Preparation and Characterization of Metal Organic Framework (MOF) Materials

by

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is 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.

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ABSTRACT

One of the metal-organic framework (MOF) material known as MOF-2, with the formula of $Zn_2(BDC)_2$ (where Zn = zinc, BDC = benzenedicarboxylic acid) is commonly synthesized at room temperature. In current project, MOF-2 was synthesized using solvothermal method at higher temperature. The current project attempted to study the effect of different temperature and time of synthesis on MOF-2. Several characterization analysis have been performed on the MOFs samples to determine the properties of MOF-2 that have been produced which included Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), and Particle Size Analyzer (PSA). The study demonstrated differences as well as similarities of MOF-2 properties for different synthesis parameters.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

1.1   Background

Metal-Organic Frameworks (MOFs) are defined as compounds that consist of metal ions or clusters coordinated to organic molecules to form one-, two-, or three-dimensional structures that are composed of the tunable metal clusters and organic linkers. Employing a simple cubic topology, Figure 1.1 shows the metal ions or clusters (metal nodes) that serve as points connecting the structure meanwhile the organic linkers serve as bridges connecting the metal nodes to form three-dimensional framework.

organic linkers   metal ions or clusters   metal organic frameworks
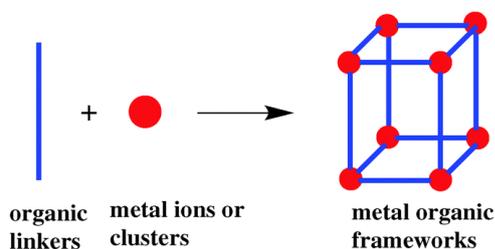
Figure 1.1   Connection of organic linkers and metal ions (or clusters) leads to a three-dimensional framework.

As a unique class of hybrid nanoporous materials, metal-organic frameworks have attracted considerable interest in recent years (Chen et al., 2010). MOFs have an exceptionally large surface areas and well-defined pores. Other than that, it display high crystalline structure, strong bonding providing robustness, linking units that are available for modification by organic synthesis (Jesse et al., 2004). Because of its characteristics, they are considered as an excellent candidates for separation, storage,

catalysis, and other evolving applications. Typically, in MOF-2 case, they are obtained either through experiment at room temperature with or without the presence of amine, or through the transformation of MOF-1. In this research, the aim is to synthesis MOF-2 at different temperature and heating time using conventional method known as solvothermal method rather than at room temperature. The effect of different temperature and time were analyzed using several characterizations analysis such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), and Particle Size Analyzer (PSA) to examine MOF's surface morphology, thermal stability, functional group and particle size respectively.

1.2   Problem Statement

MOFs, and other well-known materials such as silica and activated carbon have been widely applicable as adsorbents. As a new class of hybrid nanoporous material, MOFs have attracted interest in its adsorption ability due to its extremely large surface area and well defined pores. It has been claimed by a researcher that MOFs materials can exceed the performance of activated carbon when removing toxic industrial chemicals from air. MOFs unique characteristic of having uniform pores structure compared to other materials has making it a more preferable candidate in adsorption. It has also been investigated that the drawback of activated carbon in vacuum pressure swing adsorption (VPSA) is low selectivity. Hence kinetic based materials like MOFs are preferred. Furthermore, MOFs have the possibility to alter their structures and functional properties by shifting the building blocks used in their construction. With the ability to control pore dimension, shape of the channels, and chemical potential of the surface, making it possible to build the adsorbent with the desired adsorption properties (Mangano et al., 2013).

Compared to other MOFs, MOF-2 was usually synthesized at room temperature with or without the presence of triethylamine (TEA) depending on what type of zinc was used. At room temperature, they were left under continuous stirring,

however the time for stirring depends on the type of zinc used. There were only a few studies reported for synthesis of MOF-2 using solvothermal method. Solvothermal method is a conventional method that has been widely used in synthesizing MOFs.

One of the most difficult part in engineering MOFs is determining the correct synthesis parameters such as temperature, heating time, pressure, metal source, organic ligands and solvents that will yield the desired structure (Ordonez et al, 2014). So far, to the best knowledge, there is no study that has been done on synthesis parameters of MOF-2 using solvothermal method. Hence, this project will focus on the parameters affecting the characterization of MOFs which are temperature and heating time. Several characterization techniques were performed to analyze the characteristics of MOFs that have been synthesized.

1.3 Objectives

The main objectives of this project are:

i.   To synthesize metal organic frameworks material – MOF-2 using solvothermal method.

ii.   To study the effect of synthesis temperature and heating time on the formation of metal organic frameworks material – MOF-2

iii.   To characterize metal organic frameworks material – MOF-2 using different analytical techniques.

1.4   Scope of Study

The project is focusing on synthesizing MOF-2 material which is $Zn_2(BDC)_2$ where; Zn = zinc, BDC = benzenedicarboxylic acid, using solvothermal method. The effect of the synthesis temperature and time on the characteristics of the MOF-2 produced were investigated using FTIR, TGA, SEM, and PSA. Most of the experiment works were done in the Chemical Engineering laboratory and some of the characterizations were done in Mechanical Engineering laboratory, UTP.

CHAPTER 2

LITERATURE REVIEW

2.1   Porous materials

Porosity is the capability to hold a fluid. A solid can be regarded as porous if the voids in its structure are large enough to accommodate guest molecules (Yilmaz et al., 2012). In industry, the ability to bring molecules in and out of a porous material has proven to be greatly beneficial. Uniform porosity which is found in MOF supports the utilization of the pores as it allows more control of transport in and out of the structure. Yilmaz et al. (2012) stated that each new MOF has the potential to offer unique structural and chemical features that can be beneficial for an industrial application.

One of the significance of porosity is in adsorption. MOFs, and other materials such as silica and activated carbon have been widely known as adsorbents. Silica and activated carbon are types of adsorbent broadly used in the purification and separation of organic mixtures due to its high surface area and porosity (Unob et al., 2007). As a new class of hybrid material, MOFs has also attracted interest in its adsorption ability due to its characteristics of having extremely large surface area and well defined pores. Glover (2015) published a paper detailing the importance of tuning MOFs adsorbent surface chemistry to target specific adsorbate gases and he claimed that the outcome is MOFs materials can exceed the performance of activated carbon when removing toxic industrial chemicals from air. Cavenati et al, (2008) performed vacuum pressure swing adsorption (VPSA) by applying equilibrium based adsorbent (activated carbon) and kinetic based adsorbent (MOFs). The drawback of activated carbon is low selectivity. Hence kinetic based materials are preferred

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2.1.1 Metal Organic Frameworks (MOFs)

As a new member of the porous solids family, the number of publications about MOF has been increasing tremendously. There are hundreds of different MOFs that varies in structure types, with chemical flexibility and compositional diversity reported to date. MOFs can be defined as porous crystalline compounds forming 1, 2 or 3 dimensional structures with the use of metal ions. MOFs consist of metal ions and organic molecules known as ligands. Based on Chemwiki (2014), ligands can be described as ions or neutral molecules that bond to a central metal atom or ion. They act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). At least one donor atom with an electron pair is used to form covalent bonds with the central atom. It was claimed that MOFs were born from zeolites, a breakthrough supplement that works at the cellular level by trapping heavy metals and toxins and safely removing them from the body. The high specific surface area with Langmuir surface area reaching 10000 m^2/g and large pore volume up to 3 cm^3/g of MOFs led them as perfect candidates for catalysis, gas adsorption, separation of gases and other applications. The pore size and surface area can be modified by changing the synthetic conditions. In the future, it is believed that MOFs are able to replace zeolites at every level due to its large surface area to volume. Table 2.1 represents different types of MOFs with their surface area and pore volume.

