

**Synthesis, Characterization and Modification of Metal Organic
Framework-74 for CO₂ Adsorption**

by
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13850

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

MAY 2014

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CERTIFICATION OF APPROVAL

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Approved by,

(Dr. Ghulam Murshid)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

August 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the originality 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.

(LAU WEI CHENG)

ABSTRACT

Currently, CO₂ capture is a topical issue in environmental preservation and sustainable growth in development. This review highlights the recent studies on synthesis and characterization in metal organic framework (Mg-MOF-74) for CO₂ capture and also the recent advances in the development of amine functionalized Mg-MOF-74 for CO₂ capture. In this study, CO₂ adsorption on Magnesium-MOF-74 and Magnesium-MOF-74-AMP were investigated and compared.

Fitting in as fascinating class of nano-porous materials, MOFs have been considered potential candidates for CO₂ capture due to its capability of adsorption. However, water stability is often considered a big weakness of all kinds of metal-organic framework structures available for now. As such, Mg-MOF-74 does not exhibit such degradation which has a characteristic of strong coordination bond strength and remarkable as one of the highest CO₂ uptake capacity among MOFs.

Here, Mg-MOF-74 was synthesized by using magnesium nitrate, Mg(NO₃)₂·6H₂O and 2,5-dihydroxyterephthalate acid in the presence of dimethylformamide (DMF), ethanol and deionized water under conventional hydrothermal method. Thereafter, Mg-MOF-74 was grafted with 2-amino-2-methyl-1-propanol (AMP). Characterization techniques applied are Fourier transform infrared (FTIR), thermogravimetry analysis (TGA), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), and the performance of CO₂ adsorption on both MOFs is studied using BET method.

It was found that amine grafted MOF-74 (MOF-74-AMP) has higher CO₂ adsorption capacity with a reported value of 0.0046mol/g as compared to MOF-74 with a reported value of 0.002mol/g. This work may be helpful in the integration of amine-grafted MOF-74 applications in CO₂ capture.

ACKNOWLEDGEMENTS

In completion of this final year project, I would first like to acknowledge my supervisor, Dr. Ghulam Murshid, for all his help and unconditional guidance throughout the past two semesters. The advice and opportunities that he has provided me with have forever shaped my career and life.

I would like to also thank Dr. Sami Ullah for his professional and active role in directing my research toward higher-impact areas. He has been a great collaborator and always provided constructive feedback on my project.

Furthermore, I would like to thank my beloved family members starting with my father for always pushing the importance of science and math education, my mother and sisters for being patient listeners to all my struggles. This would not be possible without any of you.

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ABBREVIATIONS & NOMENCLATURES

AMP	2-Amino-2-Methyl-1-Propanol
BET	Brunauer–Emmett–Teller method
CO ₂	Carbon Dioxide gas
DMF	Dimethylformamide
ED-Mg/DOBDC	Ethylenediamine Functionalized Mg/DOBDC
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
IGCC	Integrated Gasification Combined Cycle
IR	Infrared
Mg/DOBDC	Magnesium /1,4-dioxido-2,5-benzenedicarboxylate, also named as Mg-MOF-74, CPO-27-Mg
Mg-MOF-74	Magnesium MOF-74
Mg-MOF-74-AMP	2-Amino-2-Methyl-1-Propanol Functionalized Magnesium Metal Organic Framework-74
Mg(NO ₃) ₂ ·6H ₂ O	Magnesium Nitrate
MOF	Metal Organic Framework
PXRD	Powder X-ray Diffraction
R&D	Research and Development
TGA	Thermogravimetry Analysis
TEM	Transmission Electron Microscope
VPFESEM	Variable Pressure Field Emission Scanning Electron Microscope

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Carbon dioxide (CO₂) is classified as one of the most significant greenhouse effect contributors. From year to year, the level of CO₂ emission keeps on rising till reaching a perturbation stage (Synthesis Report, 2007). Currently over three quarter of the global energy demand comes from the burning of fossil fuels support (Benson et al., 2008). Excessive emission of CO₂ into the atmosphere can cause global warming (Uniglobetravel, 2014). Therefore, adequate technologies have to be set up to avoid the release of CO₂ into the atmosphere.

Amongst these alternative technologies are adsorption based CO₂ capture, membrane processes, cryogenic methods, hydrate processes, electrochemical techniques and other niche methods, adsorption process is considered better as compared to other methods because of its simplicity of design and simple operation (Bhatnagar et al., 2006). Early applications in the 1950s depended on molecular sieves, alumina and silica materials for capturing CO₂ from air in enclosed regions (Webley, 2014).

There are two groups of adsorbents used for CO₂ removal, which are physisorbents and chemisorbents. Physisorbents act as a molecular sieve and adsorb CO₂ onto their surfaces. They have large surface area and higher porosity. However, adsorption rate of CO₂ is still low in the presence of other gases such as N₂. Chemisorbents are basically made up of amine functionalized materials which can react with CO₂ chemically. Generally, a good adsorbent should have these three characteristics: (1) high adsorption capacity, (2) high selectivity and (3) full regeneration capacity (Gargiulo et al., 2014).

Metal Organic Frameworks (MOFs) are porous structures with one, two or even three dimensional. They consist of metal ions connected to rigid organic linker. In processes like gas purification and separation processes, as well as in catalyst, large number of MOFs has been applied. (Wikipedia, 2014). MOFs with high versatility can function as functional, active and integral components in a MOF-based device due to their high porosity and structural flexibility (Liu, 2012).

Synthesis method of MOFs carried out in room temperature is proven that can be implemented to synthesize the same porous MOF in a quick manner as compared to solvothermal method (Tranchemontagne et al., 2008). Its adsorption capacity was found to be 8.61 mmol/g (37 wt%) at temperature of 25°C and pressure of 1 bar, which is higher than zeolite 13X (3.3mmol/g (14.5 wt%)) under the same conditions as reported in thesis Sabouni, 2013.

Adjusting or changing the connectivity and nature of the organic linker can produce different type of metal organic frameworks (Sabouni et al., 2013). Synthesis of MOFs with free amine can result in better adsorption capability. Several MOFs can be synthesized by grafting the pores with amine functional groups to enhance CO₂ uptake. Studies have proven that the presence of basic amino groups grafted on MOFs can increase the heat of adsorption which indicates stronger interaction with CO₂ gases (Uzun et al., 2014).

Moving forward in the synthesis of MOFs, amine grafted MOFs are said to have higher loading capacity for CO₂ adsorption (Kizzie, 2012). The focus of this study is on amine treatment on MOF-74 (metal – Magnesium). The effect on CO₂ adsorption performance of amine grafted Mg-MOF-74 is yet to well understand. Therefore, CO₂ adsorption on metal organic frameworks MOF-74 and amine-modified MOF-74 are investigated.

MOF-74 is synthesized by using 2,5-Dihydroxyterephthalic acid and Mg(NO₃)₂.6H₂O in the presence of dimethylformamide (DMF) , ethanol and deionized water. Then, free amine group, AMP known as 2-amino-2-methyl-1-propanol are grafted to MOF-74 to form amine-modified MOF-74. The hypothesis was verified through the study of CO₂ adsorption capacities using BET. This study focuses on tremendously increase in the CO₂ adsorption capacity of MOF-74 (Mg) even with water, thus leading to development in CO₂ capture application.

1.2 PROBLEM STATEMENT

Global environmental issue currently concerns on the increase in carbon dioxide concentration in the atmosphere. Among the greenhouses gases, CO₂ contributes more than 60% to the global warming. Therefore, there are several researches done on the synthesis of many metal organic frameworks (MOFs) for CO₂ adsorption including MOF-74 as well as characterization and modification of MOF frameworks.

Despite the multitude of metal organic framework structures available, many degrade in the presence of water. Water stability is often considered a major weakness for metal organic frameworks (MOFs). Structures formed via zinc-carboxylate bonding often exhibit such degradation, for example, MOF-177 and MOF-51 which attribute to weak coordination bond strength.

Therefore, in this study, CO₂ adsorption on metal organic framework, Mg-MOF-74 will be investigated through characterization and modifications which can be done to improve CO₂ adsorption capacity.

1.3 OBJECTIVE

This project will focus on the development of synthesis, characterization and modification of the potential candidate, metal organic framework, Mg-MOF-74 for CO₂ adsorption.

The three main objectives for this study are as follow:

- i. To carry out synthesis of both samples MOF-74 (m-Mg) and MOF-74 (m-Mg) functionalized by 2-amino-2-methyl-1-propanol (AMP).
- ii. To characterize the synthesized samples of MOF-74 (m-Mg) and Mg-MOF-74-AMP via FTIR, TGA, FESEM and TEM.
- iii. To study the performance of CO₂ adsorption on samples, MOF-74 (m-Mg) and Mg-MOF-74-AMP using BET.

1.4 SCOPE OF STUDY

The three main scope of study for this research will be:

- Study and familiar with the experimental procedure on synthesizing metal organic frameworks, MOF-74 (m-Mg) and modified MOF-74-AMP.
- Study on various analysis methods to identify the characteristics of MOF-74 (m-Mg) and modified MOF-74-AMP.
- Study on the CO₂ adsorption capacity of the two metal organic frameworks, MOF-74 (m-Mg) and modified Mg-MOF-74-AMP.

1.5 RELEVANCY OF PROJECT

This study is important because it has a strong relationship with the current global environmental issue in industries in which relates to the adsorption of CO₂ molecules. Modified Mg-MOF-74-AMP is believed to have more effective and better performance on CO₂ adsorption as compared to MOF-74 (m-Mg) in the condition of water exists. Hence, the study is relevant as modification on Mg-MOF-74 with amine functional group has not been widely addressed yet.

1.6 FEASIBILITY OF PROJECT

This project is feasible as it deals with narrowed scope of experiment whereby only two samples needed to be synthesized and five characterizations needed to be done on each sample. It is within capability to be executed with helps and guidance from the supervisor and the coordinator. It is positive that this project can be completed within the time allocated with the acquiring of equipment and materials needed.

1.7 ORGANIZATION OF DISSERTATION

The study presented in this dissertation focuses on improving the performance of CO₂ adsorption by metal organic framework-74 through amine modification.

Chapter 2 summarizes the literature review done on the respective areas such as adsorption technology for CO₂ separation and capture, characteristics and synthesis of Mg-MOF-74, water effect on CO₂ adsorption, functionalization, material characterization and adsorption measurements.

Chapter 3 writes about research methodology will be discussed in detailed in the form of project activities, gantt chart and key milestones of the project, experimental procedure, reagent & chemicals used, apparatus & equipment and characterization techniques.

Chapter 4 outlines the results from characterization of both samples including results of BET for CO₂.

Chapter 5, the last chapter of the dissertation concludes the entire study and offers some recommendations for the study.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION TECHNOLOGY FOR CO₂ SEPARATION AND CAPTURE

Carbon dioxide gas is one of the most omnipresent molecules under investigation in global university and even in industrial Research and Development (R&D) efforts. The urge of separating CO₂ from gas streams on a large quantity with the aim of either storing or using the purified form has emerged from recent studies and small scale contributions in the 1990s to major international efforts at demonstration scale today.

The use of adsorption technology to separate CO₂ from process gas streams is not new. Some of the alternative technologies for CO₂ capture are adsorption based CO₂ capture, membrane processes, cryogenic methods, hydrate processes, electrochemical techniques and other niche methods. These alternate technologies are being developed for CO₂ capture for such applications like post combustion flue gas, pre-combustion process gas where they are commonly found in the integrated gasification combined cycle (IGCC) process or other gasification processes, natural and biogas systems, food and beverage industry and the cement and steel making industry (Webley, 2014).

To be considered as a suitable material for the gas adsorption, there are three main properties that an adsorbent should have:

- (i) High adsorption capacity towards the target species.
- (ii) High selectivity towards the target species.
- (iii) Full regeneration capacity.

In the 1950s, molecular sieves, alumina and silica materials were used for removing trace CO₂ from air in enclosed environments. Early process work on developing pressure and temperature swing systems and development of functionalized nanoporous adsorbents depended on existing adsorbent materials from the zeolite, alumina, mesoporous silicates, carbon families and metal organic frameworks (MOFs) (Gargiulo et al., 2014; Webley, 2014). Recently, MOFs are found to be potential candidates in CO₂ capture because of their superior characteristics (Wu et al., 2013; Webley, 2014; Moellmer, 2009; Glover et al., 2010). Since the requirements on the adsorbent and process vary widely from one field to another, the application arena of CO₂ capture by adsorption is first classified.

