SYNTHESIS AND CHARACTERIZATION OF MOF-235 USING ALUMINUM PILLARED CLAY FOR CO_2 ADSORPTION

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by

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15401

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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Approved by,

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September 2015

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.

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MOHD MU’IZZUDDIN BIN MOHD PAUZI

ABSTRACT

Reducing the concentration of the carbon dioxide (CO_2) emission become one of the most urgent environment issues nowadays. By reducing the concentration of the CO_2 will lead to the lowering the concentration of greenhouse gases. The source of CO_2 emission can be concluded from natural source as well as from human source. For the natural source, CO_2 emission occurs from the decomposition, ocean release, respiration and volcanoes. Furthermore, for the human source, the CO_2 will emit from activities like cement production, deforestation and the burning of fossil fuels. One of the common technologies that had been use for reducing the CO_2 concentration is by using carbon capture and storage (CCS). Usually, CCS method is used from large point sources such as power plants are one option for reducing CO_2 emissions. Apart from CCS technique, the alternative method reducing of the CO_2 concentration also had been studied. One of the methods is known as adsorption technique. However, the adsorption of CO_2 from gas streams is still a critical issue. Apart from establishing new techniques, the exploration of capture materials with high adsorption performance and low capital cost are of paramount importance. Metal-organic frameworks (MOFs), a new class of crystalline porous materials constructed by metal-containing nodes bonded to organic bridging ligand shows a great potential as adsorbents or membrane materials in gas separation. By relating to the project title, this project will focus on synthesis, characterization and modification of MOF-235 and it is believed to give a better in the adsorption ability of CO_2. Thus, MOF-235 can be a good alternative method in reducing CO_2 emission.

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LIST OF ABBREVIATIONS

ADS	Adsorption
BET	Brunauer–Emmett–Teller method
CCS	Carbon, Capture and Storage
CO_2	Carbon Dioxide gas
DES	Desorption
DMF	Dimethylformamide
SEM	Scanning Electron Microscope
SSA	Specific Surface Area
FTIR	Fourier Transform Infrared
IR	Infrared
MK-10	Montmorillonite K-10
MT	Montmorillonite
MOF	Metal Organic Framework
PLIC	Pillared Interlayered Clay
TGA	Thermogravimetry Analysis

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Carbon dioxide (CO_2) is classified as one of the most significant greenhouse effect contributors. From year to year, the level of CO_2 emission keeps on rising till reaching a perturbation stage (Synthesis Report, 2007). Climate scientists have observed that CO_2 concentrations in the atmosphere have been increasing significantly over the past century, compared to the rather steady level of the pre-industrial era (International Energy Agency, 2014). A report by 49 researchers from 10 countries said, “Global CO2 emissions from burning fossil fuels will rise to a record 36 billion metric tons (39.683 billion tons) this year” (Reuters, 2013). Therefore, proper technologies need to be prepared and set up to in order reduce the releasing of CO_2 to the atmosphere.

Amongst these alternative technologies are adsorption based CO_2 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). The current inventions that most of the researcher stressed are by using metal organic framework (MOFs). MOFs very good in the CO_2 adsorption because of their unique properties, such as their highly diversified structures, large range in pore sizes, very high surface areas, and specific adsorption affinities, make MOFs excellent candidates for use in the construction of molecular sieve membranes with superior performance (Li, Liang et al. 2010).

Besides that, the pillared interlayered clays (PILCs) also one of the interesting material that widely used for the CO_2 adsorption. PILCs present, in general, lower structural regularity than, for instance, the more usual zeolites, but PILCs structural regularity is higher than other important classes of adsorbent materials, such as activated carbons (Pires and Pinto 2010). The development of inorganic pillared interlayered clays, an important category of high surface area materials, has created remarkable new opportunities in the field of the synthesis and applications of clay-based solids (Gil and Gandía 2003). Because of its large pores, the early interest in PILC was in the possibility of replacing zeolite as the catalyst for fluid catalytic cracking (Linda, Ralph et al. 1996). The Aluminum pillared clay (Al-PILC) also known as Montmorillonite (MT) is most famous in the PILC-research (Molinard and Vansant 1995).

The focus of this study is synthesized the MOF-235 and modified the MOF-235 by using MT. The effect on CO_2 adsorption performance of coated MOF-235 on MT is yet to well understand. Therefore, CO_2 adsorption on MOF-235 and modified MOF-235 by using MT are investigate. MOF-235 is available commercially as well as MT. The MT that used in this project is Montmorillonite K-10 (MK-10). The MOF-235 was coated on the MK-10 by using wet impregnation method. The hypothesis was proved through the study of CO_2 adsorption capacity using CO_2 adsorption study. This study focused on the increasing of the adsorption capacity of MOF-235 through its modification thus leading the development in CO_2 removal application.

1.2 Problem Statement

The increasing in carbon dioxide concentration nowadays became one of the largest global environment issues. Among the greenhouses gases, CO_2 contributes more than 60% to the global warming. Hence, some method must be set up to reduce the concentration of this gas. Several researches have studied regarding the synthesizing of the metal organic frameworks (MOFs) for CO_2 adsorption including MOF-235 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.