Table 2.1   Different types of MOFs with surface area and pore volume

MOF	Surface area (m^2/g)	Pore volume (cm^3/g)
MOF – 177	3875	1.59
MOF – 5	2205	1.22
MOF – 1	1794	0.65
IRMOF – 3	1568	1.07
IRMOF – 62	1814	0.99
MOF – 199	1264	0.75
MOF – 74	632	0.39

2.1.1.1 Synthesis Technology

In preparation of MOFs, there were different methods and operating conditions that have been applied by the different researchers as shown in Table 2.2.

Table 2.2   Preparation of different MOFs

MOFs	Technology	Temperature	Time	Reference
Ni-MOF-74	Hydrothermal	100℃	1 day	Wu et al., (2013)
$Cu(BDC)(TED)_{0.5}$	Solvothermal	120℃	1 ½ day	Lee et al., (2007)
$Zn(BDC)(TED)_{0.5}$	Solvothermal	120℃	2 days	Lee et al., (2007)
$Cu(BDC)(TED)_{0.5}$	Conventional	120℃	1 ½ day	Tan et al., (n.d.)
$Ni(BDC)(TED)_{0.5}$	Conventional	120℃	2 days	Tan et al., (n.d.)
$Co(BDC)(TED)_{0.5}$	Conventional	120℃	2 days	Tan et al., (n.d.)
MOF-500	Conventional	100℃	1 day	Sudik et al., (2006)

2.1.1.2 Characterization techniques

Table 2.3 displays the different characterization techniques used on MOF in past researches.

Table 2.3   Different characterization techniques used in research

Technique	Reason	Reference
FESEM (S4800, Hitachi)	To evaluate morphologies of the sample	Liu et al., (2014)
XRD (D8 Advance, Bruker)	To characterize crystal structure	
FESEM (S4800, Hitachi)	To characterize morphology and thickness of the sample	Huang et al., (2014)
XRD (D8 Advance, Bruker)	To identify phase purity and crystallinity	
TGA (Perkin-Elmer)	To evaluate the thermal stability of the sample	

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PXRD	To confirm structural integrity of the sample	Chen et al., (2010)
High pressure adsorption analyzer (HPVA-100)	To get pressure gas isotherm graph	

2.1.1.3 MOF-2

2.1.1.3.1   Synthesis method for MOF-2

MOFs were frequently synthesized using conventional solvothermal method by heating a mixture of metal salt and organic linker in a solvent that typically contains formamide to temperatures near or above the boiling point of the solvent (Getachew et al., 2014). This method is widely used since it is commonly used to synthesize other porous materials and often yield crystals suitable for XRD.

However, some researchers synthesized MOF-2 at room temperature. This was done under stirring for few hours or up to days. The presence of amine is depends on the metal salt used. Usually when zinc acetate dehydrate is used instead of zinc nitrate hexahydrate, no amine is needed.

Table 2.4 represents the technologies that have been used to prepare $Zn_2(BDC)_2$. In this project, the effect of temperature and time on synthesis of MOF-2 were investigated.

Table 2.4   Preparation technology for MOF-2

MOFs	Technology	Temperature	Time	Reference
$Zn_2(BDC)_2$	-	Room temperature	24 hours	Getachew et al., (2014)
$Zn_2(BDC)_2$	-	Room temperature	-	Li et al., (1998)
$Zn_2(BDC)_2$	Solvothermal	105℃	24 hours	Li et al., (2011)
CdMOF-2.	Microwave	120℃	48 hours	Hu, M. (2011)

CHAPTER 3

METHODOLOGY

3.1   Project Flowchart

Figure 3.1 shows the work flow of the project in final year project 2.

Experiment

⇨ Perform laboratory work to obtain samples

Data collection

⇨ Send the samples to characterization
⇨ Collect and analyze the results

Assessment

⇨ Prepare and submit progress report, dissertation and technical paper
⇨ Viva

Final Report

⇨ Prepare and submit hard bound of project dissertation
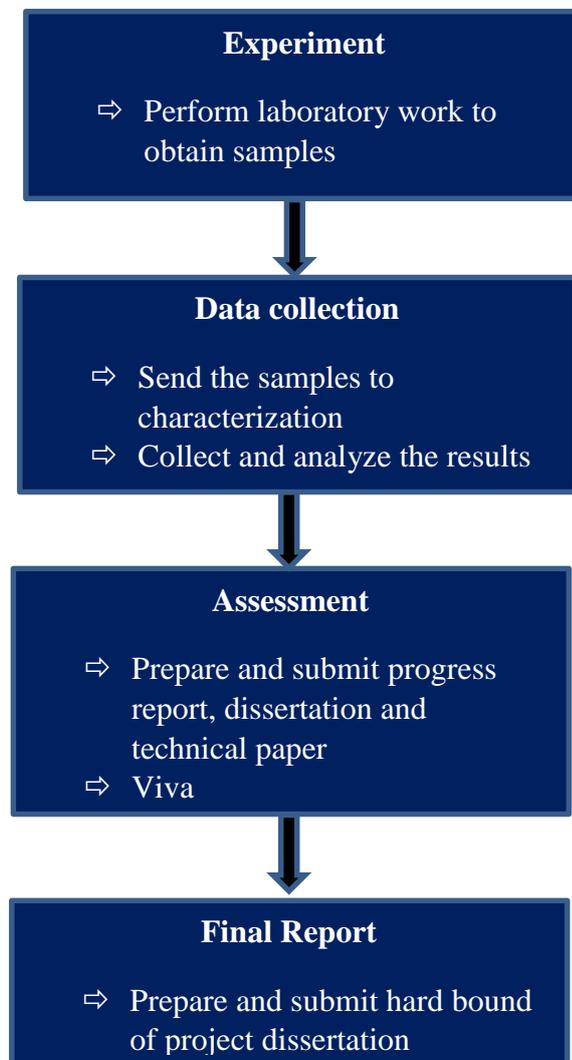
Figure 3.1   Project Flow chart

3.2   Gantt Chart

Figure 3.2 Gantt Chart displays the period allocation for each work progress.

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Experimental work	█	█	█	█	█	█	█								
2	Submission of progress work															
3	Project work continues								█	█	█	█	█			
4	Pre-SEDEX															
5	Submission of draft final report															
6	Submission of dissertation (soft bound)															
7	Submission of Technical Paper															
8	Viva															
9	Submission of Project Dissertation (hard bound)															