2.2 MOF-74

2.2.1 Characteristics of MOF-74

Metal organic frameworks are materials constitute of different metal ions linked by multi-functional organic linkers into one, two or three dimension structures (Gargiulo et al., 2014; Sabouni, 2013). MOF-74 structure is made of organic linker, 2,5-dihydroxyterephthalate linkers. The solvent molecule (water or DMF) can be easily removed under vacuum, increasing the concentration of of unsaturated coordinative metal cations. Among the current MOF structures, MOF-74 presents more co-ordinately unsaturated metal sites that can provide extra number of binding sites to gas molecules (Glover et al., 2010; Wu et al., 2013). Excellent results in CO₂ capacity and high selectivity of CO₂/CH₄ by MOF-74 were obtained from experiments (Liu et al., 2012).

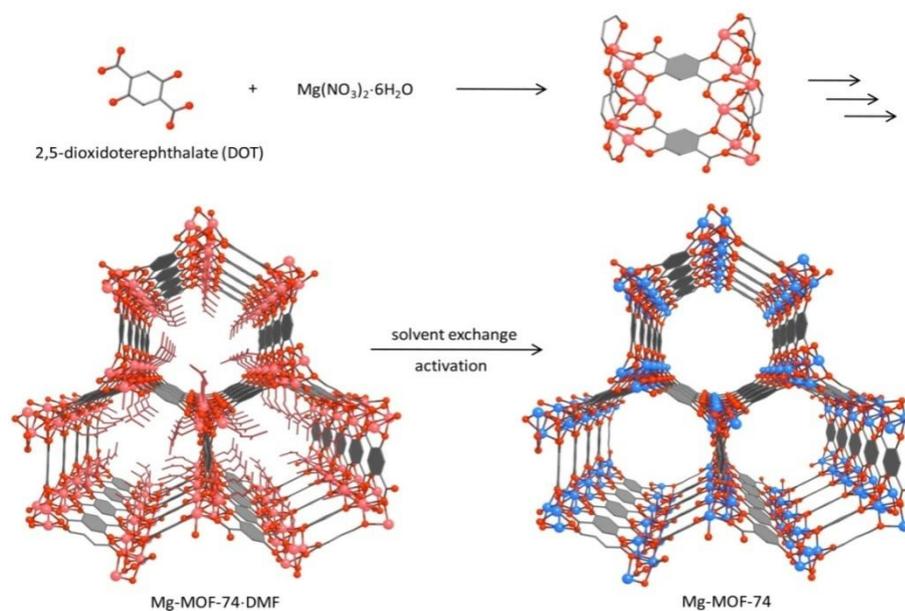
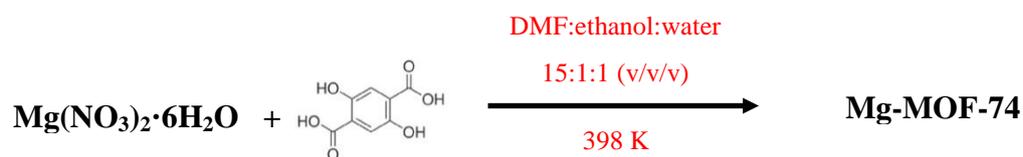


Figure 2.1: Mg-MOF-74 sample analogs.

2.2.2 Synthesis of Magnesium-MOF-74 (Mg-MOF-74)

In conventional hydrothermal method, a homogeneous solution was prepared by dissolving the mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.439 g, 5.62 mmol) and 2,5-dihydroxyterephthalic (0.338 g, 1.7 mmol) in a ratio 15:1:1 mixture of DMF (135 mL), ethanol (9 mL), and water (9 mL) under sonication. Subsequently, the autoclaves were placed in a 398K oven for 21 hours. Upon reaching room temperature, the mother liquor was decanted and replaced with fresh methanol five times over the next two days. Lastly, heat the sample to 523K under vacuum. The samples were let to cool down to room temperature and stored (Wu et al., 2013; Glover et al., 2010).



2.3 WATER EFFECTS ON CO₂ ADSORPTION

At most of the time, hydrocarbon flue gas is saturated with water by 5%-7% on volume basis. Therefore, it is very crucial to study effects of humidity on CO₂ uptake capacity. Many MOFs are found to have bad performance on CO₂ adsorption in the presence of water. Majority display a significant decrease in the CO₂ adsorption capacities after exposure to more than 60% relative humidity.

2.4 FUNCTIONALIZATION

2.4.1 Amine Functionalization

Addition of free amines to MOFs provides more sites for highly effective CO₂ adsorption even in the presence of water. Study was done on post-synthesis amine modification of Mg-MOF-74 to generate a functional nanoporous adsorbent with a capability of regeneration and improved stability to enhance CO₂ capture (Choi et al., 2012).

Liu et al. (2012) found that at low pressure region, amine-functionalized MOF has large CO₂ uptake. On the other side, amine functionalization can also decrease the volume of free sites if amine molecules are used in excess. In fact, it may reduce the CO₂ capture efficiency.

2.4.2 Synthesis of Modified MOF-74-Amine

Functionalization with ethylenediamine was performed based on the recent paper by Lei (2013). About 40ml anhydrous toluene and 1.0g ethylenediamine (Fisher) was added into flask with 200mg of solid dry Mg/DOBDC (Mg-MOF-74) sample. The contents were stirred at 400 rpm under reflux. After 12 hours, the mixture was washed with 100ml of deionized water and then 100ml of ethanol. The filtered material was put under drying for 14 hours at room temperature to yield ethylenediamine functionalized Mg/DOBDC (Mg-MOF-74) which was named as ED-Mg/DOBDC.

2.5 MATERIAL CHARACTERIZATION

Characterization techniques used to analyse sample are fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) (Wu et al.,2013; Chen et al., 2010). The structure of MOF will be analyzed by using X-ray diffractometer. The morphology of samples will be analyzed by using FESEM. Furthermore, TGA was used to analyse the thermal degradation and weight loss of the synthesized MOFs.

Moellmer (2009) states that the microporous solids' surface area results gained from BET method on adsorption isotherm do not show the actual internal surface area. Bae et al. (2009) also suggest that comparison of the experimental BET surface area with the calculated value can provide the surface area deviations from the perfect geometric of crystal structure.

2.6 ADSORPTION MEASUREMENTS

Gargiulo (2014) proved that amine functionalization can actually make MOFs more selective towards CO₂. The performance of MOFs on CO₂ adsorption will be studied by using Brunauer–Emmett–Teller (BET) method. The performance on CO₂ adsorption can be analysed from the graph of CO₂ adsorption isotherm.

CHAPTER 3

METHODOLOGY

3.1 PROJECT ACTIVITIES

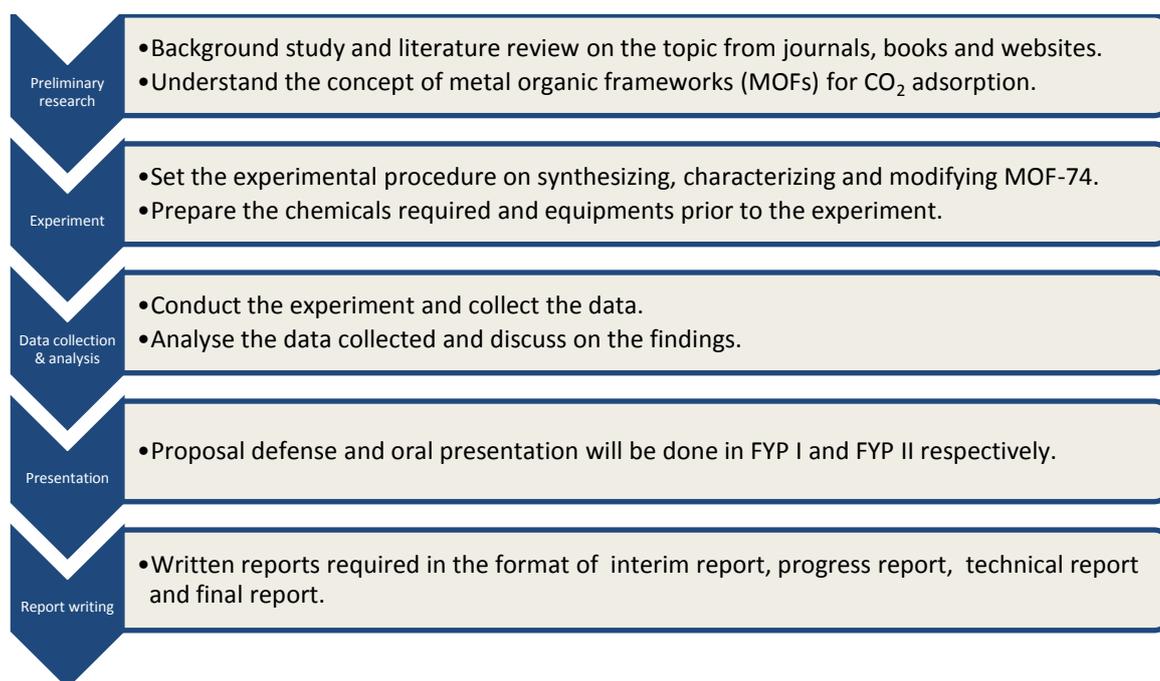


Figure 3.1: Project Activities Flowchart

3.2 GANTT CHART & KEY MILESTONE

3.2.1 Gantt Chart & Key Milestone (FYP I)

Table 3.1: FYP (I) Gantt Chart

No.	Details	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of title and allocation	■	■												
2	First meeting with supervisor			■											
3	Preliminary project work				■	■	■	■							
4	Submission of extended proposal							◆							
5	Proposal defense								■						
6	Project work I: Synthesis of MOF-74 (1 st Batch)							■	◆						
7	Project work II: Synthesis of MOF-74 (2 nd Batch)								■	■	◆				
8	Project work III: Synthesis of MOF-74 (3 rd Batch)										■	■	◆		
9	Submission of interim draft report													◆	
10	Submission of final interim report														◆

■ Process

◆ Key Milestone

3.2.2 Gantt Chart & Key Milestone (FYP II)

Table 3.2: FYP (II) Gantt Chart

No.	Project Activities	Week No.													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Characterization of MOF-74 (TGA, FTIR)	■	◆												
2	Characterization of MOF-74 (TEM, FESEM, BET)			■	■	◆									
3	Project work VI: Synthesis of MOF-74-AMP (1 st Batch)						◆								
4	Project work V: Synthesis of MOF-74-AMP (2 nd Batch)							◆							
5	Submission of progress report								◆						
6	Characterization of MOF-74-AMP (TEM, FESEM, BET)							■	◆						
7	Characterization of MOF-74-AMP (TGA, FTIR)									■	■	◆			
8	Pre-SEDEX											◆			
9	Submission of dissertation draft report												◆		
10	Submission of dissertation (soft bound report)													◆	
11	Submission of technical paper													◆	
12	Viva Presentation														◆
13	Submission of project dissertation (hard bound report)														◆

■ Process

◆ Key Milestone

3.3 RESEARCH METHODOLOGY

3.3.1 Sample Preparation of Mg-MOF-74

- 1) 1.424g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.334g of 2,5-dihydroxyterephthalic acid are weighed and placed inside a beaker.
- 2) A mixture in a ratio of 15:1:1(v/v/v) of DMF(135ml), ethanol(9ml) and deionized water(9ml) is prepared.
- 3) $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2,5-dihydroxyterephthalic acid mixture is dissolved in the mixture of DMF, ethanol and deionized water under sonication for about half an hour.
- 4) The mixture is placed into an autoclave and put into an oven at 125°C for 26 hours.
- 5) The mixture is cooled down to room temperature and the mother liquor is removed and replaced with methanol twice per day over next three days.
- 6) Mixture is then evaporated using different temperatures, 60°C for an hour and 110°C for 10 hours to result in yellow microcrystalline powder. Small portion of the powder is taken from each temperature for characterization purpose.
- 7) The sample is heated under vacuum to 260°C for 12 hours.
- 8) The sample is left to cool down to room temperature and stored.