The adsorption of CO_2 was focused in this study. The modified of MOF-235 by using MK-10 is considered as new adsorbents. The MOF-235 contains high pore volume and surface area in previous studies. Furthermore, the alternative adsorbents are needed to develop for the active and economical material which provide higher CO_2 adsorption rate.

1.3 Objectives and Scope of Study

This study will be investigated the improvement of properties, characterization and investigated of prepared MOF-235 and modified MOF-235 by using MK-10 in order to enhance the CO_2 capture capability.

The objectives of this project are:

1. To synthesis of MOF-235 and MOF-235 by using MK-10.
2. To characterize the MOF-235 and Modified MOF-235 via SEM, FTIR, TGA and BET for CO_2 adsorption.
3. To analyze the capability of CO_2 adsorption of MOF-235 and Modified MOF-235 via characteristic results.

This project involved the synthesis of samples, characterization of samples and a CO_2 adsorption experiment. In addition, the synthesis and adsorption experiment were conducted in CO_2 laboratory while the characterization was done by the authorized personnel

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

1. Study and familiar with the experimental procedure on synthesizing metal organic frameworks, MOF-235 and Modified MOF-235 by using MK-10.
2. Study on various analysis methods to identify the characteristics of MOF-235 and Modified MK-10.
3. Study on the CO_2 adsorption capacity of the two metal organic frameworks, MOF-235 and Modified MOF-235.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 CO_2 Capture and Storage

In order to reduce the emission of CO_2 to the atmosphere, CO_2 capture and storage (CCS) have been used. Usually, post-combustion, pre-combustion and oxyfuel combustion are the three main categories of CO_2 capture technologies (Foundation, 2007). Post-combustion are the CO_2 end-of-pipe separation from the flue gas mostly consist of N_2 and CO_2. Before the absorbent is brought into contact with the flue gas, it is cooled down first. Then, CO_2 will be attached to the absorbent. In the second process, to release concentrated CO_2 and regenerate the absorbent, the liquid solution is heated. Roughly, 80 to 90 percent of the CO_2 can be captured by using this technology (Foundation, 2007).

Figure 2.1 shows different technologies and associated materials for CO_2 separation and capture (Li et al., 2011). Capturing CO_2 by porous material is an alternative approach among the CCS technologies due to its energetic efficiency and technical feasibility. Metal-organic frameworks (MOFs) have shown greater potential rather than other CCS technologies as they have high specific surface areas (SSAs), pore volume and tuneable pore size.

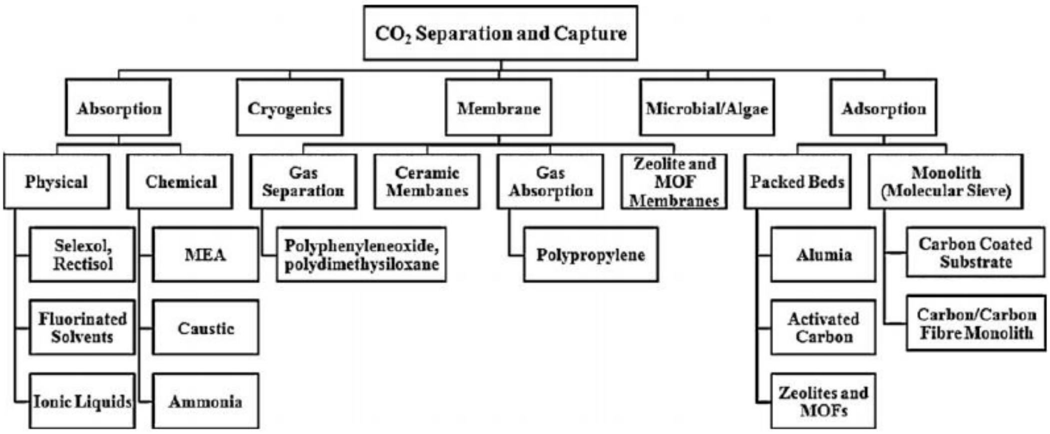


Figure 2.1 Different technologies and associated for CO_2 separation and capture (Thiruvenkatachari, 2009)

According to Li et al (2011), stated that the critical CO_2 capture capacity of MOFs is directly related to CO_2 measurement at room temperature and high pressure. It’s been found that the total pore volume of MOFs is effectively correlated with CO_2 amount which could be adsorbed at high pressure. Hence, it’s been concluded that the surface area directly related to CO_2 storage capability.

This study will be used BET method to determine the rate of CO_2 adsorption of impregnation MOF-235 on aluminum pillared clay. Since, many studies have been stated that Brunauer–Emmett–Teller (BET) method is related with isotherm adsorption analysis due to their pore volume and surface area of the adsorbents (Lili et al., 2012; Guo & Fang., 2014)

2.2 Adsorption of CO_2 Using MOFs

Metal-organic frameworks (MOFs) are a class of crystalline porous materials which has been emerged in the past two decades. According to Stephen Caskey, MOFs consist of metal ions or clusters, containing nodes linked by multidirectional organic linkers/ligands and assembled through strong coordination bonds in the network structure. The network can be 1-D, 2-D and 3-D extended, periodic structures (Caskey, 2009). The structure of MOFs could easily be tuned and modified using a building-block approach thus resulting in porous material with high surface area and low-density (Jung et al., 2013). They have a great potential in advancing a variety of applications such as gas storage, adsorption separation, catalysis and gas sensing (Mu et al., 2010).

