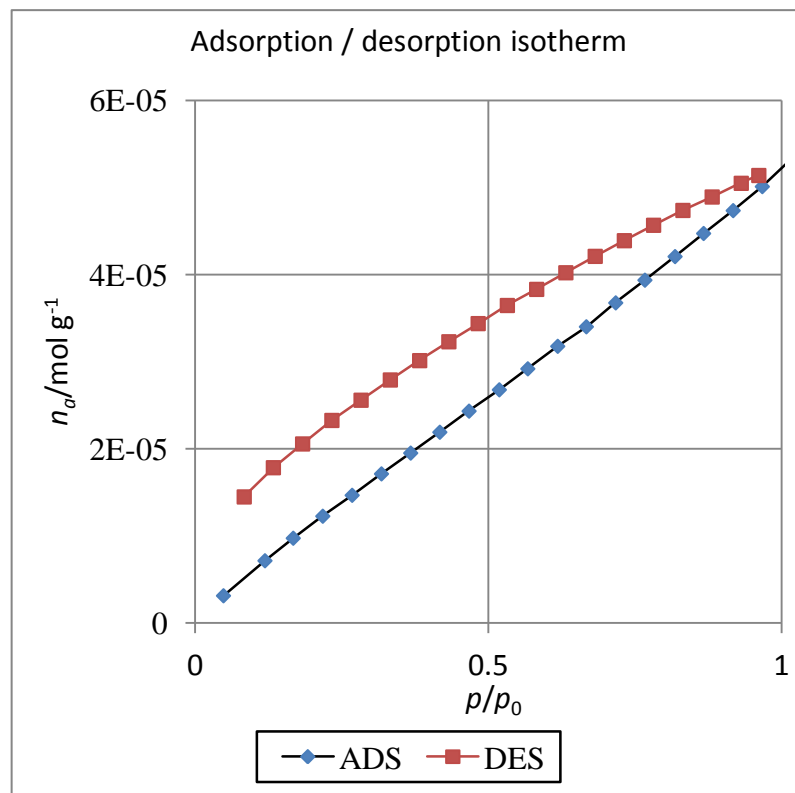


FIGURE 4.12 CO₂ adsorption and desorption isotherm at 298 K

FIGURE 4.13 shows adsorption and desorption isotherm of N₂ at 77 K. The adsorption isotherm is type II isotherm. The sorption of N₂ reaches near-saturation at relatively low pressures and then increases very slowly up to 1 atm. The adsorption of N₂ was the highest at relative pressure of 0.98 atm which is 0.575 mmol/g. The BET surface area and total pore volume of N₂ adsorption is 14.8 m²/g and 0.0199 cm³/g. Getachew et al. (2014) reported that MOF-2 have surface area of 361 m²/g and total pore volume of 0.227 cm³/g. Saha et al. (2012) studies reported that the BET surface area of MOF-2 for N₂ adsorption is 39 m²/g.