3.3.2 Experimental Procedure Flow Chart

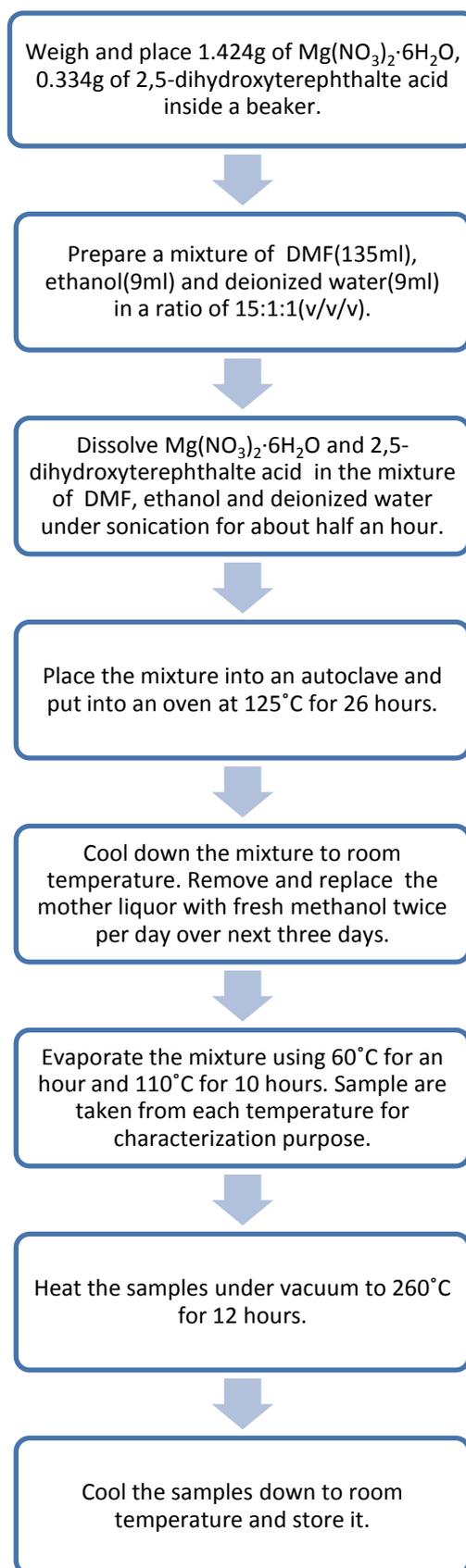


Figure 3.2: Flow Chart of Experimental Procedure

3.3.3 Sample Preparation of Mg-MOF-74-AMP (Lei, 2013)

- 1) About 40ml anhydrous toluene and 1.0g of 2-amino-2-methyl-1-propanol (AMP) was added into beaker with 200mg of solid dry Mg-MOF-74 sample.
- 2) The contents of the beaker were stirred at 400rpm under reflux at 110°C for 12 hours.
- 3) Then, the content of mixture was washed and filtered with 100ml of deionized water and then 100ml of ethanol.
- 4) The filtered material was dried at room temperature for 14 hours to yield amine functionalized MOF-74 named as Mg-MOF-74-AMP.

3.3.4 Reagent and Chemicals

List of chemicals that are used in the experiment:

- 1) Magnesium Nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
- 2) 2,5-Dihydroxyterephthalic acid
- 3) Dimethylformamide (DMF)
- 4) 2-amino-2-methyl-1-propanol (AMP)
- 5) Ethanol
- 6) Deionized Water
- 7) Methanol
- 8) Anhydrous toluene

3.3.5 Apparatus & Equipments

Below are the lists of apparatus and equipments used in this project.

Table 3.3: List of Apparatus

<i>List</i>	<i>Apparatus</i>	<i>Function</i>
1.	Beaker	To hold chemicals and reagents.
2.	Spatula	To transfer chemicals and reagents from bottle to beakers.
3.	Weighing machine	To measure the weight of chemicals in solid form required for MOF-74 synthesis.
4.	Measuring cylinder	To measure the weight of chemicals in liquid form accurately.
5.	Pipette	To measure liquid in less than 10ml.

Table 3.4: List of Characterization Equipments

<i>Equipment</i>	<i>Graphical Diagram</i>	<i>Function</i>
Thermal Gravimetry Analyzer (TGA)		To determine the weight change of a material with temperature change. To find out degradation temperature.
Fourier Transform Infrared Spectroscopy (FTIR)		To identify unknown materials, determine the quality of a sample and quantity of components in a mixture.
Transmission Electron Microscope (TEM)		To observe the compound's morphology and porosity at nano-crystal level.
Field Emission Scanning Electron Microscopy (FESEM)		To observe small structures on the surface of cells and material.
Brunauer-Emmett-Teller (BET) method		To measure CO ₂ uptake capacity and the specific surface area of finely divided and porous solids.

3.3.6 Characterization Techniques

TGA Analysis

Thermogravimetric Analysis (TGA) was carried out in a 100ml/min flowing air atmosphere at a heating rate of 10°C/min from the temperature of 50°C to 200°C using Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer. Degradation temperature of the samples could be observed from the TGA profile.

FTIR Analysis

Fourier Transform Infrared (FTIR) spectrum was obtained from Nicolet FTIR Impact 400 system. About 2mg of the lab samples were grounded with 460 mg of potassium bromide (KBr) under atmosphere. The mixture was then transferred to a die kit and pressed into a pellet. This analysis technique was used to identify unknown materials, determine the quality of the samples and quantity of components in the samples.

TEM Analysis

Zeiss Libra 200 Transmission Electron Microscope (TEM) was used to analyze the geometry and chemical of Mg-MOF-74 particles at atomic level. The TEM instrument was operated at 200 kV. The general morphology of the samples of MOFs was studied for individual nanocrystals.

FESEM Analysis

The crystal morphology of the samples was observed using a Zeiss Supra55 Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM). The VPFESEM instrument is operated at an accelerating voltage of 2kV.

BET for CO₂ Analysis

The CO₂ adsorption isotherms of the sample were obtained from BEL Japan BELSORP-minill. Before sample was sent for characterization, pretreatment was required for sample preparation using BELPREP-vacll instrument.

CHAPTER 4

RESULTS & DISCUSSION

4.1 SYNTHESIS OF MG-MOF-74

From the synthesis of lab samples, these are the results of Mg-MOF-74 obtained from the first, second and third batch of Mg-MOF-74 synthesis.



Figure 4.1: Mg-MOF-74 (in powder form)

The amount of Mg-MOF-74 synthesized and stored as follows:

Table 4.1: Amount of Mg-MOF-74 Synthesized

<i>No.</i>	<i>Batch</i>	<i>Amount of Mg-MOF-74 Synthesized (mg)</i>
1	First	0.75
2	Second	0.36
3	Third	0.38

The Mg-MOF-74 obtained from the first batch of synthesizing is dried up according to different temperatures, which are 60°C, 110°C and 260°C respectively. The reason behind drying up the sample using different temperature is to observe the change in MOF-74 structure with temperature. For temperature of 60°C, the sample is put into oven for 1 hour. About 0.35mg of MOF-74 is taken from the evaporating dish. After that, the temperature is set to 110°C and the sample is further dried up for another 10 hours. Same procedure is followed where small portion of the sample is transferred into small container. The sample is heated under vacuum to 260°C for 12 hours. The remaining MOF-74 sample synthesized from the second and third batches will be used to synthesize modified MOF-74-Amine.

4.2 CHARACTERIZATION OF MG-MOF-74

4.2.1 Fourier Transform Infrared (FTIR)

It is very important to identify and analyse the major characteristic of Mg-MOF-74 infrared spectrum. There will be no qualities of the features being discussed in this study. Refer thesis of Burkholder, for detailed information. The spectra obtained from both the synthesized MOF-74 at 60°C and 110°C respectively were analyzed in this project according to absorption peaks. Refer Appendix 10 & 11 for FTIR spectra results.

From the two graphs generated from FTIR analysis, both are showing the almost similar spectra. According to the table of Characteristic IR Absorptions, sharp peaks at 3400.28 cm⁻¹ and 3411.97 cm⁻¹ respectively indicate that both are having bond of O-H stretch or H-bonded. The functional groups are either alcohols or phenols. In addition, both compounds contain C-H stretch which represents functional group of alkanes (2926.37 cm⁻¹ and 2927.57 cm⁻¹ respectively).

In the frequency range from 2500 cm⁻¹ to 2000 cm⁻¹, several minor peaks can be observed from MOF-74 synthesized at 60°C.

Peak listings are provided below:

[strong (s), medium (m), weak (w), broad (br), narrow (n) and sharp (sh).]

Mg-MOF-74 at 60°C: IR 3400.28 (s), 2926.37 (m), 2854.77 (m), 2749.62 (w), 2495.94 (w), 2434.78 (br), 2183.31 (w), 2107.07 (w), 1583.13 (sh), 1460.41 (sh), 1418.81 (sh), 1370.40 (s), 1237.46 (s), 1210.22 (sh), 1123.47 (s), 914.14 (s), 888.47 (sh), 821.05 (sh), 673.59 (br), 660.42 (n), 634.79 (w), 587.61 (s), 508.18 (m), 485.04 (m), 460.08 (m) cm^{-1} .

Mg-MOF-74 at 110°C: IR 3411.97 (s), 2927.57 (m), 2855.16 (m), 2495.57 (w), 1586.62 (sh), 1459.41 (s), 1417.95 (sh), 1369.91 (s), 1236.69 (sh), 1209.76.47 (sh), 1122.93 (n), 1031.06 (m), 913.87 (w), 888.26 (sh), 820.82 (sh), 660.60 (w), 633.05 (w), 588.34 (m), 509.79 (n), 484.53 (m), 460.18 (n).

Ranging from 1600 cm^{-1} to 450 cm^{-1} , there are number of peaks present. The bonds exist in both MOF-74 are N-H bend (1583.13 cm^{-1} , 1586.62 cm^{-1}); C-H bend (1460.41 cm^{-1} , 1459.41 cm^{-1}); C-C stretch (in-ring) (1418.81 cm^{-1} , 1417.95 cm^{-1}); C-H rock (1370.4 cm^{-1} , 1369.91 cm^{-1}); C-O stretch (1237.46 cm^{-1} , 1236.69 cm^{-1}); O-H bend (914.14 cm^{-1} , 913.87 cm^{-1}); C-H “oop” (888.47 cm^{-1} , 888.26 cm^{-1}); C-H bend.

The functional groups are 1° amines, alkanes, aromatics, alcohols, carboxylic acids and alkynes. The peaks displayed by both samples synthesised at different temperatures, which are 60°C and 110°C respectively fall within the similar ranges, a result which agree with the results published for Mg/DOBDC (Kizzie, 2012; Diaz-Garcia et al., 2014).

4.2.2 Thermogravimetric Analysis (TGA)

In Thermogravimetric Analysis (TGA) measurement, the exchange of materials between the sample and the immediate surrounding has to be possible.

The TGA curve of synthesized Mg-MOF-74 at 60°C is shown in Figure 4.4. The first weight loss produced around 122°C . This can be due to the removal of solvent (DMF or water) from the cavities. The next major weight loss in the range of 400°C to 650°C corresponds to the organic ligand decomposition and therefore indicates the thermal stability of Mg-MOF-74 framework synthesized at 60°C in air atmosphere (Botas et al., 2010).