Basically, MOFs have been studied widely for three main reasons. First and foremost, these materials possess high surface areas, for instance, MOF-177 = $4500m^2/g$ (Chae et al., 2004), MOF-5 = $3000m^2/g$ (Eddaoudi et al., 2002), (Yaghi, Rosi, et al., 2003) and Cu-MOF = $3200m^2/g$ (Seki, 2001) and controlled porosity. It makes them good candidates for gas storage and catalysis. Secondly, some MOFs may have attraction for certain gases and, therefore, MOFs could be used in gas separation. For example, Seki's Cu-MOF that has a methane sorption capacity of 212 cm^3 STP g^{-1}, which is superior to the sorption capacity of zeolite 5A and nearly the same as activated carbon AX-21 (Seki, 2001). Third, in terms of chemical composition, MOFs are highly flexible. Thus, it allows the addition of functional groups which could change the pore size and chemical properties of the MOF (Perez, Balkus, Ferraris, & Musselman, 2009).

There are two types of MOFs which are rigid and flexibility or dynamics. Rigid MOFs generally have comparatively stable and robust porous frameworks. The porous frameworks have permanent porosity. For flexible MOFs, have dynamic and "soft" frameworks which respond to external stimuli, for example, temperature, pressure and guest molecules (Li et al., 2011). Due to their adjustable pore sizes, controllable pore surface properties, and large surface areas, MOFs are the ideal adsorbents or membrane materials for gas storage and separation. Most MOFs have higher pore volumes and surface areas than other porous material, such as zeolites and activated carbon. The total pore volume of MOFs is proportional to the amount of adsorbed CO_2 at high pressure.

2.3 MOF-235

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). An iron terephthalate (MOF-235), one of the metal-organic frameworks (MOFs), has been used for the removal of CO_2 via adsorption. The adsorption capacities of MOF-235 are much higher than those of an activated carbon. The performance of MOF-235 having high adsorption capacity is remarkable because the MOF-235 does not adsorb nitrogen at liquid nitrogen temperature. The solvent molecule (water or DMF) can be easily removed under vacuum, increasing the concentration of unsaturated coordinative metal cations.

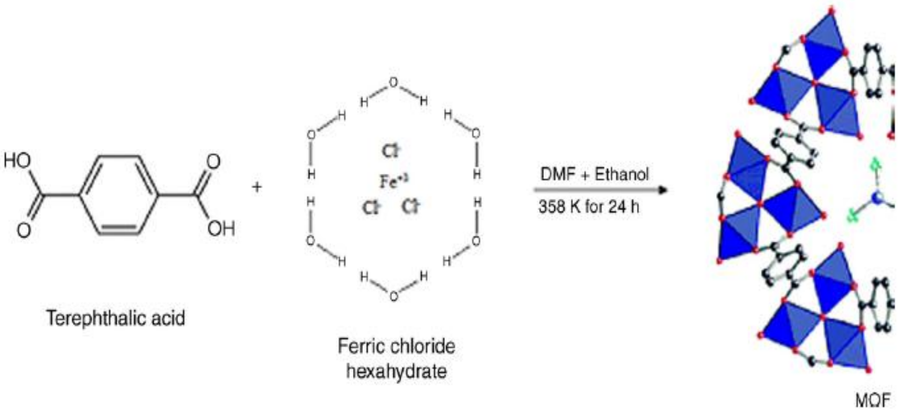


Figure 2.3 MOF-235 sample analogs (Anbia et al., 2012)

2.4 Montmorillonite

Aluminum pillared clay or montmorillonites are one of the more abundant semiotic clays in nature. They are characterized by the substitution of Al^{3+} in the octahedral sheet by Mg^{2+}, resulting in a negative layer charge that is compensated by hydrated cations adsorbed in the interlamellar space. These cations can easily be substituted by others present in solution.

Barrer and MacLaeod studied the enhancement of the adsorption capacity of smectites when exchanged with tetraalquilammonium salts. Careful calcination of the exchanged clay leads to interesting materials with permanent microporosity across a range of molecular sizes. Lahav et. Al. reported as PILCs (Pillared Inter-Layered Clays) because the calcined oxocations act as pillars that prop up clay layers. Since the work of Brindley and Sempels and Lahav et. al. different oxocations of Al, Zr, Ti, La, Ga, Fe and Cr have been used. Mixed pillars (Ga-Al, Ga-La) have been used to improve thermal stability. Several reviews on the topic have been reported.

PILCs are attractive as adsorbents or catalysts either as catalysts or as catalyst supports. Their widespread use has been delayed by difficulties in obtaining a uniform and reproducible product at a pilot scale because of the many parameters involved in the preparation process that influence PILCs' properties. The first Al-PILC was a coarse-grained material consisting of aggregates with rather well-order clay lamellae, while the second Al-PLIC was prepared in a way that led to fine grains comprising aggregates of randomly stacked lamellae. The latter material showed very fast cation uptake, which is a property of high practical value.