Figure 3.2   Gantt Chart

3.3   Key Project Milestones

Figure 3.3 represents the important dates for each work title.
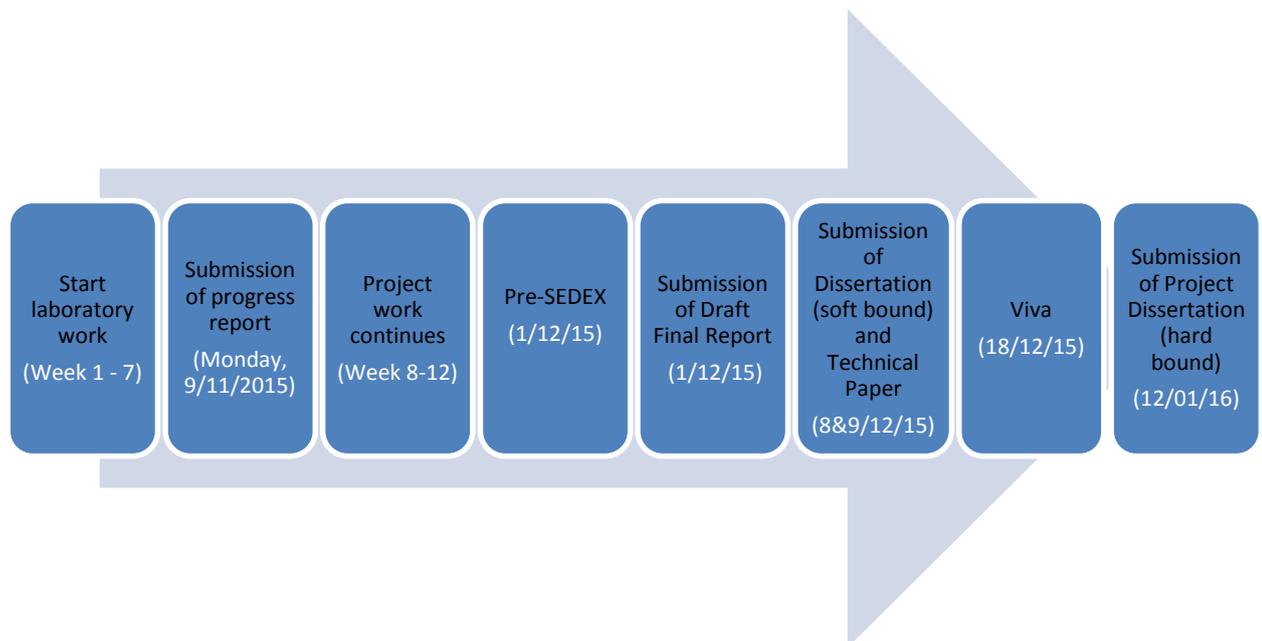
Figure 3.3   Key Project Milestones

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3.4   Material, Apparatus and Equipment

Table 3.1 shows the chemical and material used in the experiment.

Table 3.1   Chemical and material for experiment

No	Material
1	Zinc(II) nitrate hexahydrate
2	H_2BDC
4	DMF
5	Ethanol
6	Acetone
7	Filter paper
8	Aluminium foil
9	Paraffin film

Table 3.2 represents apparatus used in the experiment.

Table 3.2   Apparatus for experiment

No	Apparatus	Quantity
1	Spatula	1
2	250mL beaker	1
3	120mL beaker	1
4	100mL beaker	1
5	100mL measuring cylinder	1
6	10mL measuring cylinder	1
7	Stirring rod	1
8	Filter funnel	1
9	Retort stand	1
10	Petri dish	1
11	Plastic dropper	1
12	Magnetic stirrer bar	1

Table 3.3 displays equipment used in the experiment.

Table 3.3   Equipment for experiment

No	Apparatus	Quantity
1	Weighing balance	1
2	Magnetic hot plate stirrer	1
3	Ultrasonic device	1
4	Oven	1
5	Vacuum oven	1

3.5   Synthesis of MOF-2 material

3.5.1 Preparation of MOF-2 material

1) H_2BDC (0.83 g, 5.0 mmol), zinc(II) nitrate hexahydrate (1.31 g, 5 mmol), and 50 mL of DMF were mixed in the 150 mL beaker.
2) The 150 mL beaker was wrapped with a layer of paraffin film, then the mixture were stirred using magnetic hot plate stirrer to dissolve all solids.
3) The mixture were subjected to ultrasonic treatment at 50℃ for 3 hours until clear solution is obtained.
4) The mixture were then be transferred to vessels and placed in oven to be heated at certain temperature for certain time.
5) Step 1 to 4 was repeated several times with different temperature and synthesis time according to Table 3.4.
6) The sample undergone centrifugation and then was filtered with filter paper.
7) The sample was placed on petri dish to be completely dried under vacuum oven at 100℃ overnight.

Table 3.4   Temperature and synthesis time

Sample	Temperature (°C)	Synthesis time (hour)
1	60	24
2		48
3	80	24
4		48
5	100	24
6		48
7	120	24
8		48

3.5.2   Characterization of MOFs

3.5.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR (model: 8400S, brand: Shimadzu) was used to identify functional group and bonding in the sample.

3.5.2.2 Scanning Electron Microscopy (SEM)

SEM (model: Pro X, brand: Phenom) was used to evaluate the surface morphology of the sample material.

3.5.2.3 Thermal Gravimetric Analysis (TGA)

TGA (model: PYRIS 1, brand: Perkin Elmer) was used to check the thermal stability of the sample.

3.5.2.4 Particle Size Analysis

Particle Size Analyzer (model: MS2000, brand: Mastersizer) was used to measure the particle size of the sample.

CHAPTER 4

RESULT AND DISCUSSION

4.1   Weight of the sample

The weight gain of the samples synthesized under different synthesis time and temperature from the experiment were tabulated in Table 4.1. From Table 4.1, it is observed that the highest weight gain was obtained at synthesis condition of 100℃ for 48 hours while at 60℃, either the solution was heated for 24 or 48 hours, there were no crystal formed. It can be deduced that at temperature of 60℃ and below is not the appropriate temperature to synthesize MOF-2. At lower temperature, the energy supplied was not enough to optimize the formation of metal-ligand bond (Zn-BDC) through condensation process meanwhile at elevated temperature of higher than the boiling point of water, the chemical reaction involving water molecules and metal clusters in MOF could lead to hydrolysis process where ligands were displaced. At temperature more than the boiling point of water, water molecules started to dissociate into H^+ and OH^- that then displaced some ligand, which was BDC bond in the Zn-BDC which resulted in lower weight gain at 120℃ compared to at 100℃ .

Table 4.1   Weight of the samples

Sample	Temperature (°C)	Synthesis time (hour)	Weight (grams)
1	60	24	No crystal formed
2		48	
3	80	24	0.2700
4		48	0.5277
5	100	24	0.6718
6		48	0.7569
7	120	24	0.6100
8		48	0.6832

4.2   Fourier Transform Infrared Spectroscopy

The infrared regions used in FTIR analysis is mid-IR; between 500 to 4000 cm^{-1}, which is the most widely used region to determine the structure of organic and biochemical species. The samples were mixed with potassium bromide and turned into pellet before being analyzed with FTIR. The graphs for FTIR analysis were obtained, and the respective functional groups were determined based on the peak from the graphs, using Appendix A and B as reference.
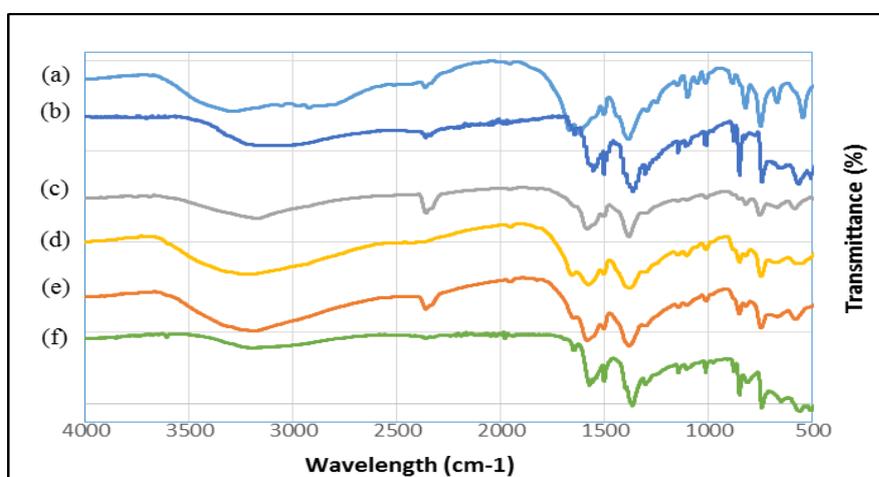

Figure 4.1   FTIR spectrum for MOF-2 synthesized at a) 80 °C, 24 hours, b) 80 °C, 48 hours, c) 100 °C, 24 hours, d) 100 °C, 48 hours, e) 120 °C 24 hours, and f) 120 °C 48 hours.