(i) Sample of Mg-MOF-74 synthesized at 60°C

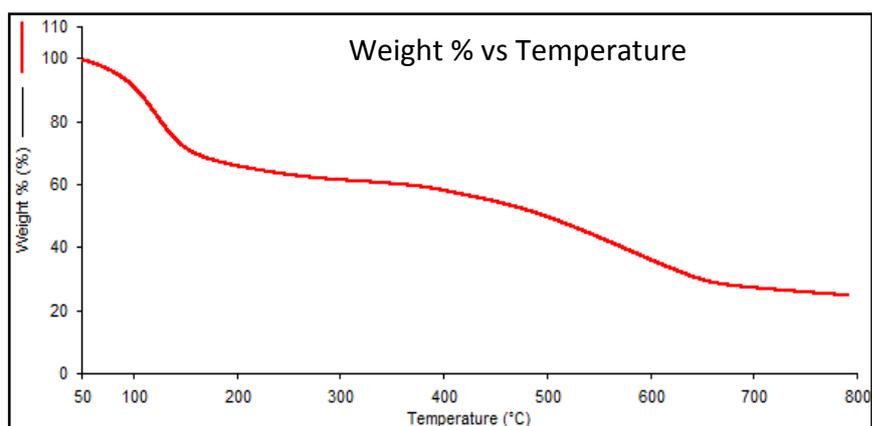


Figure 4.2: Weight% vs Temperature of Mg-MOF-74 sample synthesized at 60°C

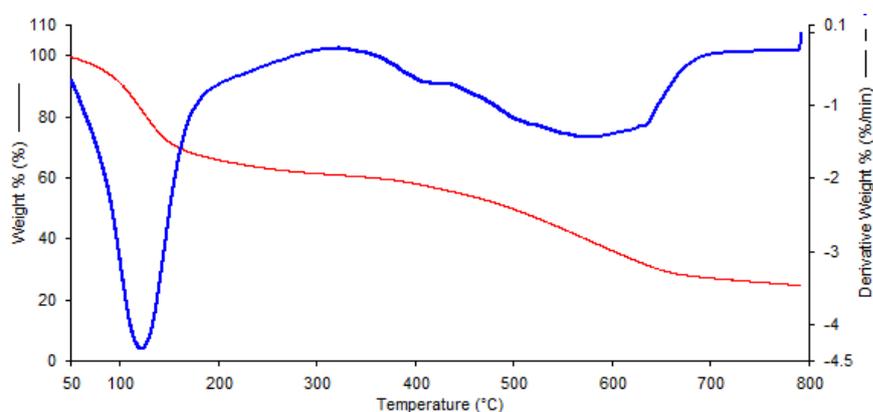


Figure 4.3: TGA curve of Mg-MOF-74 sample synthesized at 60°C

(ii) Sample of Mg Mg-MOF-74 synthesized at 110°C

The TGA curve (Figure 4.5) generated from Mg-MOF-74 synthesized at 110°C produces an almost similar trend as that at 60°C.

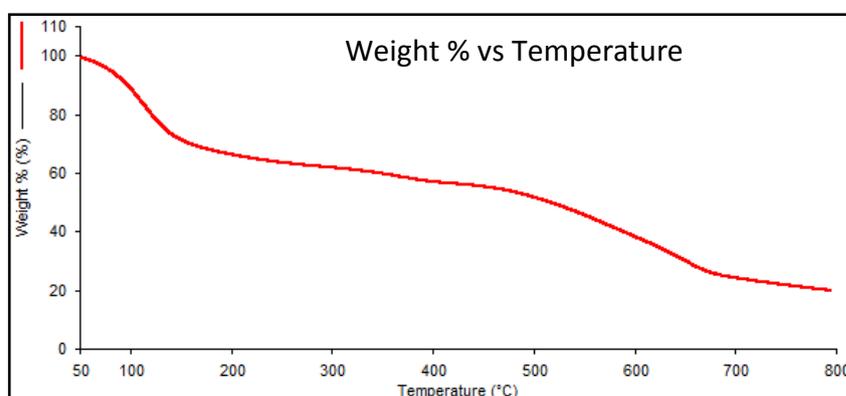


Figure 4.4: Weight% vs Temperature of Mg-MOF-74 sample synthesized at 110°C

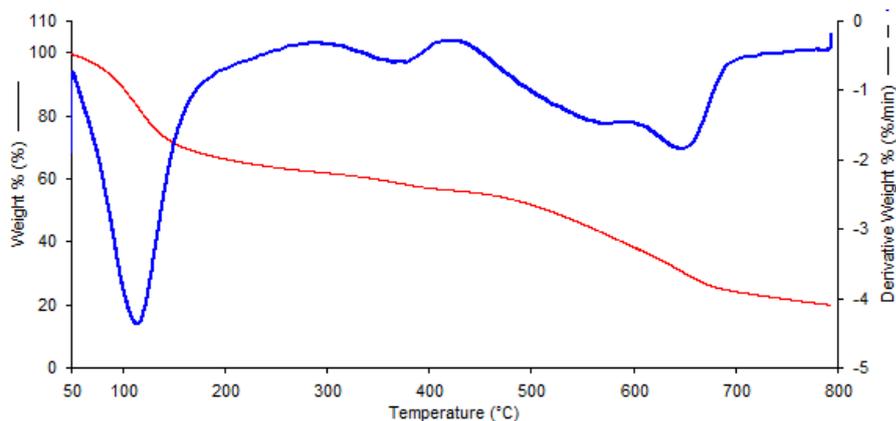


Figure 4.5: TGA curve of Mg-MOF-74 sample synthesized at 110°C

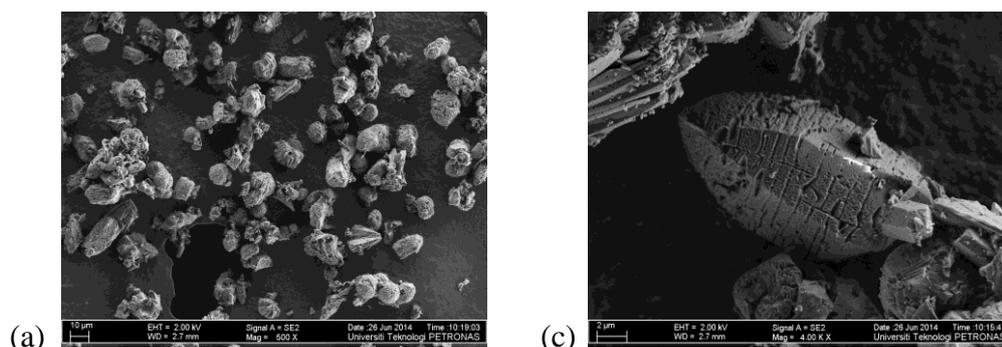
The first weight loss which is caused by the removal of solvent (DMF or water) from cavities is observed at 112°C from the curve above (Figure 2). Secondly, the temperature range involving major weight loss (ligand decomposition) changes to 500°C - 680°C, indicating the thermal stability of Mg-MOF-74 synthesized at 110°C (Botas et al., 2010).

Thus, it can be concluded that Mg-MOF-74 framework synthesized at higher temperature would possess a greater thermal stability in air atmosphere.

4.2.3 Field Emission Scanning Electron Microscope (FESEM)

The crystal morphology of the both sample were observed by a Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Model: Zeiss Supra55 VP) at an accelerating voltage of 2kV.

The working distance to observe sample Mg-MOF-74 is set to be 2.7mm. Several images were collect under the VPFESEM equipment with different magnifications.



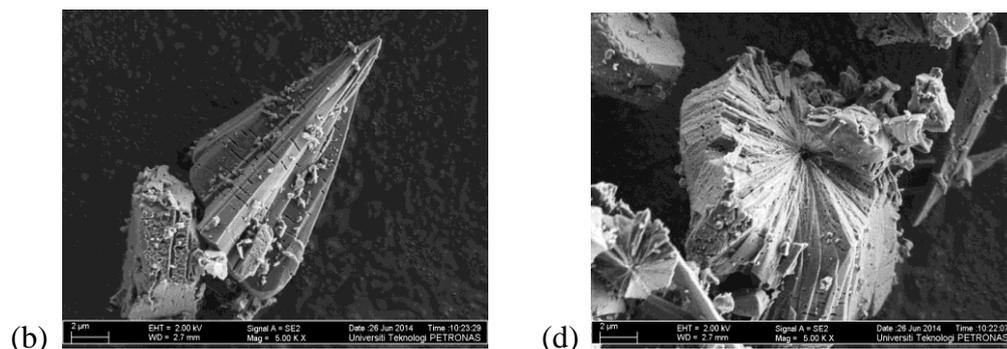


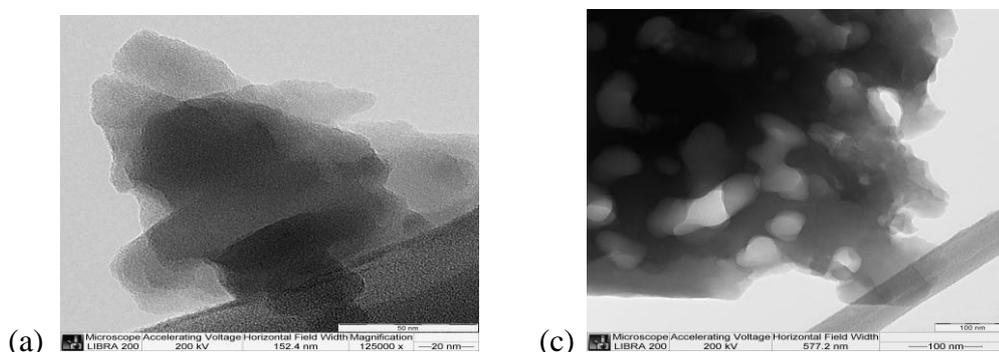
Figure 4.6: FESEM of Mg-MOF-74 lab sample – Magnification of (a) 500 (b) 5k (c) 4k (d) 500

Figures above show the images of Mg-MOF-74 obtained from VPFESEM. Based on the above figures, it can be observed that the crystal structure of Mg-MOF-74 sample prepared in this study are mostly in shuttle like form, an observation similar to results reported by Bao, 2011. Here, particle sizes are with an average size of $16\mu\text{m}$ (in the range of 4 - $28\mu\text{m}$) and also in tetra sharp form.

4.2.4 Transmission Electron Microscope (TEM)

TEM images are obtained from Transmission Electron Microscope (TEM, Model: Zeiss Libra 200) with an accelerating voltage of 200kV.

A range from 59nm to 577.2nm of horizontal field width is used to observe the sample cell.



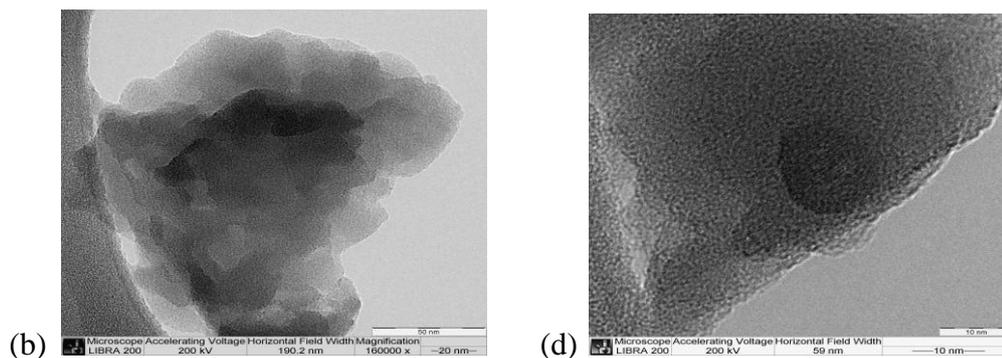


Figure 4.7: TEM of Mg-MOF-74 lab sample – Magnification of (a) 125k (b) 160k – Horizontal field width of (c) 577.2nm (d) 59nm

The figures above are the representative TEM images observed for the Mg-MOF-74 samples. The images are taken at several magnifications such as 80000x, 125000x, and 160000x. The rest of the images are provided in Appendix. TEM images provide information on the physical structure of the Mg-MOF-74 synthesized. The compound's morphology and porosity were observed at the nano-crystal level. It closely related to its adsorption characteristics.

Figure 4.7(a) and (b) are taken at different magnifications, at 125000x and 160000x respectively, showing structure of more like solid granular which agrees to the results showed in the paper of Siddiqui (2013). The particles in figure 4.7(c) and (d) display some porosity in their structure. Results of TEM in this study are similar as the results reported previously (Siddiqui, 2013).