2.5 Modified MOF-235

The applications and potentials of thin film coatings of metal–organic frameworks (MOFs) supported on various substrates are discussed in this few decades. Because the demand for fabricating such porous coatings is rather obvious, in the past years several synthesis schemes have been developed for the preparation of thin porous MOF films. Interestingly, although this is an emerging field seeing a rapid development a number of different applications on MOF films were either already demonstrated or have been proposed.

Lately, many researchers focuses on the fabrication of continuous, thin porous films, either supported on solid substrates or as free-standing membranes. The availability of such two-dimensional types of porous coatings opened the door for a number of new perspectives for functionalizing surfaces. Also for the porous materials themselves, the availability of a solid support to which the MOF-films are rigidly (in a mechanical sense) anchored provides access to applications not available for the typical MOF powders with particle sizes of a few μm.

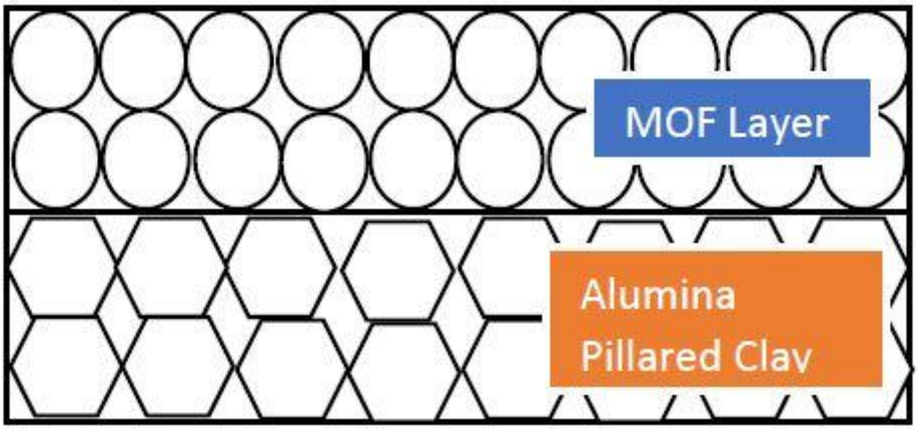


Figure 2.5 MOF layer coated on Montmorillonite

2.6 Material Characterization

Characterization techniques used to analyze sample are Fourier Transform Infrared Spectroscopy (FTIR), Thermal Gravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM) (Wu et al., 2013; Chen et al., 2010). The texture and morphology of MOF will be analyzed by using SEM. Furthermore, TGA was used to analyze the thermal degradation and weight loss of the synthesized MOFs.

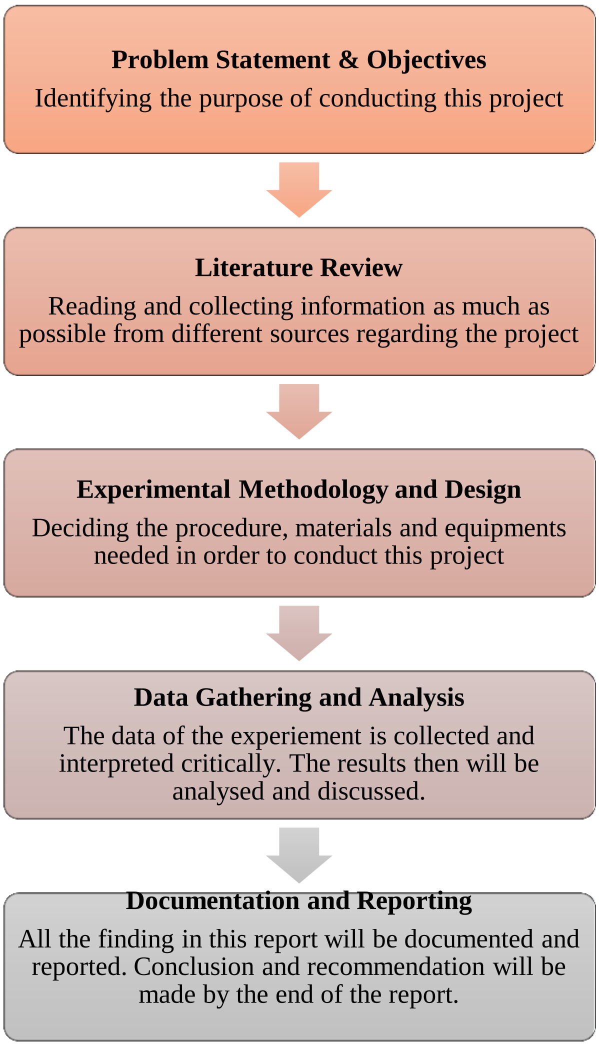
Moellmer (2009) states that the microporous solids’ surface area results gained from BET method on adsorption isotherm do not show the actual internal surface area. Bae et al. (2009) also suggest that comparison of the experimental BET surface area with the calculated value can provide the surface area deviations from the perfect geometric of crystal structure. The FTIR will show us the functional group of the substance that we analyzed. From the FTIR results, we can know either the functional group of Modified MOF-235 is change or not compare to the original MOF-235.