Based on Figure 4.1, all MOF-2 samples exhibited similar pattern where the transmittance peak fell under the same wavelength range which led to same functional groups and bonds. The functional groups and bonds found in the FTIR spectrum confirmed the existence of the MOF-2 compound. The analyzed bonds included =C-H bend, C-N stretch, C-H, C=C, N-H bend, and O-H. The bonds and functional groups found in FTIR spectrum were listed in Table 4.2. The plots for each samples and their respective functional groups and bonds analyzed can be found in appendix.

Table 4.2:   Bond and functional group of MOF-2 found in FTIR spectrum

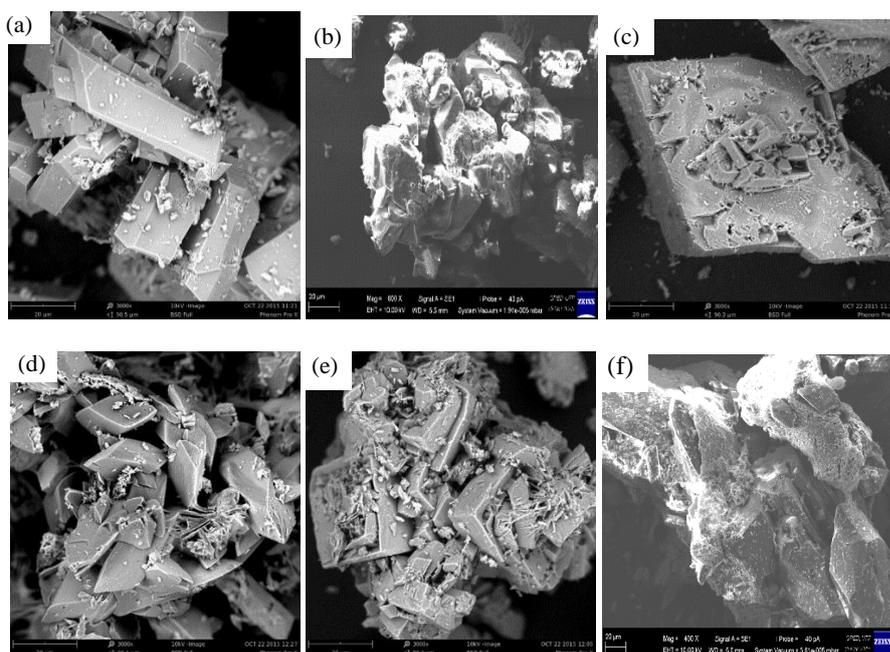| Wavelength (cm^{-1})	Bond	Functional group
1000-650	=C-H bend	Alkenes
1250-1020	C-N stretch	Aliphatic amine
1470-1340	C-H	Alkanes
1680-1610 1650-1580	C=C N-H bend	Alkenes 1° amines
2400-2300	Not available	Not available
3300-2500	O-H	Hydrogen bonded alcohol, phenols

4.3   Scanning Electron Microscopy

Figure 4.2.   SEM images of MOF-2 synthesized at a) 80 ℃, 24 hours, b) 80 ℃, 48 hours, c) 100 ℃, 24 hours, d) 100 ℃, 48 hours, e) 120 ℃ 24 hours, and f) 120 ℃ 48 hours.

As shown in Figure 4.2, the MOFs that have been synthesized using different temperature and time display different SEM images. The images showed the growth of MOF-2 was not uniform and there was polydispersity in shape and size. The shape was seen to be rectangular with slanting structure for all samples.

These SEM results did not produce similar shape to the one synthesized at room temperature as reported by Getachew et al. (2014) or the one synthesized using solvothermal method by Li et al. (2011). However, Figure 4.2 d) resembled SEM image for MOF-2 reported by Aiyappa et al. (2013).

4.4   Thermal Gravimetric Analysis

In TGA, nitrogen gas was used with the temperature rate of 5℃/min. Usually in TGA curves for MOF-2, there were three steps of weight loses observed. The first step of weight loss represents the loss of water molecules, the second weight lost is corresponding to the volatilization of the discrete DMF molecules in the framework, while the last step refers to the decomposition of the MOF-2 framework.
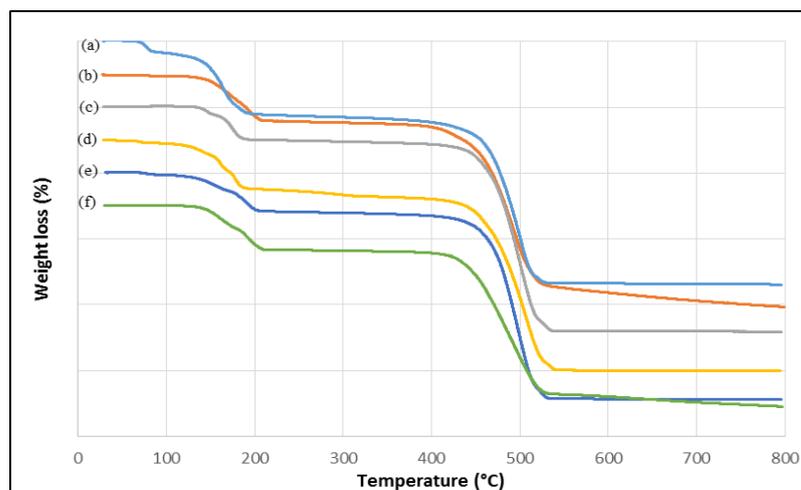

Figure 4.3.   TGA curves of MOF-2 synthesized at a) 80 ℃, 24 hours, b) 80 ℃, 48 hours, c) 100 ℃, 24 hours, d) 100 ℃, 48 hours, e) 120 ℃ 24 hours, and f) 120 ℃ 48 hours.

The first step of weight loss were not visible in the TGA plots because all water molecules present in the samples have been eliminated in vacuum oven, except for Figure 4.3 a), since during the experiment, the pump with the vacuum oven was not functioning. Figure 4.3 a) displayed similar TGA plots as reported by Li, et al. (2011) and Getachew, et al (2014) that have dried the samples naturally. Overall, all the curves have similar pattern to each other.

The first step of weight loss for Figure 4.3 a) was observed around 60℃ (4.07wt%), the second step was below 200℃ (18.28wt%), and the third step of weight

loss was above 400℃ (45.36wt%). Figure 4.3 b) first step of weight loss was seen around 160 ℃ (13.75wt%) and the second step of weight loss at above 400℃ (48.96wt%). The TGA data represented in Figure 4.3 c) has weight losses at 140℃ (10.02wt%), and same as previous data, above 400℃ (56.74wt%). MOF-2 synthesized at 100℃ for 48 hours shown in Figure 4.3 d) exhibited similar graph style as in Figure 4.3 c) where the first step of weight loss observed around 130℃ (11.08wt%), and final weight loss above 400℃ (55.56wt%). For Figure 4.3 e), first weight loss at 130℃ (13.83wt%) and second weight loss at 440℃ (52.06wt%) meanwhile Figure 4.3 f) has weight loss at 140℃ (13.51wt%) and at 420℃ (43.01wt%).

Table 4.2 tabulated the total weight loss for each samples in TGA where the highest weight loss was at 80℃ 24 hours.