4.2.5 BET for CO₂

BET for CO₂ – Mg-MOF74

Weight of MP sample cell + weight of stopper = 11.9124 g + 0.7807 g = 12.6931 g

Weight of MP sample cell + weight of funnel = 29.6148 g

Weight of Mg-MOF-74 before moisture removing = 0.2928 g

Weight of MP sample cell + weight of stopper + weight of Mg-MOF-74 (after moisture removed) = 12.9156 g

Weight of Mg-MOF-74 after moisture removed = 0.2225 g

The sample of Mg-MOF-74 was sent for BET gas adsorption for CO₂. The following are the results obtained:

Table 4.2: CO₂ Gas Adsorption Capacity of Mg-MOF-74 sample

Sample	Weight of Mg-MOF-74 after moisture removed (g)	CO ₂ Gas Adsorption at 106.22kPa (mol/g) <i>(CO₂ isotherm at 25°C, 298.2K)</i>
Mg-MOF-74	0.2225	0.002

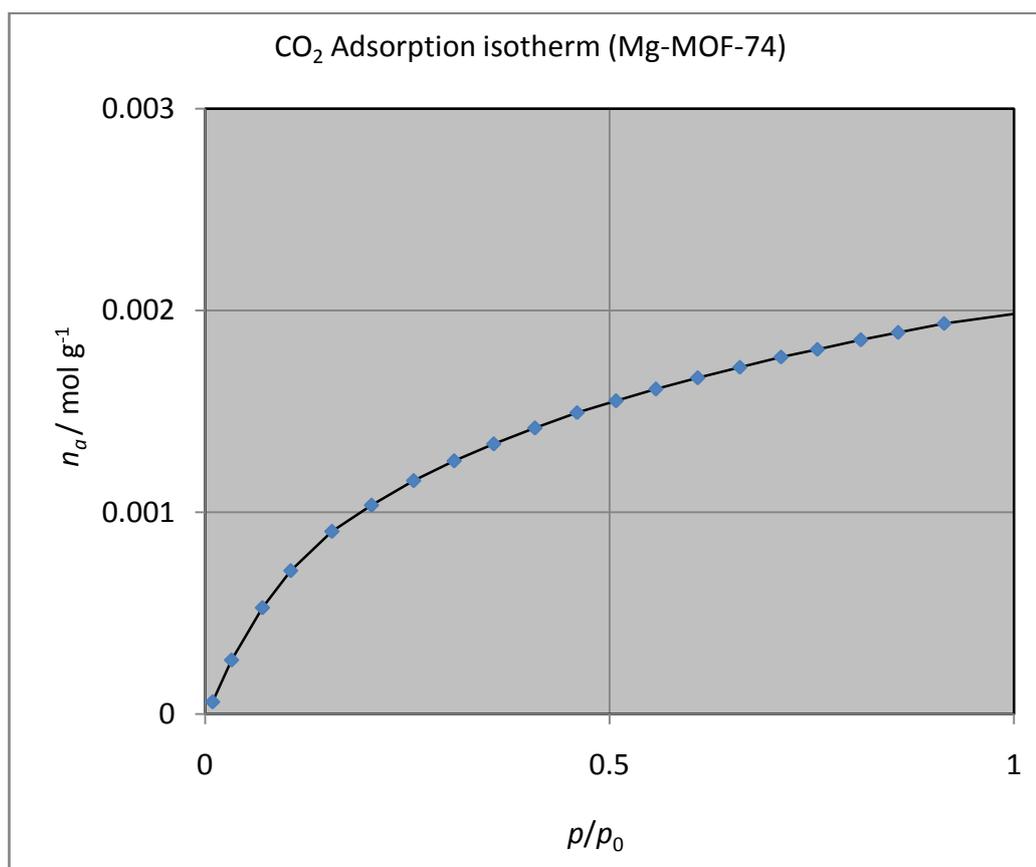


Figure 4.8: CO₂ Adsorption Isotherm on Mg-MOF-74

The graph above shows the CO₂ adsorption isotherm on Mg-MOF-74 sample at 25°C (298.2K). The CO₂ adsorption isotherm on Mg-MOF-74 gradually increases in CO₂ uptake at P/P₀ from 0 to 1. The steeper the slope of the isotherm, the stronger the interaction of CO₂ with the sample Mg-MOF-74. In the low pressure region, a steep slope can be observed from the graph and it is considered as a remarkable characteristic of microporous materials, Mg-MOF-74 (Bao, 2011). The CO₂ gas adsorption capacity of sample at 298.2k and 106.22kPa is achieved at 0.002mol/g which deviates from the recently reported value of 0.008mol/g at 298K and 1 bar (Bao, 2011). Further investigation on the value gained in this study has to be done in future work.

4.3 SYNTHESIS OF MG-MOF-74-AMP

Synthesized material from earlier stage was stored and used to further modify with amine. In this study, 2-Amino-2-methyl-1-propanol (AMP) is used as the amine on Mg-MOF-74 modification. The synthesis method of Mg-MOF-74-AMP follows the experimental procedure in thesis done previously by Lei, 2013. Synthesis of Mg-MOF-74 was done in two batches. The amount of material synthesized from the two batches is 0.65 and 0.75mg respectively.

4.4 CHARACTERIZATION OF MG-MOF-74-AMP

4.4.1 Fourier Transform Infrared (FTIR)

Similar procedure was applied to analyse the infrared spectrum of modified Mg-MOF-74 (Mg-MOF-74-AMP). There will be no qualities of the features being discussed. Refer thesis of Burkholder, for detailed information. The spectrum obtained from the synthesized Mg-MOF-74-AMP was analyzed according to absorption peaks. Refer to Appendix 12 for the FTIR spectrum result.

Peak listings are provided below:

[strong (s), medium (m), weak (w), broad (br), narrow (n) and sharp (sh).]

Mg-MOF-74-AMP: IR 3419.53 (s), 1589.12 (m), 1423.46 (sh), 1236.62 (sh), 1210.89 (sh), 1124.01 (m), 888.99 (sh), 821.39 (sh), 601.72 (br).

According to the table of Characteristic IR Absorptions, Mg-MOF-74-AMP has sharp peak at 3419.53 which is identical to infrared spectrum of Mg-MOF-74. Amine modified Mg-MOF-74 shows an IR peak at 1589.12 (N-H bend) belongs to functional group of 1° amines.

Ranging from 1500 cm^{-1} to 450 cm^{-1} , there are number of peaks present. The bonds exist are C-C stretch (in-ring) (1423.46 cm^{-1}); C-N stretch (1236.62 cm^{-1}); C-O stretch (1210.89 cm^{-1}); C-N stretch (1124.01 cm^{-1}); C-H “oop” (888.99 cm^{-1}) and N-H wag (821.39 cm^{-1}).

The functional groups are aromatics, aromatics amines, alcohols, carboxylic acids, aliphatic amines and 1°, 2° amines. Most of the peaks are identical to the previous result gained from Mg-MOF-74 but some additional peaks were discovered where those peaks are believed to be the effects of modification done on Mg-MOF-74 with AMP (Diaz-Garcia et al., 2014).

4.4.2 Thermogravimetric Analysis (TGA)

Figure 4.8 displays the TGA curve of amine modified Mg-MOF-74, named Mg-MOF-74-AMP. It is clearly interpreted from the graph of derivative weight vs temperature that the weight loss due to the removal of solvent produced at around 130°C. Thus, evacuation of the as-synthesized material was performed at this temperature so that AMP modified Mg-MOF-74 can be referred as Mg-MOF-74-AMP. Within the range of 450°C to 550°C, the second major weight loss occurs. This range of temperature is lower than the reading obtained from unmodified Mg-MOF-74, indicating amine modified Mg-MOF-74 possesses lower thermal stability. This provides an additional prove which is Mg-MOF-74-AMP has higher porosity (Siddiqui, 2013).

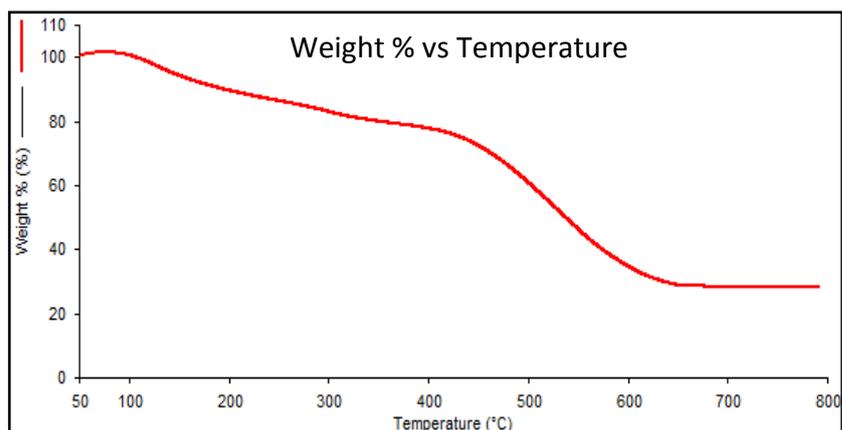


Figure 4.9: Weight% vs Temperature of Mg-MOF-74-AMP sample

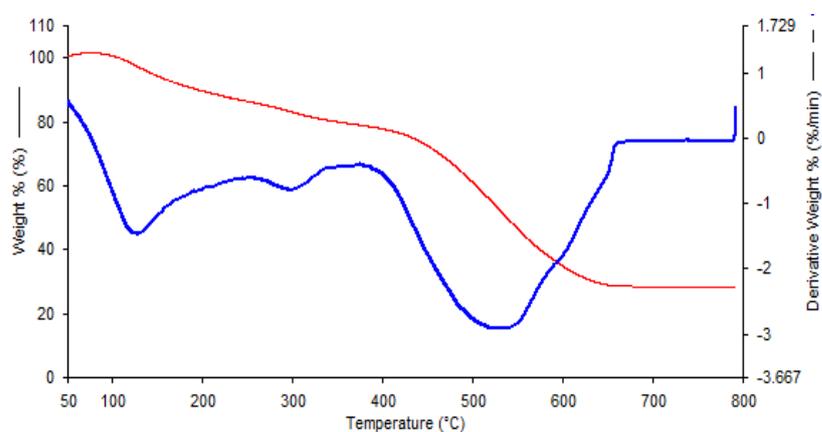


Figure 4.10: TGA curve of Mg-MOF-74-AMP sample

4.4.3 Field Emission Scanning Electron Microscope (FESEM)

Here, different working distance is applied to observe the crystal morphology of amine treated Mg-MOF-74, namely Mg-MOF-74-AMP which is 2.5mm. The FESEM images of the sample obtained are as follow.

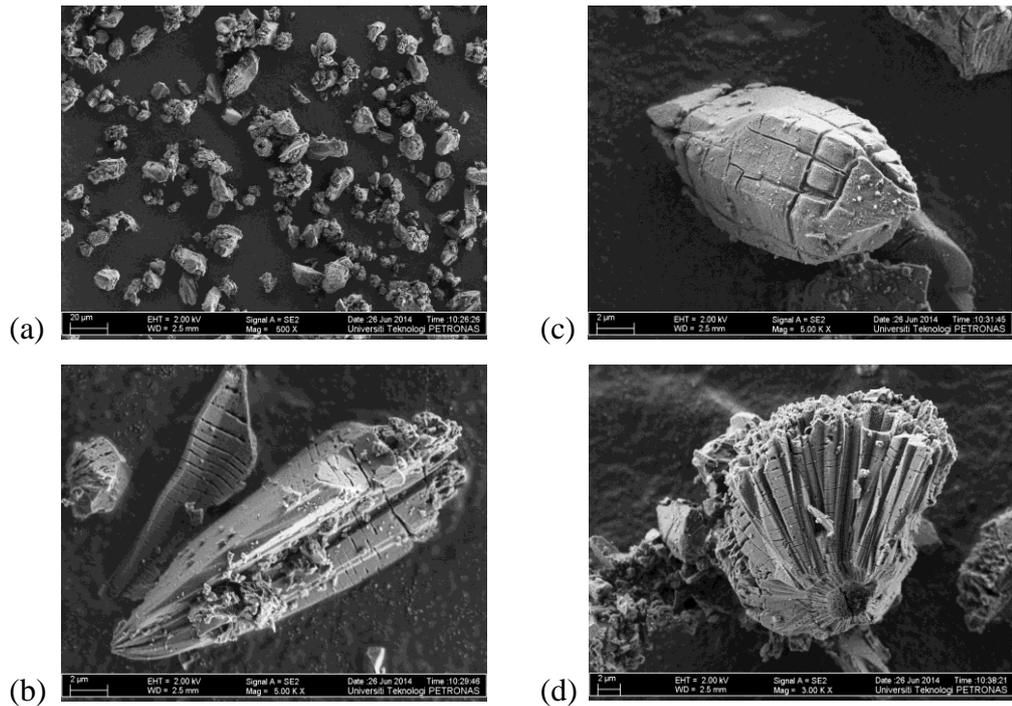


Figure 4.11: FESEM of Mg-MOF-74-AMP lab sample – Magnification of (a) 500 (b) (c) 5k (d) 3k

From the FESEM images of amine treated Mg-MOF-74, the crystal morphology is very different from the non-amine treated Mg-MOF-74. Figure 4.9(a) can be seen that particles are of similar shape compared to figure 4.6(a) with 5-26 μm in length and 2-5 μm in diameter, agreed with the FESEM results obtained from thesis of Li, 2013. Whereas, from figure 4.9(b), (c) and (d), deposits of rod-like particles on the surface were found and it is also stated in Li, 2013 when SBA-15-ex is grafted with amine. This can be explained that organic component has changed the surface affinity of Mg-MOF-74, creating more sites for CO₂ adsorption. In addition, more cracks can be seen on the crystal surface, indicating the increase of crystal surface area. In fact, when there is an increase in surface area, more unsaturated sites are available for the adsorption of CO₂ to take place. Thus, it can lead to increment of CO₂ adsorption capacity if MOFs are treated with amine which has been proved in previous works.