CHAPTER 3

METHODOLOGY AND PROJECT WORK

3.1 Project Process Flow

This is the process flow for this research project that must be followed so that the objectives of the study can be achieved.



Problem Statement & Objectives
Identifying the purpose of conducting this project

Literature Review
Reading and collecting information as much as possible from different sources regarding the project

Experimental Methodology and Design
Deciding the procedure, materials and equipments needed in order to conduct this project

Data Gathering and Analysis
The data of the experiement is collected and interpreted critically. The results then will be analysed and discussed.

Documentation and Reporting
All the finding in this report will be documented and reported. Conclusion and recommendation will be made by the end of the report.

Figure 3.1 Project Activities Flowchart

3.2 Gantt Chart & Key Milestone

Table 3.2 Gantt chart

No.	Details	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	**Project work 1:** Synthesis of MOF-235 (1st Batch)	🟨	🟨	🟨											
2	**Project work 2:** Synthesis of MOF-235 (2nd Batch)			🟨	🟨	🟨									
3	**Project work 3:** Synthesis of modified MOF-235					🟨	🟨	🟨							
4	Characterization submission and results								🟨	🟨					
5	Submission of Progress Report								◆						
6	Characterization submission and results continues									🟨	🟨				
7	Pre-SEDEX											◆			
8	Submission of Draft Report											◆			
9	Submission of Soft Bound Dissertation												◆		
10	Submission of the technical paper												◆		
11	Viva Oral Presentation													◆	
12	Submission Of Project Dissertation														🟨

🟨 Key Milestone

◆ Process

3.3 Experimental Methodology

3.3.1 Synthesis and Preparation of MOF-235

Chemical Substances

1. Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$)
2. Terepthalic Acid ($C_8H_6O_4$)
3. Dimethylforamide (DMF)
4. Ethanol (C_2H_6O)

Experiment Procedures

1) An exact amount of terepthalic acid (0.614 g) is weighted by using micro-balance and then mixed with 180 ml of DMF.
2) The mixture is stirred for 10 minutes by using magnetic stirrer until a clear solution is formed.
3) 0.6 g of iron chloride is added into solution and then is stirred for another 5 minutes.
4) The reaction mixture of 90 ml and 90 ml of ethanol are mixed together.
5) 360 ml of the mixture is loaded into Teflon-lined Autoclave and is placed in electic oven (85 °C) for 24 hours.
6) Orange powder of MOF-235 is collected by centrifuge and washed by using 50% of DMF and 50% of ethanol mixture for 3 times.
7) The product is dried overnight and is stored in glass vial.

3.3.2 Synthesis and Preparation of Modified MOF-235

The aluminum pillared clay is available commercially. The aluminum pillared clay that had been used is Montmolrillonite-K10 (MT). For this project, the MOF-235 will be modified with MT by using 5%, 10% and 15% of MOF-235 to MT.

The following procedure is the synthesizing modified MOF-235 by using 5% of MOF-235 to MT:

1) 3 g of MT is treated in an aqueous solution dissolve with sodium hydroxide. The concentration of sodium hydroxide is set at 0.05M and stirred for 8 hours at 200 rpm in room temperature.
2) Then, 5% of MOF-235 to MT by mass ratio is added to the solution. Means, if 3g of MT is used; then the amount of 5% MOF needed is 0.15g.
3) The mixture is continued stirring for another 24 hours at 160 °C. The expectation is that the MOF-235 distributes uniformly on the MT.
4) After that, the final product is collected by centrifuge and washed with extra distilled water 7 times.
5) To remove any adsorbed guest, the modified MOF-235 is dried at 150°C for 12 hours in vacuum oven.

The same procedure is repeated by using 10% and 15 % of MOF-235.

3.4 Characterization Technique for MOF-253 and Modified MOF-235

In this project, there are four characterization need to be made. First, characterization is made by using BET for CO_2 adsorption. BET (Brunauer, Emmett and Teller) can evaluate the value of superficial specific surface area of the material by using the principle of the inert gas adsorption. In this project the gas that had been used is CO_2 gas by varying the relationship between the partial pressure of CO_2 and its vapor pressure to the adsorption capacity of material.

On the other hand, the characterization can also be done by using Scanning Electron Microscope (SEM) where those instruments can analyze the samples morphology and surface texture. SEM is an electron microscope that allows ultra-high resolution electron imaging up to x 1,000,000. Meanwhile, SEM uses energetic electrons to produce high resolution, black and white images in the realms of 10 micrometer to 100 micrometer, providing the morphology, compositional and crystallographic information on the samples. Also, the SEM can produce three-dimensional images.

Thermogravimetric analysis (TGA) is used to measure the weight gain or loss during a heating or cooling process. TGA thermal curve is displayed with the X-axis as the time or temperature and the Y-axis as the weight (mg) or the weight percent (%). FT-IR analysis is to analyze the different in functional group for both samples which is MOF-235 itself and modified MOF-235.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis Results

Referring to the Gantt Chart for this project, the project is working as planned chart of this project, all the project work are going as planned. The MOF-235 was successfully synthesized with in the time. The total amount of MOF-235 in 1st batch and 2nd batch that was collected is 0.4843g. The orange powder of MOF-235 needs to be stored in moisture free condition because as we know that the MOF-235 will degrade in the present of moisture. The figure below is the MOF-235 that was synthesized.