Table 4.3   Total weight loss (%) for MOF-2 in TGA

Sample	Temperature (℃)	Synthesis time (hour)	Total weight loss (%)
a)	80	24	73.95
b)		48	70.72
c)	100	24	68.33
d)		48	70.12
e)	120	24	68.98
f)		48	61.03

4.5   Particle Size Analysis

The particle size of MOF-2 at different synthesis parameters was tested at refractive index of 1.500.
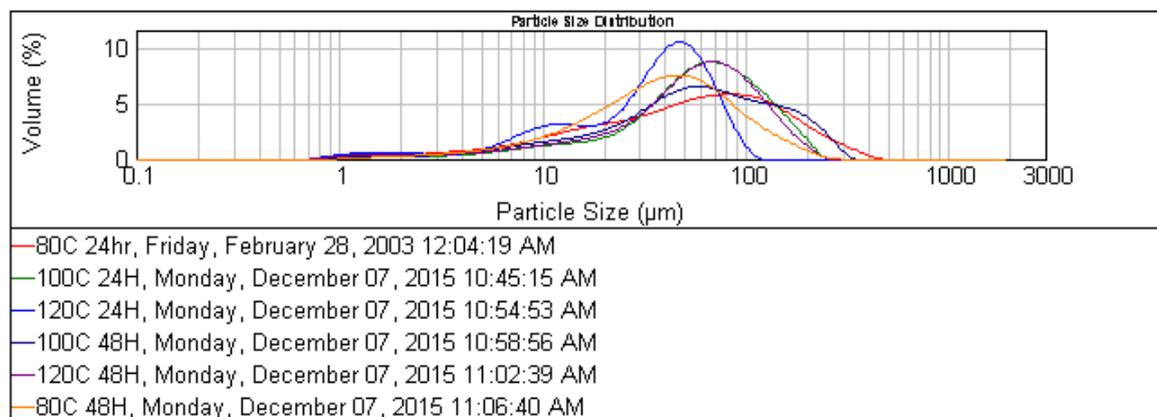

Figure 4.4   Particle Size Distribution

Figure 4.4 presented the particle size distribution of MOF-2. It could be seen that each samples has distinct particle size distribution with the average specific surface area of 0.288 m^2/g, surface weighted mean of 20.865μm and volume weighted mean of 49.684 μm. Table 4.4 showed the particle size diameter for each sample.

Table 4.4   Particle size of MOF-2

Sample	Temperature (°C)	Synthesis time (hour)	Particle size, diameter (μm)
a)	80	24	55.862
b)		48	39.187
c)	100	24	60.470
d)		48	57.589
e)	120	24	36.436
f)		48	56.867

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CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1   Conclusion

According to the study, it can be concluded that the temperature of 60℃ and lower is not suitable to synthesize MOF-2 as it will not produce any crystal. Meanwhile 100℃ was found to be the optimum temperature with the highest weight gain. For the characterization, FTIR spectrum found that all the MOF-2 samples contained =C-H bend, C-N stretch, C-H, C=C, N-H bend, and O-H bonds. SEM images showed polydispersity in shape and size for each samples. TGA graphs observed the step of weight losses for the samples at below 100℃, above 100℃, and above 400℃ while the particle size distribution exhibited different particle size for each samples.

5.2   Recommendation

In future work, this project can be further improved by running more synthesis' parameters of temperature and time so that the parameters can be studied in more details. Other than that, the characteristics of the MOFs can be analyzed using various techniques such as X-ray Diffraction (XRD), Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM).   Furthermore, the application of the MOFs in separation, drug delivery, catalysis and storage should be analyzed as well.

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APPENDICES

Table of Characteristic IR Absorptions

frequency, cm^{-1}	bond	functional group
3640–3610 (s, sh)	O–H stretch, free hydroxyl	alcohols, phenols
3500–3200 (s,b)	O–H stretch, H–bonded	alcohols, phenols
3400–3250 (m)	N–H stretch	1°, 2° amines, amides
3300–2500 (m)	O–H stretch	carboxylic acids
3330–3270 (n, s)	–C≡C–H: C–H stretch	alkynes (terminal)
3100–3000 (s)	C–H stretch	aromatics
3100–3000 (m)	=C–H stretch	alkenes
3000–2850 (m)	C–H stretch	alkanes
2830–2695 (m)	H–C=O: C–H stretch	aldehydes
2260–2210 (v)	C≡N stretch	nitriles
2260–2100 (w)	–C≡C– stretch	alkynes
1760–1665 (s)	C=O stretch	carbonyls (general)
1760–1690 (s)	C=O stretch	carboxylic acids
1750–1735 (s)	C=O stretch	esters, saturated aliphatic
1740–1720 (s)	C=O stretch	aldehydes, saturated aliphatic
1730–1715 (s)	C=O stretch	α, β–unsaturated esters
1715 (s)	C=O stretch	ketones, saturated aliphatic
1710–1665 (s)	C=O stretch	α, β–unsaturated aldehydes, ketones
1680–1640 (m)	–C=C– stretch	alkenes
1650–1580 (m)	N–H bend	1° amines
1600–1585 (m)	C–C stretch (in–ring)	aromatics
1550–1475 (s)	N–O asymmetric stretch	nitro compounds
1500–1400 (m)	C–C stretch (in–ring)	aromatics
1470–1450 (m)	C–H bend	alkanes
1370–1350 (m)	C–H rock	alkanes
1360–1290 (m)	N–O symmetric stretch	nitro compounds
1335–1250 (s)	C–N stretch	aromatic amines
1320–1000 (s)	C–O stretch	alcohols, carboxylic acids, esters, ethers
1300–1150 (m)	C–H wag (–CH$_2$X)	alkyl halides
1250–1020 (m)	C–N stretch	aliphatic amines
1000–650 (s)	=C–H bend	alkenes
950–910 (m)	O–H bend	carboxylic acids
910–665 (s, b)	N–H wag	1°, 2° amines
900–675 (s)	C–H "oop"	aromatics
850–550 (m)	C–Cl stretch	alkyl halides
725–720 (m)	C–H rock	alkanes
700–610 (b, s)	–C≡C–H: C–H bend	alkynes
690–515 (m)	C–Br stretch	alkyl halides

m=medium, w=weak, s=strong, n=narrow, b=broad, sh=sharp

Appendix A   IR absorption table

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes $\left(>C=C<_H\right)$	3010–3095	Medium
		675–995	Strong
C—H	Alkynes (—C≡C—H)	3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
C=C	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C≡N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO$_2$	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

Appendix B   IR absorption table
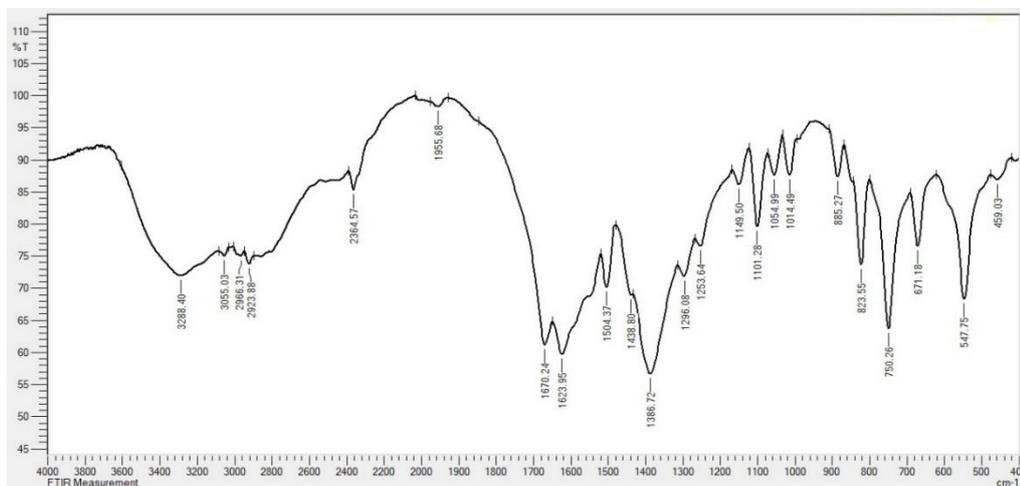
Peak	Bond	Functional group
750.26	=C-H bend	Alkenes
1101.28	C-N stretch	Aliphatic amine
1386.72	C-H	Alkanes
1623.95	C=C	Alkenes
	N-H bend	1° amines
3288.40	O-H	Hydrogen bonded alcohol, phenols