4.4.4 Transmission Electron Microscope (TEM)

TEM images of Mg-MOF-74-AMP are shown in figures below. TEM images confirm the structure of the sample.

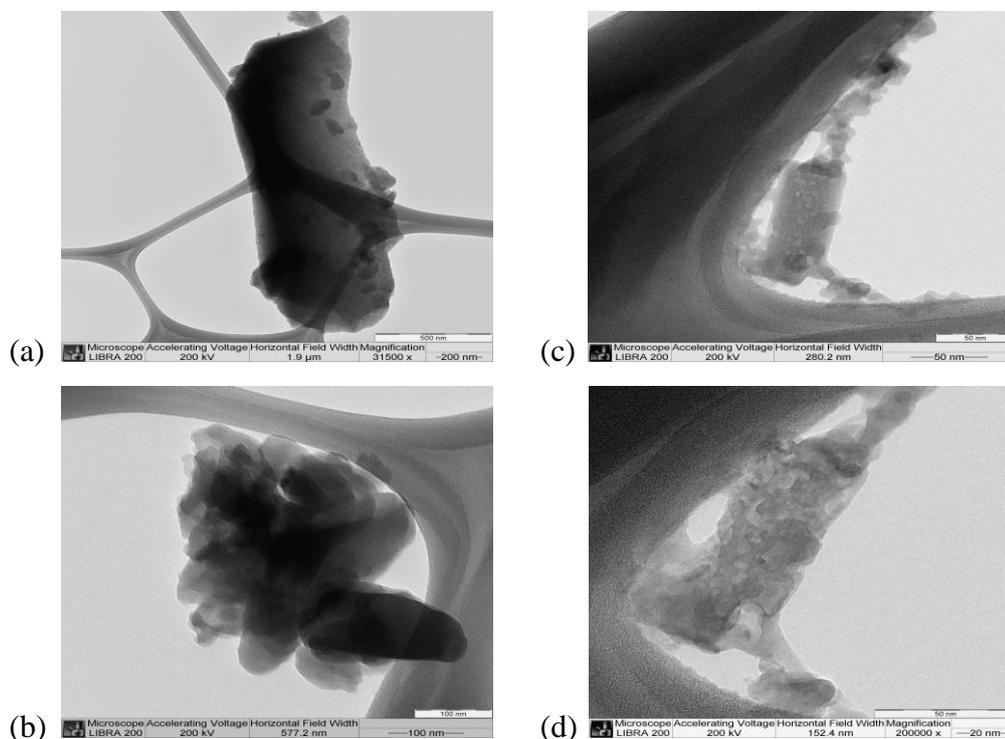


Figure 4.12: TEM of Mg-MOF-74-AMP lab sample – Magnification of (a) 31.5k (d) 200k; - Horizontal field width of (b) 577.2nm (c) 280.2nm

The images are taken at several magnifications such as 31500x, 200000x, and horizontal field width of 577.2nm and 280.2nm.. The rest of the images are provided in Appendix. The images are different than that of Mg-MOF-74. Figure 4.10(a) and (b) displayed an unknown solid material which is believed to be the organic component, AMP added to Mg-MOF-74. Figure 4.10(c) and (d) are recommended to be studied in future work.

4.4.5 BET for CO₂

BET for CO₂ – Mg-MOF74-AMP

Weight of MP sample cell + weight of stopper = 11.7581 g + 0.7948 g = 12.5529 g

Weight of MP sample cell + weight of funnel = 29.9054 g

Weight of Mg-MOF-74-AMP before moisture removing = 0.2907 g

Weight of MP sample cell + weight of stopper + weight of Mg-MOF-74-AMP (after moisture removed) = 12.7434 g

Weight of Mg-MOF-74-AMP after moisture removed = 0.1905 g

The sample of Mg-MOF-74 was sent for BET gas adsorption for CO₂. The following are the results obtained:

Table 4.3: CO₂ Gas Adsorption Capacity of Mg-MOF-74-AMP sample

Sample	Weight of Mg-MOF-74-AMP after moisture removed (g)	CO ₂ Gas Adsorption at 103.58kPa (mol/g) (CO ₂ isotherm at 25 °C, 298.2K)
Mg-MOF-74-AMP	0.1905	0.0046

Besides, CO₂ gas adsorption isotherm of modified Mg-MOF-74 with AMP was measured at 25°C. From this data, we can investigate the potential of Mg-MOF-74-AMP to serve as an adsorbent for CO₂ capture.

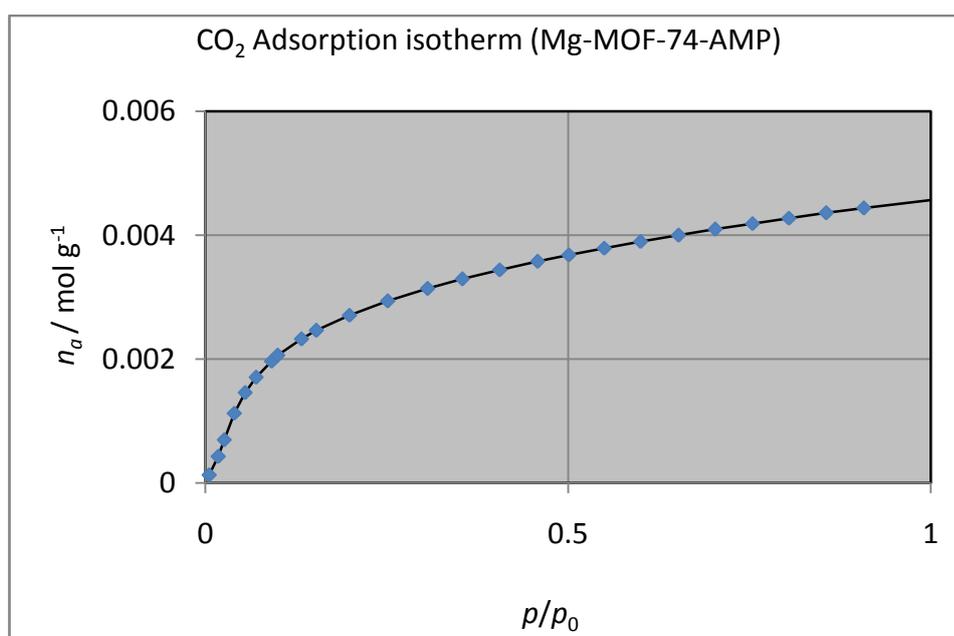


Figure 4.13: CO₂ Adsorption Isotherm on Mg-MOF-74-AMP

Figure below demonstrates the comparative graph of CO₂ adsorption isotherms on Mg-MOF-74 and amine modified Mg-MOF-74, named Mg-MOF-74-AMP.

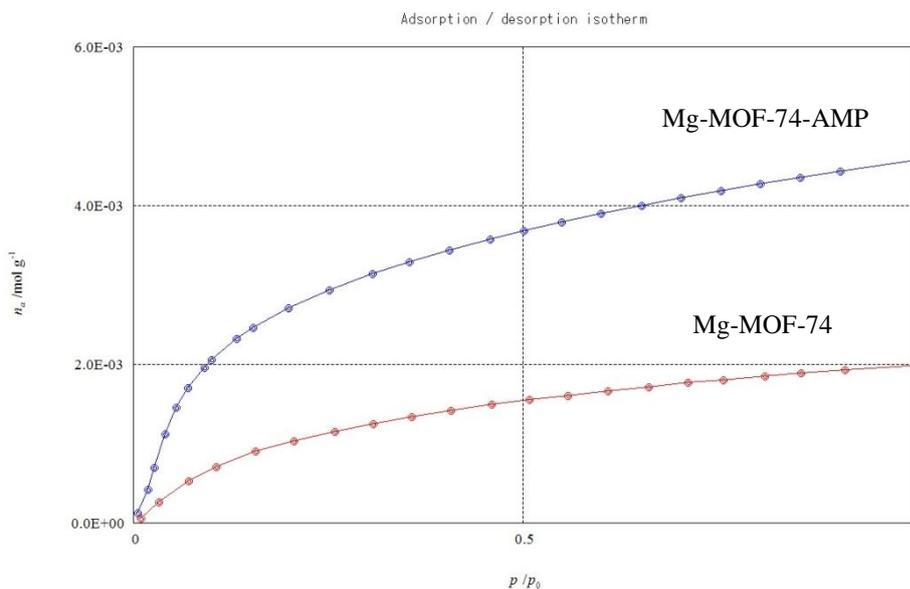


Figure 4.14: Comparative Graph of CO₂ Adsorption Isotherms on Mg-MOF-74 and Mg-MOF-74-AMP

From various previous studies done, amine treated MOFs are proven to have a better CO₂ adsorption capacity. The result of CO₂ uptake of Mg-MOF-74 treated with AMP appears to be higher than Mg-MOF-74 which turned up to be the expected result gained.

From the figure, CO₂ adsorption isotherm on Mg-MOF-74-AMP has a sharp rise in CO₂ uptake at P/P_0 from 0.05 to 0.25, indicating in the low pressure region, the uptakes of CO₂ are significantly higher in Mg-MOF-74-AMP, in which representing strong adsorption of CO₂ onto Mg-MOF-74-AMP. The CO₂ uptake at 298.2k and 103.58kPa is attained at 0.0046mol/g, which is twice the CO₂ uptake of Mg-MOF-74.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

As a conclusion, this project is important as it deals with overcoming the major weakness of metal organic frameworks, water stability and Mg-MOF-74 has a better adsorption among the MOFs. Project activities on synthesis of metal organic framework, Mg-MOF-74 as well as the characterization and modification were conducted to study on the characteristics and CO₂ adsorption on both samples in order to improve on CO₂ adsorption technology.

Mg-MOF-74 functionalized by 2-amino-2-methyl-1-propanol (AMP) is believed to be one of the effective ways to decrease the CO₂ concentration in the atmosphere due to its effective and better performance on CO₂ adsorption. Both samples are characterized by FTIR, TGA, FESEM, TEM and BET method. From the results gained, CO₂ uptake capacity was improved by 100% after amine modification which has achieved the ultimate objective of this study. The CO₂ gas adsorption capacity increases from 0.002mol/g to 0.0046mol/g after AMP was added to Mg-MOF-74.

As a recommendation, future work may be done to study on BET for N₂ adsorption isotherm analysis of Mg-MOF-74-AMP and also study on manipulating the amount of AMP grafted on Mg-MOF-74. Types of amine used in Mg-MOF-74 modification may be listed as one of the future works. The most important is the integration of MOF-74 applications in various industries.