Figure 4.1(a) Collected MOF-235

The modified of MOF-235 is synthesized by using the MK10. The total amount of MOF-235 will be distributed to three different sample of modified MOF-235. The three sample of modified MOF-235 are 5%, 10% and 15% of MOF-235 to the MK10. The percentage of MOF-235 to the MK10 is based on the mass ratio. The mass ratio for the modified MOF-235 to MK10 is defined in the table below.

Table 4.1(a) Mass ratio of modified MOF-235 to montmorillonite-K10

Percentage of MOF-235	Amount of MOF-235	Amount of MK10
5%	0.15g	3.0g
10%	0.30g	3.0g
15%	0.15g	1.0g

The figure below is the modified MOF-235 that was synthesized by using 5%, 10% and 15% of MOF-235 respectively. The final amount of modified MOF-235 that was collected is stated in Table 3. The final amount modified MOF-235 is decrease due to the some impurities that was removed during the dilution and drying process.

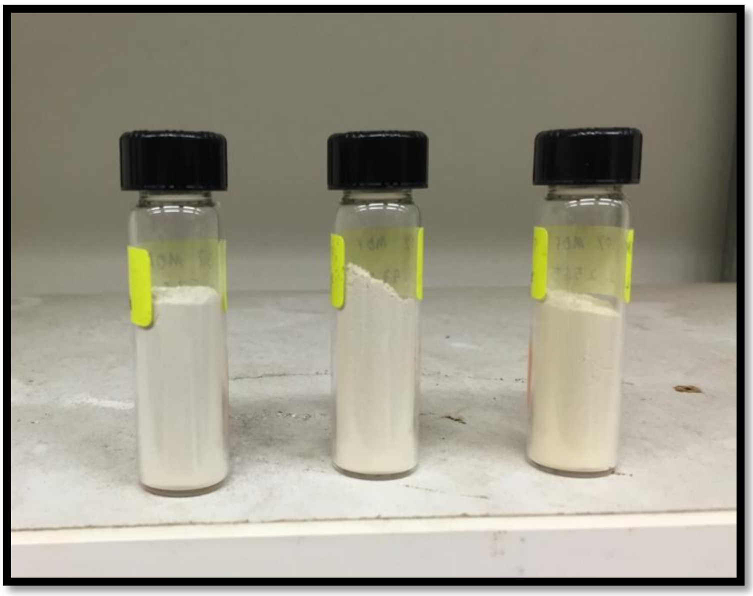


Figure 4.1(b) Collected Modified MOF-235

Table 4.1(b) The final amount of MOF-235

Percentage MOF-235 used	**Amount of modified MOF-235**
5%	2.5490g
10%	2.4727g
15%	0.2565g

4.2 Characterization Results

4.2.1 Scanning Electron Microscope (SEM)

Figure 4.2.1 (a), 4.2.1 (b), 4.2.1 (c), 4.2.1 (d) and 4.2.1 (e) shows the comparison between the SEM images of MOF-235, MK-10, 5% MOF-235/MK-10, 10% MOF-235/MK-10 and 15% MOF-235/MK-10 respectively.

The image from Figure 4.2.1 (a), we can assume that the particles of MOF-235 have octahedron morphology and not much different with diamond-like shape. MOF-235 obtained the basic octahedron structure but there are many defect on the structure of the particles itself and also the edge of the particles is not sharp. In the meanwhile, the image captured as illustrated in the Figure 4.2.1 (b) reveals that the majority of the particles had a lamellar morphology. The MK-10 structure can be seen that the particle consisting mainly of flake-like particles.

Hence, for the Figure 4.2.1 (c), 4.2.1 (d) and 4.2.1 (e) we can conclude that the diamond-like shape indicated as MOF-235 and flake-like shape indicated as MK-10. The MOF-235 and MK-10 is not chemically bond but they physically bond each other.