Appendix C   FTIR data for MOF-2 at 80℃, 24 hours

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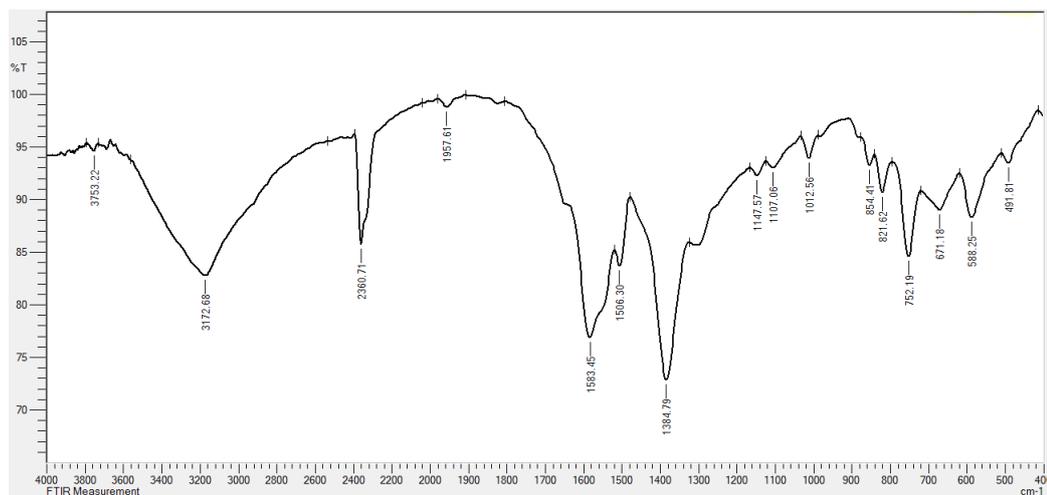
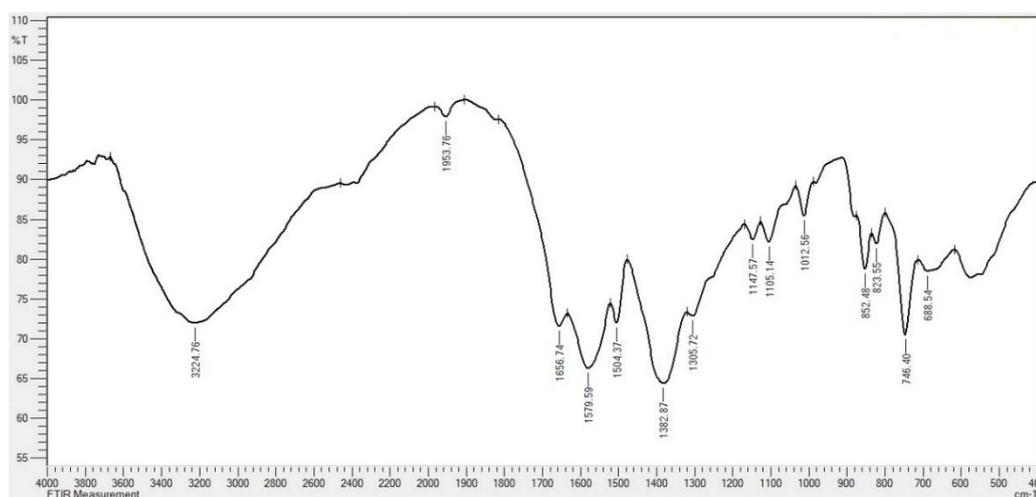| Peak	Bond	Functional group
752.19	=C-H bend	Alkenes
1384.79	C-H	Alkanes
1583.45	C=C	Aromatic rings
3172.68	O-H stretch	Carboxylic acid

.Appendix D   FTIR data for MOF-2 at 100℃, 24 hours
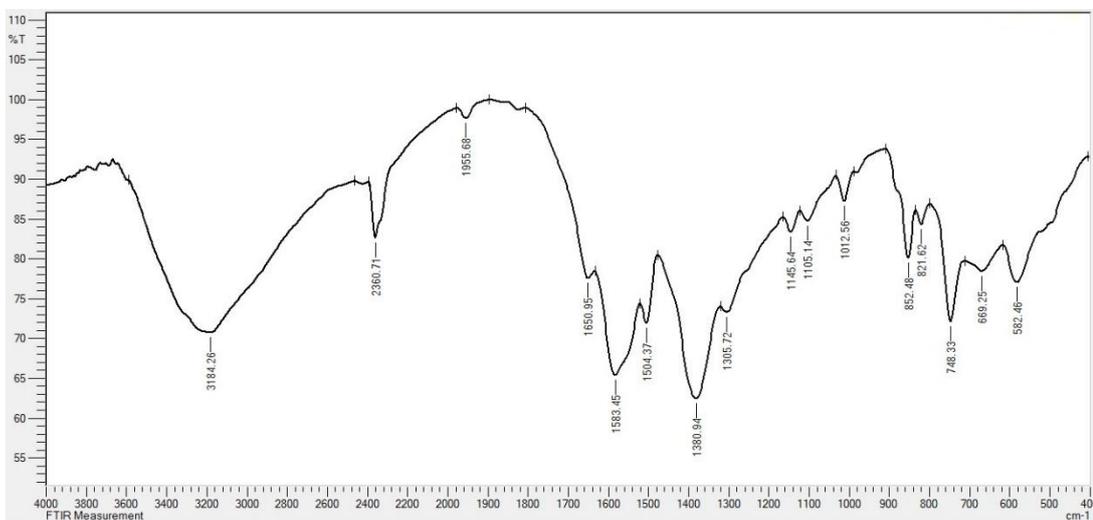
Peak	Bond	Functional group
748.33	=C-H bend	Alkenes
1380.94	C-H	Alkanes
1583.45	C=C	Aromatic rings
3184.26	O-H stretch	Carboxylic acid

Appendix E   FTIR data for MOF-2 at 120℃, 24 hours
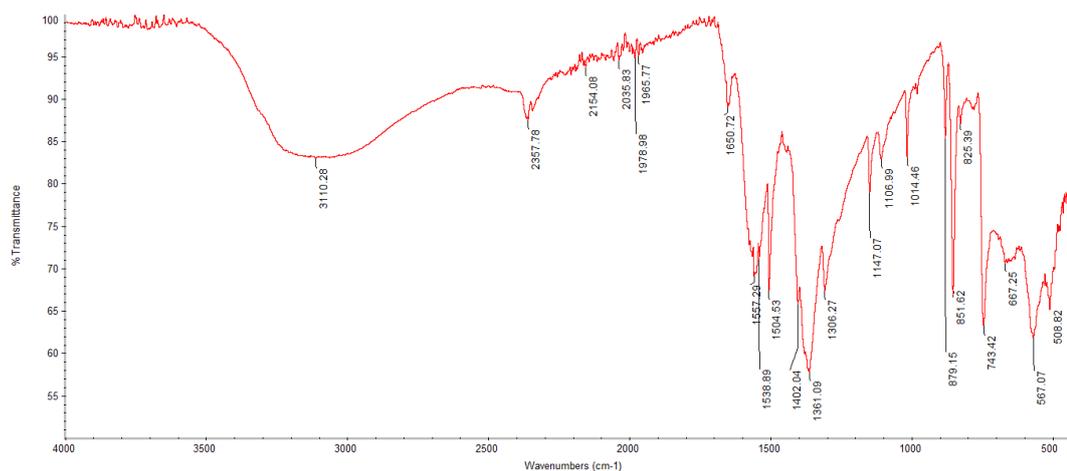
Peak	Bond	Functional group
743.42	=C-H bend	Alkenes
1361.09	C-H	Alkanes
1557.29	C=C	Aromatic rings
3110.28	O-H stretch	Carboxylic acid