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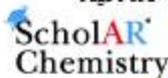
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separation. *Microporous and Mesoporous Materials*, 180, 114-122. doi:
<http://dx.doi.org/10.1016/j.micromeso.2013.06.023>

APPENDICES

Appendix 1: MSDS of Magnesium Nitrate

Material Safety Data Sheet		Page 1 of 2
MSDS # 429.00	Magnesium Nitrate	
Section 1: Product and Company Identification		
Magnesium Nitrate		
Synonyms/General Names: Magnesium nitrate, hexahydrate		
Product Use: For educational use only		
Manufacturer: Columbus Chemical Industries, Inc., Columbus, WI 53925.		
24 Hour Emergency Information Telephone Numbers		
CHEMTREC (USA): 800-424-9300 CANUTEC (Canada): 613-424-6666		
Scholar Chemistry: 5100 W. Henrietta Rd, Rochester, NY 14586; (866) 260-0501; www.ScholarChemistry.com		
Section 2: Hazards Identification		
White powder, no odor.		
DANGER! Strong oxidizer and body tissue irritant		
Target organs: None known.		
This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).		
Section 3: Composition / Information on Ingredients		
Magnesium Nitrate (13446-18-9), >99%		
Section 4: First Aid Measures		
<i>Always seek professional medical attention after first aid measures are provided.</i>		
Eyes:	Immediately flush eyes with excess water for 15 minutes, lifting lower and upper eyelids occasionally.	
Skin:	Immediately flush skin with excess water for 15 minutes while removing contaminated clothing.	
Ingestion:	Call Poison Control immediately. Rinse mouth with cold water. Give victim 1-2 cups of water or milk to drink. Induce vomiting immediately.	
Inhalation:	Remove to fresh air. If not breathing, give artificial respiration.	
Section 5: Fire Fighting Measures		
Oxidizing agent. When heated to decomposition, emits acrid fumes of NOx.		
Protective equipment and precautions for firefighters: Use foam or dry chemical to extinguish fire. Firefighters should wear full fire fighting turn-out gear and respiratory protection (SCBA). Cool container with water spray. Material is not sensitive to mechanical impact or static discharge.		
Section 6: Accidental Release Measures		
Use personal protection recommended in Section 8. Isolate the hazard area and deny entry to unnecessary and unprotected personnel. Sweep up spill and place in sealed bag or container for disposal. Wash spill area after pickup is complete. See Section 13 for disposal information.		
Section 7: Handling and Storage Yellow		
Handling: Use with adequate ventilation and do not breathe dust or vapor. Avoid contact with skin, eyes, or clothing. Wash hands thoroughly after handling.		
Storage: Store in Oxidizer Storage Area [Yellow Storage] with other oxidizers and away from any combustible materials. Store in a cool, dry, well-ventilated, locked store room away from incompatible materials.		
Section 8: Exposure Controls / Personal Protection		
Use ventilation to keep airborne concentrations below exposure limits. Have approved eyewash facility, safety shower, and fire extinguishers readily available. Wear chemical splash goggles and chemical resistant clothing such as gloves and aprons. Wash hands thoroughly after handling material and before eating or drinking. Use NIOSH-approved respirator with a dust cartridge.		
Exposure guidelines: Magnesium Nitrate: OSHA PEL: Not Available, ACGIH: TLV: Not Available, STEL: Not Available.		

Appendix 2: MSDS of 2,5-Dihydroxyterephthalic acid



- MATERIAL SAFETY DATA SHEET -

SECTION 1 - CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

MSDS Name : 2,5-Dihydroxyterephthalic acid
Company Identification : Clearsynth Labs Pvt. Ltd.
413 Laxmi Mall, New Link Road, Andheri (W),
Mumbai-400 053, INDIAIA
For Information call : +91-22-26355700
For emergencies call : +91-22-26355699
For further enquiries : info@clearsynth.com

SECTION 2 - COMPOSITION, INFORMATION ON INGREDIENTS

CAS#	Chemical Name	%	EINECS#	Haz Symbols	RISK PHRASES
610-92-4	2,5-Dihydroxyterephthalic acid	>95%	-	-	-

Hazard Symbols: XN
Risk Phrases: 22

SECTION 3 - HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Harmful if swallowed.

Potential Health Effects

The toxicological properties of this material have not been investigated. Use appropriate procedures to prevent opportunities for direct contact with the skin or eyes and to prevent inhalation. Compound is Non-hazardous, Non-Toxic/Non-Flammable.

SECTION 4 - FIRST AID MEASURES

Eyes:

Immediately flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids.

Skin:

Flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes.

Ingestion:

Do NOT induce vomiting. If conscious and alert, rinse mouth and drink 2-4 cupfuls of milk or water.

Inhalation:

Remove from exposure and move to fresh air immediately.

Notes to Physician:

SECTION 5 - FIRE FIGHTING MEASURES

General Information:

As in any fire, wear a self-contained breathing apparatus in pressure-demand, MSHA/NIOSH (approved or equivalent), and

Appendix 3: MSDS of Dimethylformamide (DMF)



MATERIAL SAFETY DATA SHEET

DIMETHYLFORMAMIDE

PRODUCT IDENTIFICATION

Chemical Name and Synonyms:

N,N-Dimethylformamide

Chemical Family:

Amide

Chemical Formula:

$\text{HCON}(\text{CH}_3)_2$

Product Use:

Laboratory solvent

Manufacturer's Name and Address:

Caledon Laboratories Ltd.

40 Armstrong Avenue

Georgetown, Ontario L7G 4R9

Telephone No.:

(905) 877-0101

Fax No.:

(905) 877-5555

Emergency Telephone No.:

CANUTEC (613) 995-5555

HAZARDOUS INGREDIENTS OF MATERIALS

Ingredients	%	TLV Units	CAS No.
<i>N,N</i> -Dimethylformamide	99	10 ppm	68-12-2

PHYSICAL DATA

Physical State:

Liquid

Odour and Appearance:

Clear liquid; fishy, pungent odour

Odour Threshold (ppm):

0.045 ppm (good warning properties, detectable well below the TLV)

Vapour Pressure (mm Hg):

2.7 mm Hg at 20°C

Vapour Density (Air = 1):

2.51

Evaporation Rate:

0.17 (*n*-Butyl acetate = 1)

Boiling Point (°C):

153°C

Freezing Point (°C):

-61°C

pH:

6.7 (0.5M, aqueous)

Specific Gravity:

0.95

Coefficient of Water/Oil distribution:

$\log P(\text{oct}) = -0.87$

SHIPPING DESCRIPTION

UN:

2265

T.D.G. Class:

3

Pkg. Group:

III

REACTIVITY DATA

Chemical Stability:

Normally stable.

Incompatibility with other substances:

Can react vigorously with acid chlorides, oxidizing agents, chloroformates, reducing agents, halogens. Explosive with triethylaluminum when heated. Reacts violently with carbon

tetrachloride or benzene hexachloride above 65°C, or in the presence of iron, and with such oxidizing agents as chromic anhydride, magnesium nitrate, potassium permanganate, bromine, nitric acid. Methylene bisphenyl diisocyanate polymerizes violently on contact with dimethylformamide. Not corrosive to metals.

Reactivity:

Avoid elevated temperatures, sparks, open flame, all ignition sources, and incompatible materials.

Hazardous Decomposition Products:

CO_2 , NO_x

FIRE AND EXPLOSION DATA

Flammability:

Combustible liquid. Must be moderately heated for combustion to occur.

Extinguishing Media:

Carbon dioxide, alcohol foam, or dry chemical. Do not use halogenated extinguishing material. Water spray can be used to absorb heat, disperse vapours, cool containers, but is ineffective for extinguishing fire. Fight fire from upwind, from a safe distance. Firefighters must wear protective equipment and clothing (Bunker gear) sufficient to prevent inhalation of fumes or vapours and contact with skin and eyes.

Flash Point (Method Used):

58°C (CC)

Autoignition Temperature:

445°C

Upper Flammable Limit (% by volume):

15.2

Lower Flammable Limit (% by volume):

2.2

Hazardous Combustion Products:

CO_2 , NO_x , dimethyl-amine

Sensitivity to Impact:

None identified

Sensitivity to Static discharge:

No information available; vapour in the flammable range may be ignited by a electrostatic charge of sufficient energy.

TOXICOLOGICAL PROPERTIES AND HEALTH

DATA

Toxicological Data:

LD₅₀:

(oral, rat) 2,800 mg/kg; (dermal, rabbit) 5,000 mg/kg

LC₅₀:

(Inh, mouse) 3,002 ppm/2h

Effects of Acute Exposure to Product:

Inhaled:

Irritating; may cause coughing, sneezing, and shortness of breath. Readily absorbed through respiratory tract, causing gastrointestinal complications, colicky abdominal pains, loss of appetite, nausea, vomiting, nervous agitation, increased blood pressure, liver damage, damage to kidneys and urinary tract. In contact with skin:

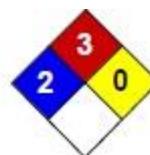
Mild irritant to skin and tissue. May cause drying and cracking of skin. May be absorbed through skin in toxic amounts, causing systemic symptoms as in "inhaled" or "ingested".

In contact with eyes:

Vapour can cause mild irritation. Liquid can cause temporary, moderate conjunctival inflammation and transient corneal damage.

Ingested:

Appendix 4: MSDS of Ethanol



Health	2
Fire	3
Reactivity	0
Personal Protection	E

Material Safety Data Sheet Ethyl alcohol 200 Proof MSDS

Section 1: Chemical Product and Company Identification	
Product Name: Ethyl alcohol 200 Proof Catalog Codes: SLE2248, SLE1357 CAS#: 64-17-5 RTECS: KQ6300000 TSCA: TSCA 8(b) Inventory: Ethyl alcohol 200 Proof CI#: Not applicable. Synonym: Ethanol; Absolute Ethanol; Alcohol; Ethanol 200 proof; Ethyl Alcohol, Anhydrous; Ethanol, undenatured; Dehydrated Alcohol; Alcohol Chemical Name: Ethyl Alcohol Chemical Formula: CH ₃ CH ₂ OH	Contact Information: Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396 US Sales: 1-800-901-7247 International Sales: 1-281-441-4400 Order Online: ScienceLab.com CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300 International CHEMTREC, call: 1-703-527-3887 For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients		
Composition:		
Name	CAS #	% by Weight
Ethyl alcohol 200 Proof	64-17-5	100
Toxicological Data on Ingredients: Ethyl alcohol 200 Proof: ORAL (LD50): Acute: 7060 mg/kg [Rat]. 3450 mg/kg [Mouse]. VAPOR (LC50): Acute: 20000 ppm 8 hours [Rat]. 39000 mg/m 4 hours [Mouse].		

Section 3: Hazards Identification
Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of Inhalation. Slightly hazardous in case of skin contact (permeator), of Ingestion.
Potential Chronic Health Effects: Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: A4 (Not classifiable for human or animal.) by ACGIH. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified PROVEN for human. DEVELOPMENTAL TOXICITY: Classified Development toxin [PROVEN]. Classified Reproductive system/toxin/female, Reproductive system/toxin/male [POSSIBLE]. The substance is toxic to blood, the reproductive system, liver, upper respiratory tract, skin, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.

Appendix 5: MSDS of Methanol



Health	2
Fire	3
Reactivity	0
Personal Protection	H

Material Safety Data Sheet Methyl alcohol MSDS

Section 1: Chemical Product and Company Identification								
Product Name: Methyl alcohol	Contact Information:							
Catalog Codes: SLM3064, SLM3952	ScienceLab.com, Inc. 14025 Smith Rd. Houston, Texas 77396							
CAS#: 67-56-1	US Sales: 1-800-901-7247 International Sales: 1-281-441-4400							
RTECS: PC1400000	Order Online: ScienceLab.com							
TSCA: TSCA 8(b) Inventory: Methyl alcohol	CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300							
CI#: Not applicable.	International CHEMTREC, call: 1-703-527-3887							
Synonym: Wood alcohol, Methanol; Methylol; Wood Spirit; Carbinol	For non-emergency assistance, call: 1-281-441-4400							
Chemical Name: Methanol								
Chemical Formula: CH ₃ OH								
Section 2: Composition and Information on Ingredients								
Composition:								
<table border="1"> <thead> <tr> <th>Name</th> <th>CAS #</th> <th>% by Weight</th> </tr> </thead> <tbody> <tr> <td>Methyl alcohol</td> <td>67-56-1</td> <td>100</td> </tr> </tbody> </table>	Name	CAS #	% by Weight	Methyl alcohol	67-56-1	100		
Name	CAS #	% by Weight						
Methyl alcohol	67-56-1	100						
Toxicological Data on Ingredients: Methyl alcohol: ORAL (LD50): Acute: 5628 mg/kg [Rat]. DERMAL (LD50): Acute: 15800 mg/kg [Rabbit]. VAPOR (LC50): Acute: 64000 ppm 4 hours [Rat].								
Section 3: Hazards Identification								
Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator). Severe over-exposure can result in death.								
Potential Chronic Health Effects: Slightly hazardous in case of skin contact (sensitizer). CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for mammalian somatic cells. Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Classified POSSIBLE for human. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to eyes. The substance may be toxic to blood, kidneys, liver, brain, peripheral nervous system, upper respiratory tract, skin, central nervous system (CNS), optic nerve. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.								
Section 4: First Aid Measures								

Appendix 6: MSDS of 2-amino-2-methyl-1-propanol (AMP)



801465 2-Amino-2-methyl-1-propanol
for synthesis

For general questions please contact our
Customer Service:

Merck KGaA
Frankfurter Str. 260
64293 Darmstadt
Germany
Phone: +49 6161 72-0
Fax: +49 6161 72 2000

29 April 2014

Product number	Packaging	Qty/Pk
8014650250	Glass bottle	250 ml
8014651000	Glass bottle	1 l
8014652500	Glass bottle	2.5 l
8014659026	Plastic container	25 l