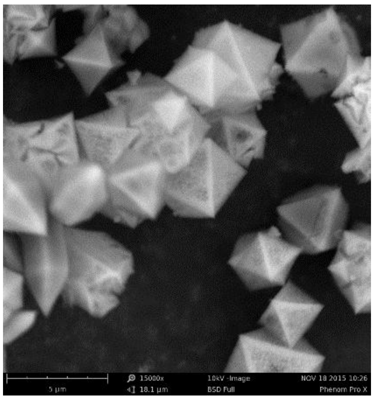


Figure 4.2.1(a) SEM image of MOF-235

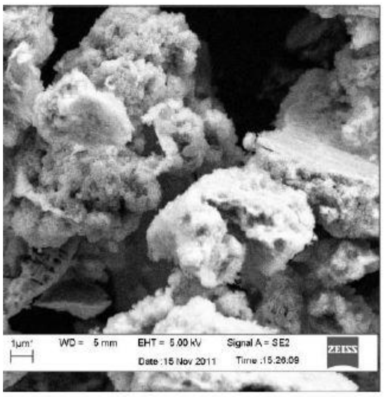


Figure 4.2.1(b) SEM image of MK-10

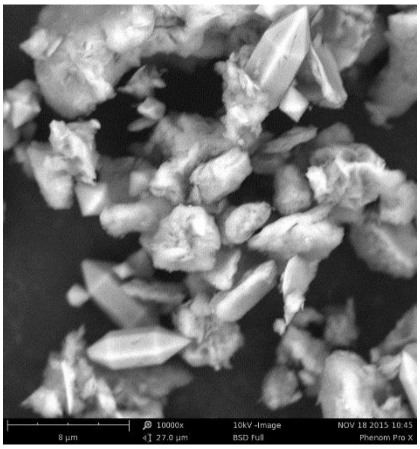


Figure 4.2.1(c) SEM image for 5% MOF-235/MK-10

Figure 4.2.1(d) SEM images for 10% MOF-235/MK-10

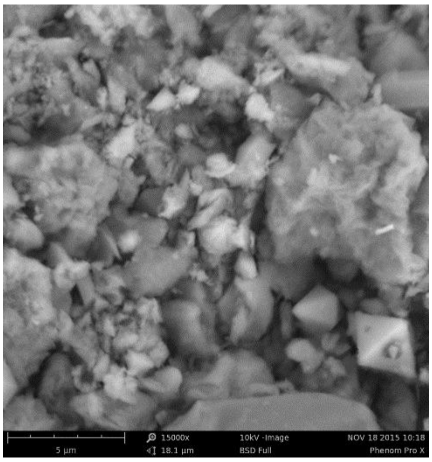


Figure 4.2.1(e) SEM image for 15% MOF-235/MK-10

4.2.2 Termogravimetric Analysis (TGA)

Figure 4.2.2 (a), 4.2.2 (b), 4.2.2 (c), 4.2.2 (d) and 4.2.2 (e) shows TGA curves recorded for the MOF-235, MK-10, 5% MOF-235/MK-10, 10% MOF-235/MK-10 and 15% MOF-235/MK-10. The total weight losses for the samples are described in the table below when heated up to 800°C.

It is clear form this figures that all the samples released physically moisture content when it heated up at 100°C. A very strong and stable sample had obtained as the TGA curves show that all the sample did not decomposed when heat it up to 800°C. The percentage weight losses for all the samples are slightly decrease at 800°C due to the structure change of the particles.