Appendix F   FTIR data for MOF-2 at 80℃, 48 hours

Peak	Bond	Functional group
746.40	=C-H bend	Alkenes
1382.87	C-H	Alkanes
1579.59	C=C	Aromatic rings
3224.76	O-H stretch	Carboxylic acid

Appendix G   FTIR data for MOF-2 at 100℃, 48 hours
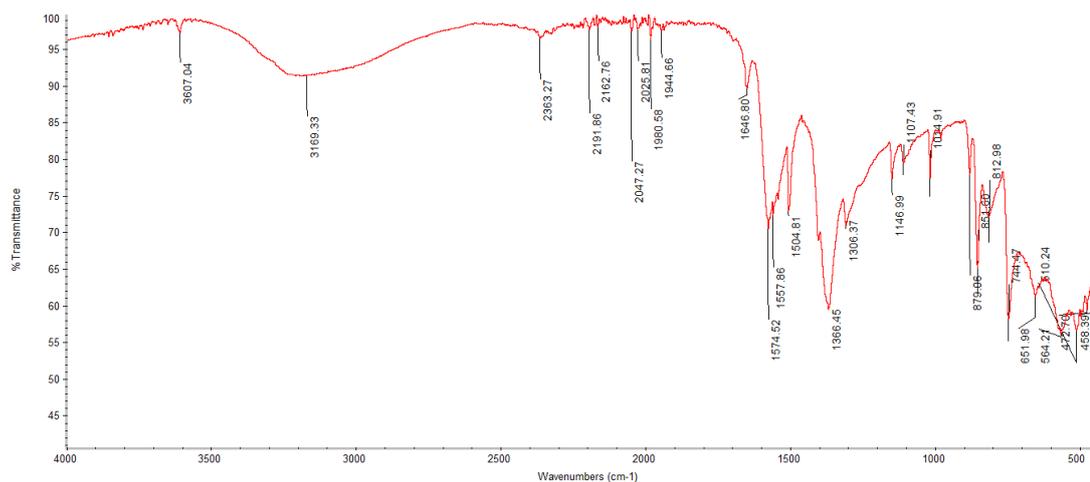
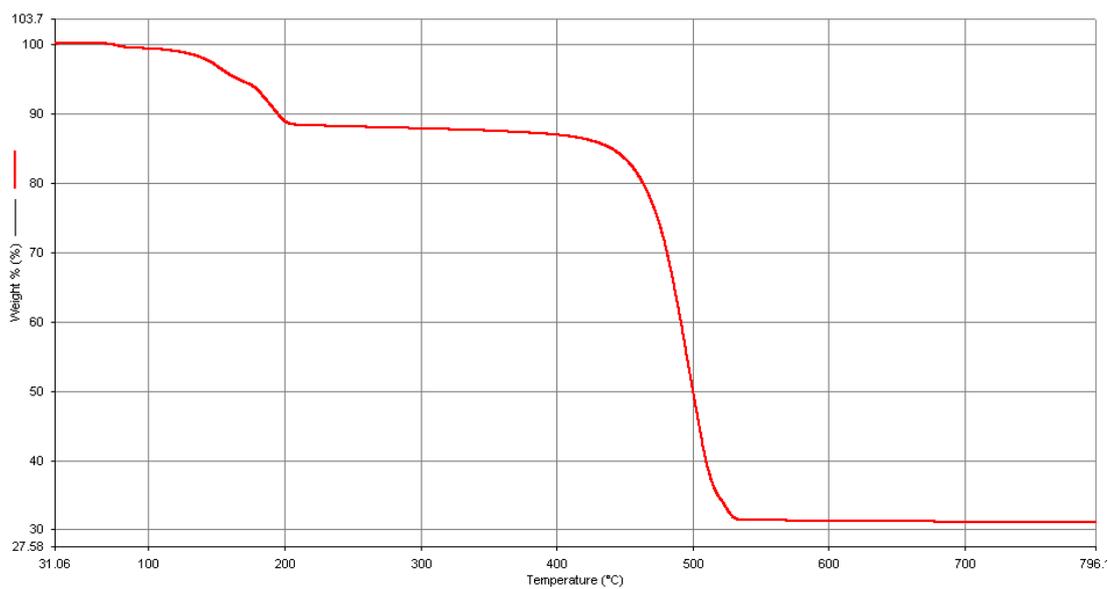| Peak	Bond	Functional group
744.47	=C-H bend	Alkenes
1366.45	C-H	Alkanes
1574.52	C=C	Aromatic rings
3169.33	O-H stretch	Carboxylic acid