Product information	
<i>Synonyms</i>	Isobutanolamine
<i>Hill Formula</i>	C ₄ H ₁₁ NO
<i>HS Code</i>	2922 19 85
<i>EC number</i>	204-709-8
<i>Molar mass</i>	89.14 g/mol
<i>EC index number</i>	603-070-00-6
<i>CAS number</i>	124-68-5

Chemical and physical data	
<i>Ignition temperature</i>	438 °C
<i>Melting point</i>	30 - 31 °C
<i>Molar mass</i>	89.14 g/mol
<i>Density</i>	0.96 g/cm ³ (26 °C)
<i>pH value</i>	11.3 (10 g/l, H ₂ O)
<i>Boiling point</i>	166 °C (1013 hPa) (anhydrous)

Appendix 7: MSDS of Toluene



Health	2
Fire	3
Reactivity	0
Personal Protection	H

Material Safety Data Sheet Toluene MSDS

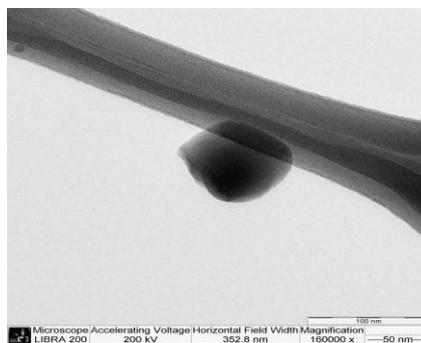
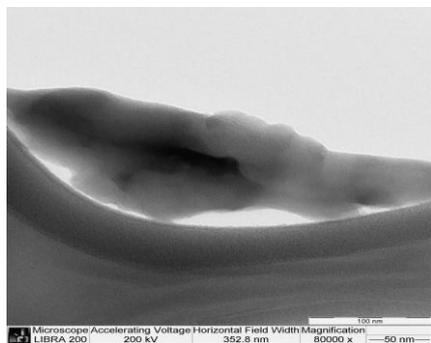
Section 1: Chemical Product and Company Identification	
Product Name: Toluene Catalog Codes: SLT2857, SLT3277 CAS#: 108-88-3 RTECS: XS5250000 TSCA: TSCA 8(b) Inventory: Toluene CI#: Not available. Synonym: Toluol, Tolu-Sol; Methylbenzene; Methacide; Phenylmethane; Methylbenzol Chemical Name: Toluene Chemical Formula: C6-H5-CH3 or C7-H8	Contact information: Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396 US Sales: 1-800-901-7247 International Sales: 1-281-441-4400 Order Online: ScienceLab.com CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300 International CHEMTREC, call: 1-703-527-3887 For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients		
Composition:		
Name	CAS #	% by Weight
Toluene	108-88-3	100
Toxicological Data on Ingredients: Toluene: ORAL (LD50): Acute: 636 mg/kg [Rat]. DERMAL (LD50): Acute: 14100 mg/kg [Rabbit]. VAPOR (LC50): Acute: 49000 mg/m 4 hours [Rat]. 440 ppm 24 hours [Mouse].		

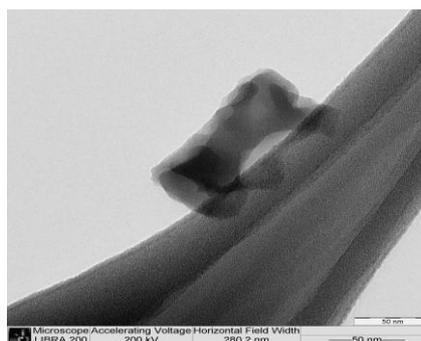
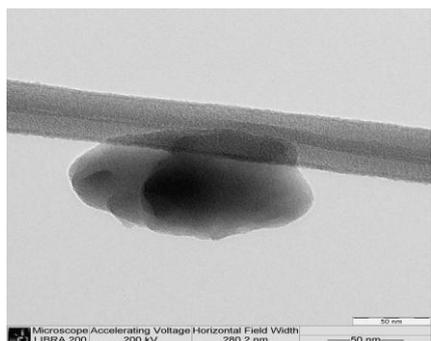
Section 3: Hazards Identification
Potential Acute Health Effects: Hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Slightly hazardous in case of skin contact (permeator). Potential Chronic Health Effects: CARCINOGENIC EFFECTS: A4 (Not classifiable for human or animal.) by ACGIH, 3 (Not classifiable for human.) by IARC. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to blood, kidneys, the nervous system, liver, brain, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

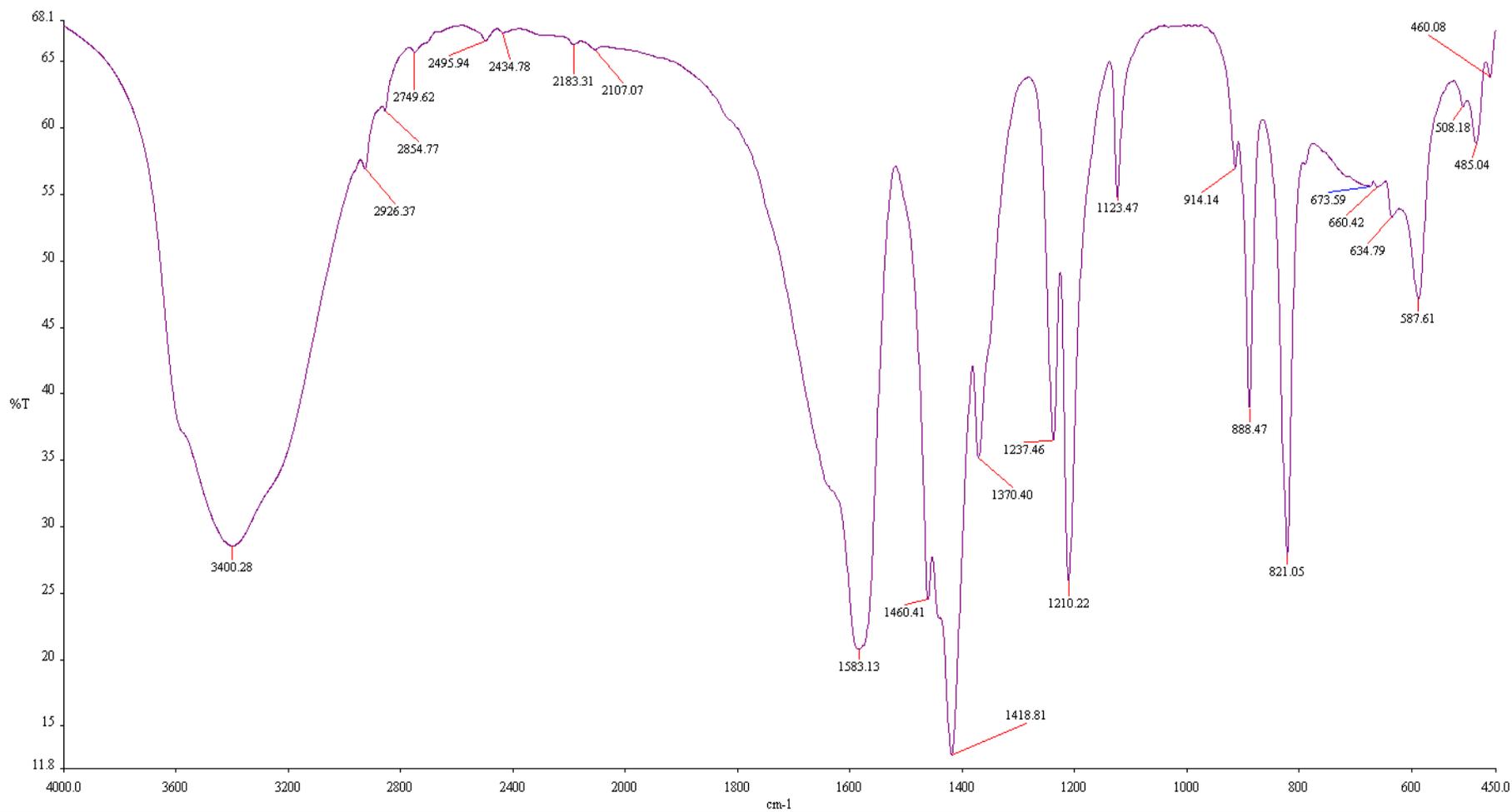
Appendix 8: TEM Images of Mg-MOF-74



Appendix 9: TEM Images of Mg-MOF-74-AMP

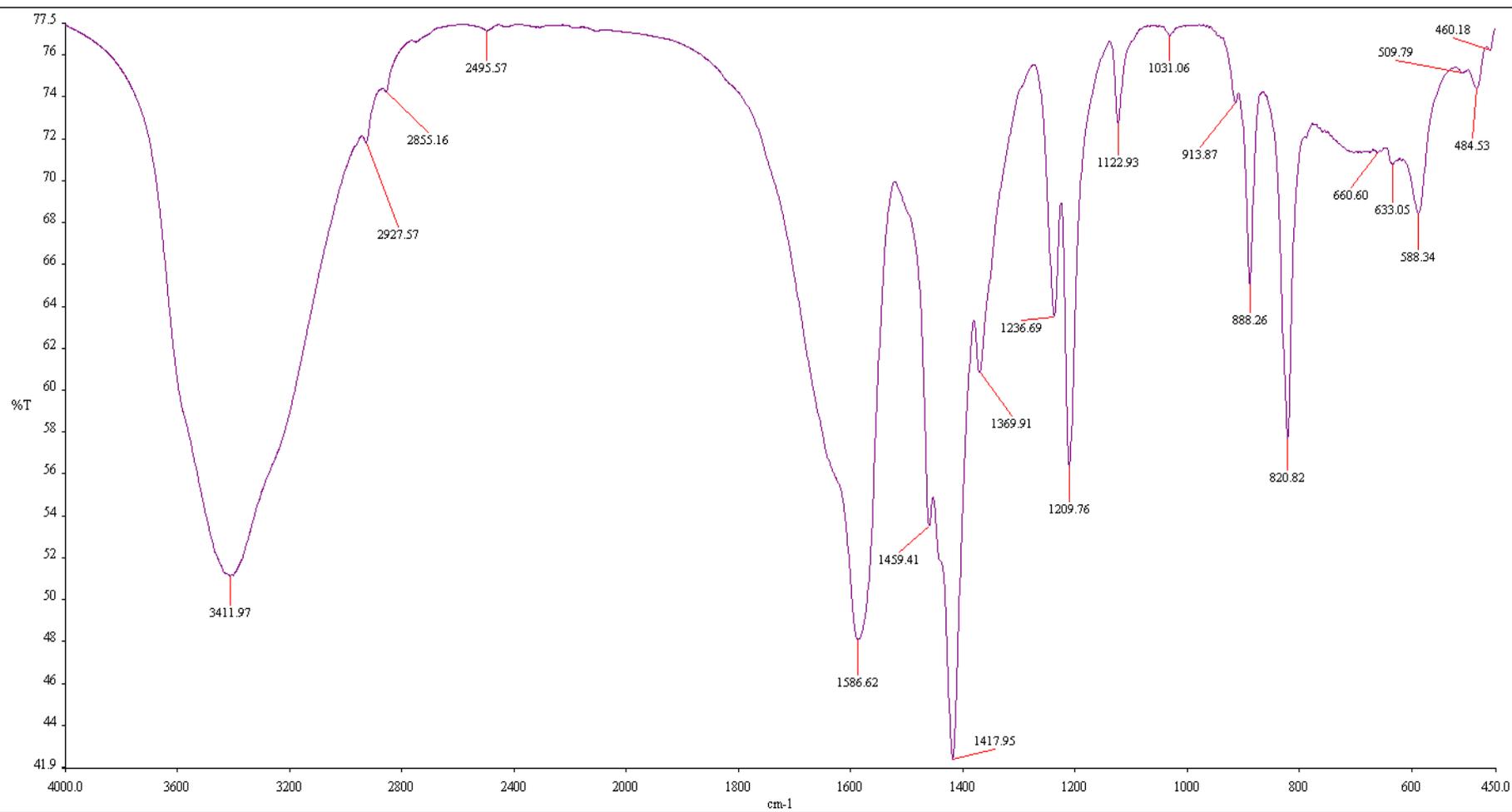


Appendix 10: FTIR spectra of Mg-MOF-74 synthesized at 60°C



Sample A (60oC).asc

Appendix 11: FTIR spectra of Mg-MOF-74 synthesized at 110°C



Sample B (110oC).asc

Appendix 12: FTIR spectrum of Mg-MOF-74-AMP