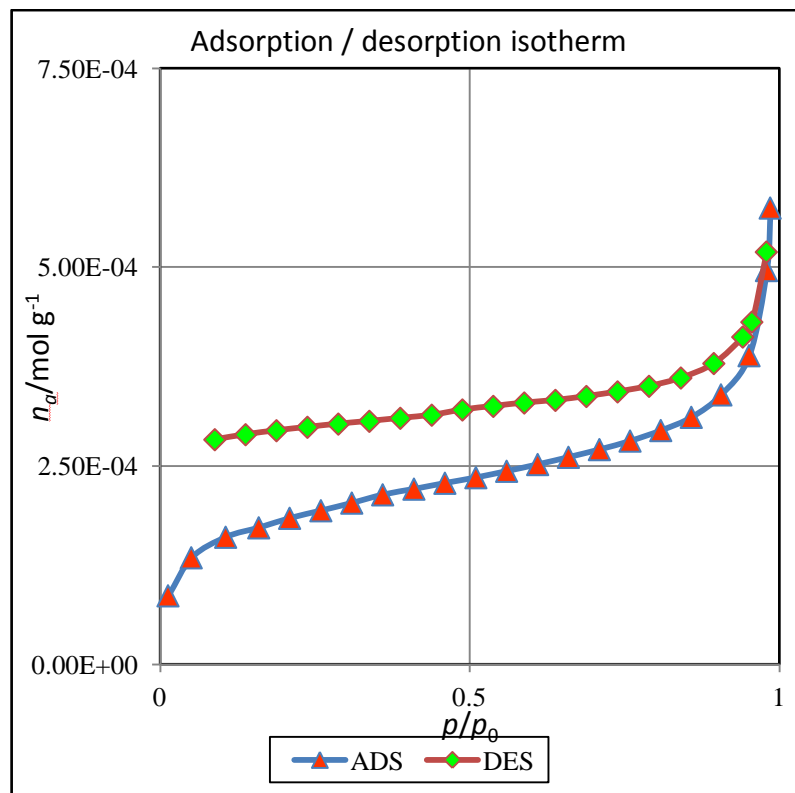


FIGURE 4.13 N_2 adsorption and desorption isotherm at 77 K

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this project, MOF have been successfully formed. It was found that MOF synthesized changed from Zn(BDC)(TED)_{0.5} to MOF-2 due to the exposure to the air longer than 36 hours. The MOF synthesized shows diversity in the size and shape of the crystal. The FTIR spectrum shows similar pattern for all MOF synthesized. The type of bonding existed in the synthesized MOF structure were aromatics C-H bond, alkoxy C-O bond, aromatic ring C=C bond, carboxylic acids O-H bond, amine N-H bond and alcohols or phenols O-H bond. TGA plots diagrams shows three steps of weight losses where water molecules, N,N-Dimethylformamide (DMF) molecules and the decomposition of the MOF-2 with the total weight loss in between 73 wt% to 84 wt%. The BET surface area of CO₂ and N₂ adsorption is 2.19 m²/g and 14.8 m²/g respectively. The total pore volume of CO₂ and N₂ adsorption is 1.1633 cm³/g and 0.0199 cm³/g.

5.2 Recommendations

A few recommendations can be drawn based on the observation during this study to prevent the change phase from Zn(BDC)(TED)_{0.5} to MOF-2. The following are some of the recommendations for future works relevant to studies of Zn(BDC)(TED)_{0.5}.

- i. The samples are to be stored immediately after the synthesis until further use to get rid of humidity in the atmosphere.
- ii. The vacuum oven used for sample heating is recommended to be operated at pressure as low as 0 bar to avoid exposure to humidity during heating.
- iii. The time exposing the sample to the atmosphere during sample characterization is to be minimized.

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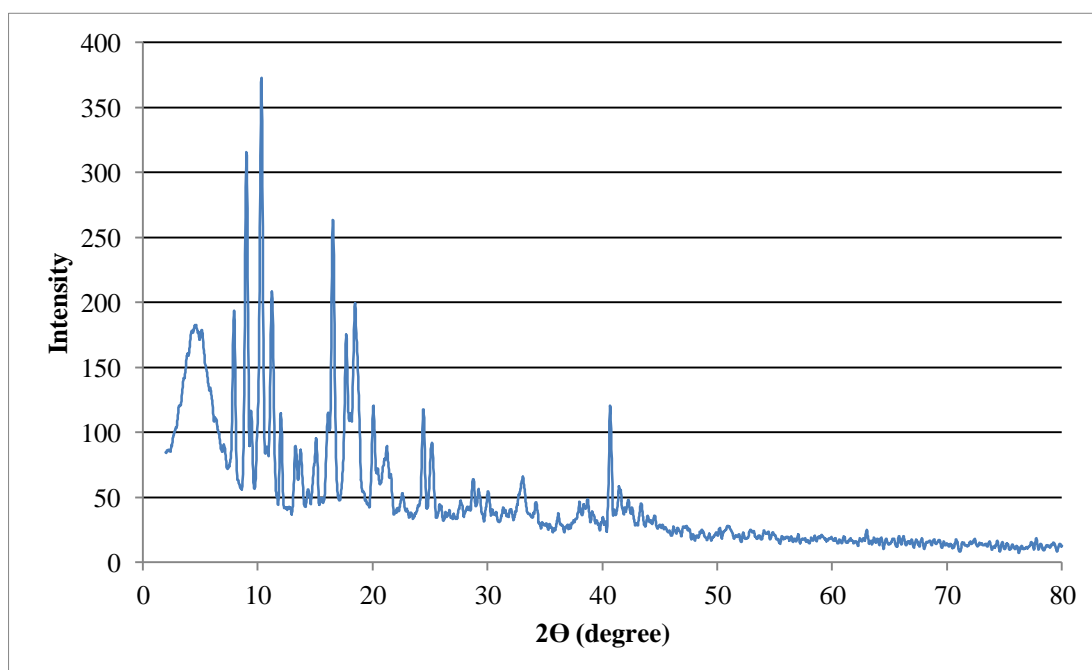
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APPENDICES

APPENDIX I. Percentage Yield Equation

$$\text{Percentage Yield} = \frac{\text{mass of actual yield}}{\text{mass of theoretical yield}} \times 100\%$$

APPENDIX II. XRD Patterns of Microwave Synthesis at 150°C for 4 hours



APPENDIX III. Spectroscopy Data Tables for FTIR Absorption