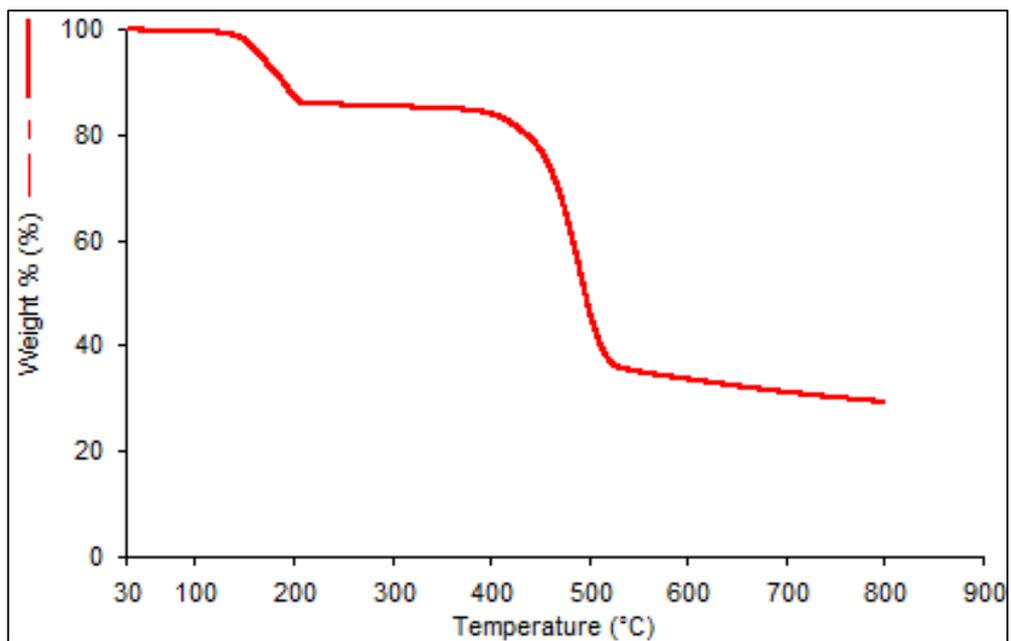Appendix H   FTIR data for MOF-2 at 120℃, 48 hours
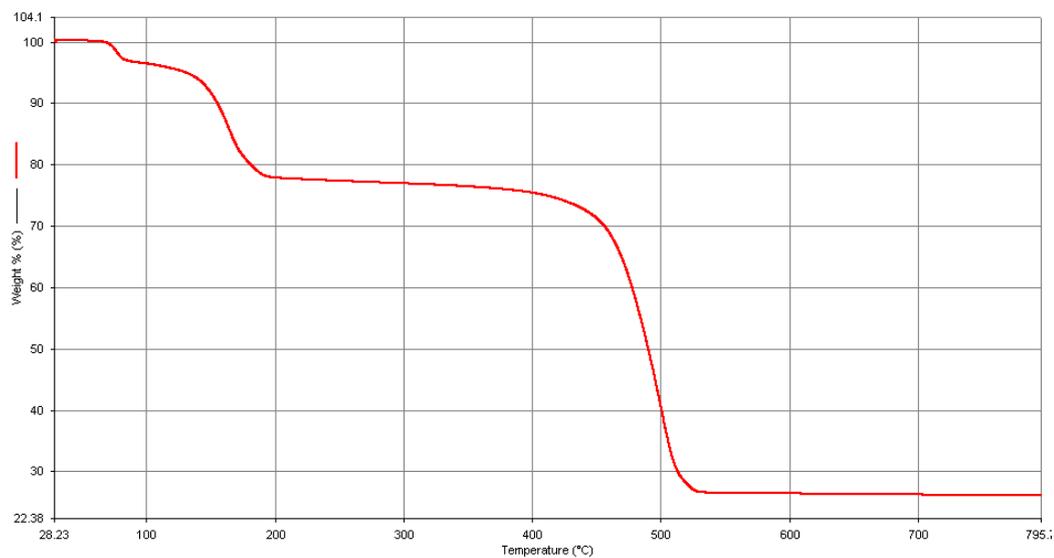
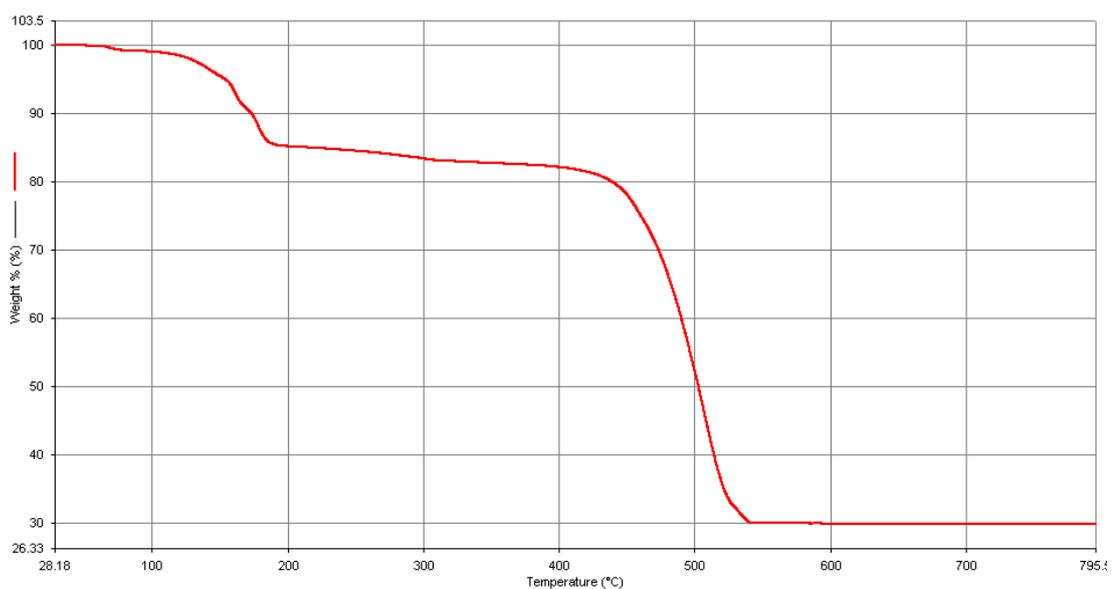Appendix I   TGA data for MOF-2 at 80℃, 24 hours
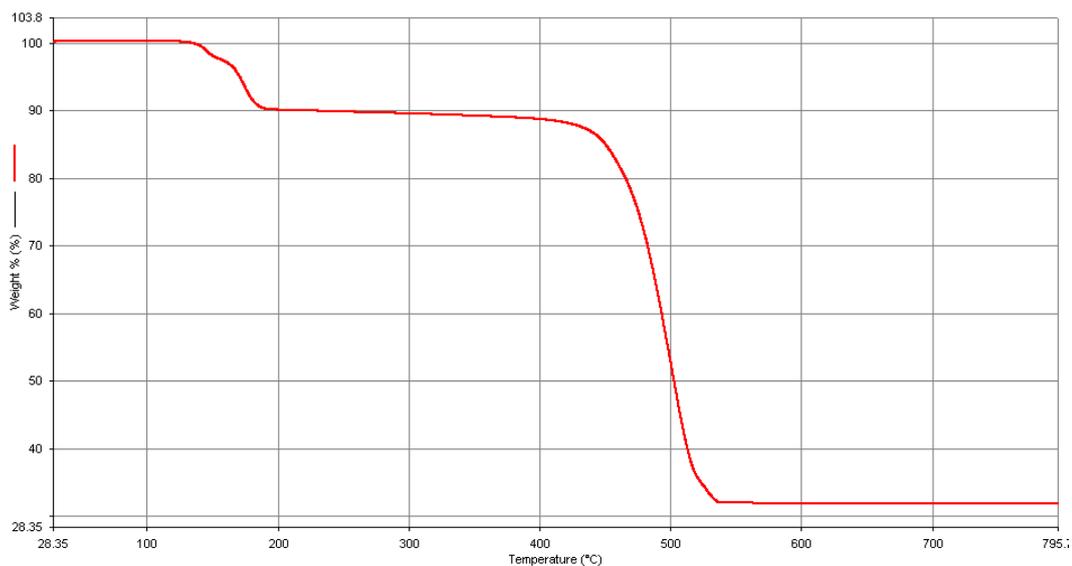
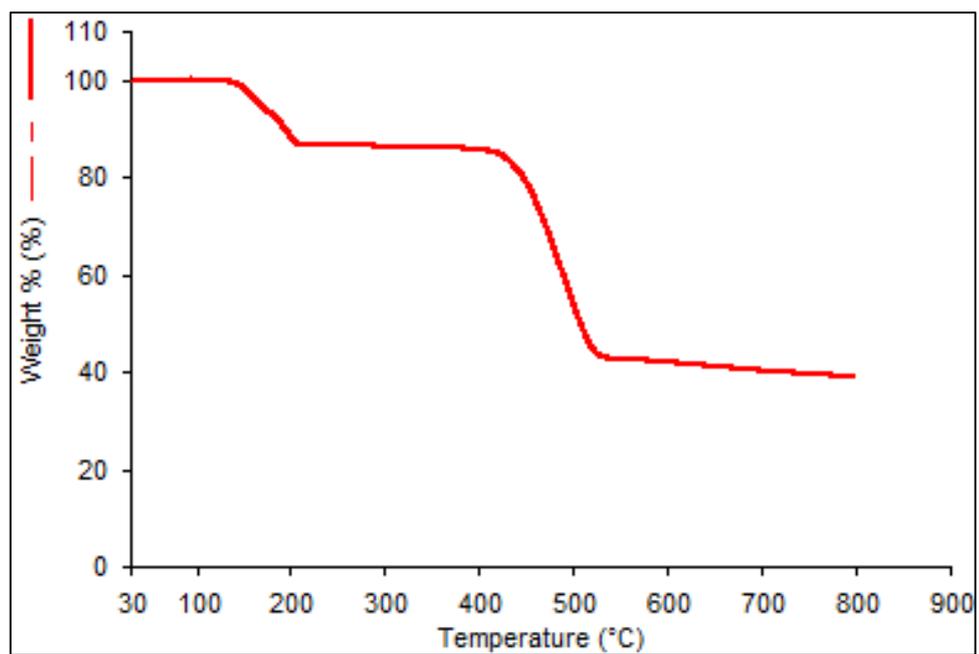Appendix J   TGA data for MOF-2 at 100℃, 24 hours

Appendix K   TGA data for MOF-2 at 120℃, 24 hours

Appendix L   TGA data for MOF-2 at 80℃, 48 hours

Appendix M   TGA data for MOF-2 at 100℃, 48 hours

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Appendix N   TGA data for MOF-2 at 120℃, 48 hours