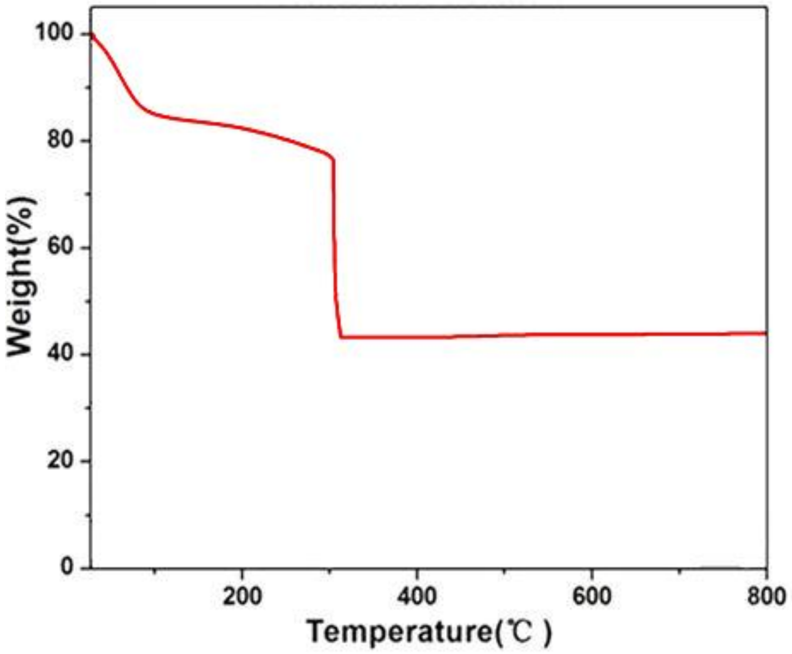


Figure 4.2.2(a) TGA curve for MOF-235

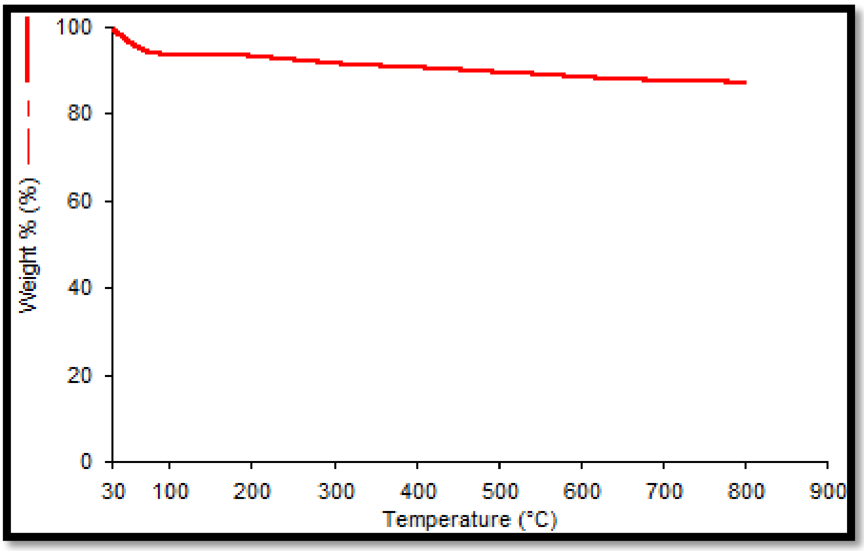


Figure 4.2.2(b) TGA curve for MK-10

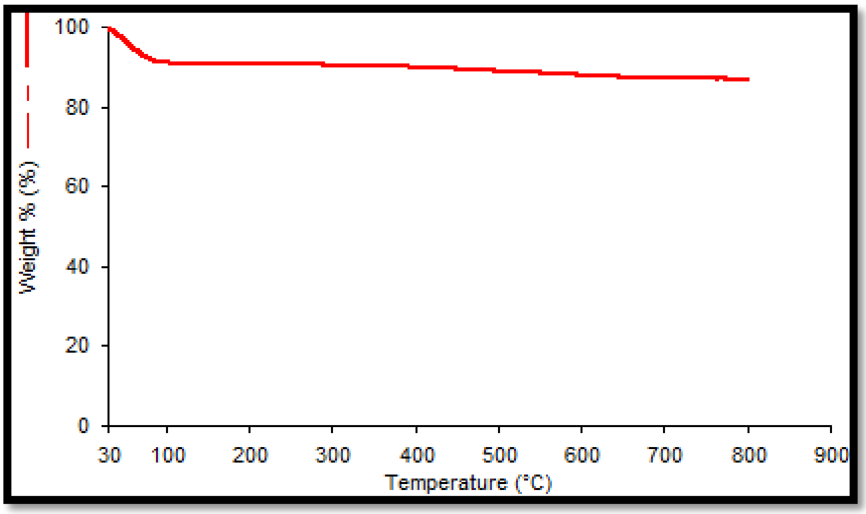


Figure 4.2.2(c) TGA curve for 5% MOF-235/MK-10

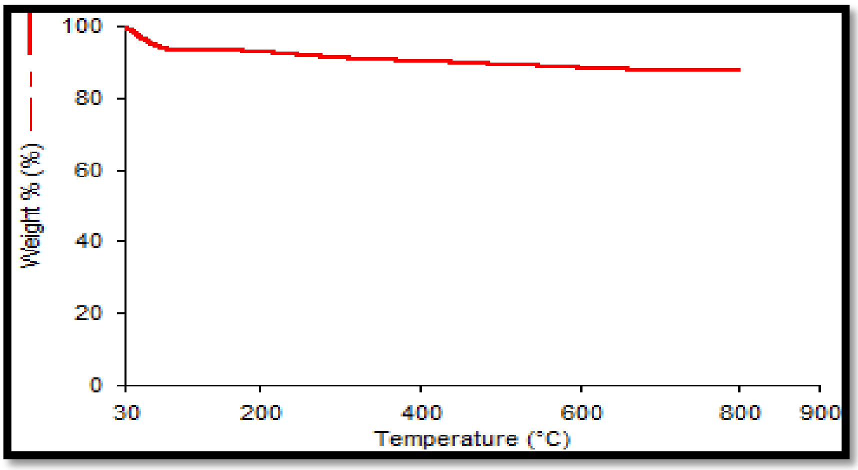


Figure 4.2.2(d) TGA curve for 10% MOF-235/MK-10

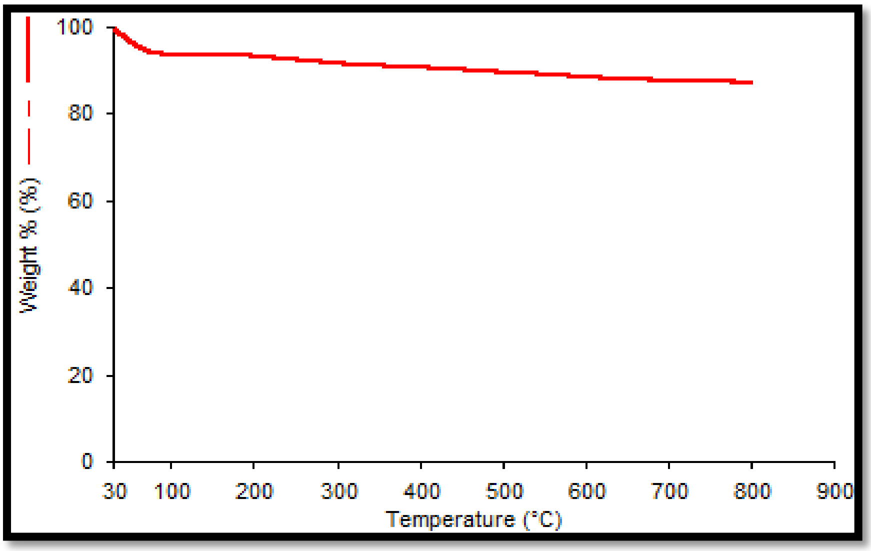


Figure 4.2.2(e) TGA curve for 10% MOF-235/MK-10

4.2.3 Fourier Transform Infrared (FTIR) Spectroscopy

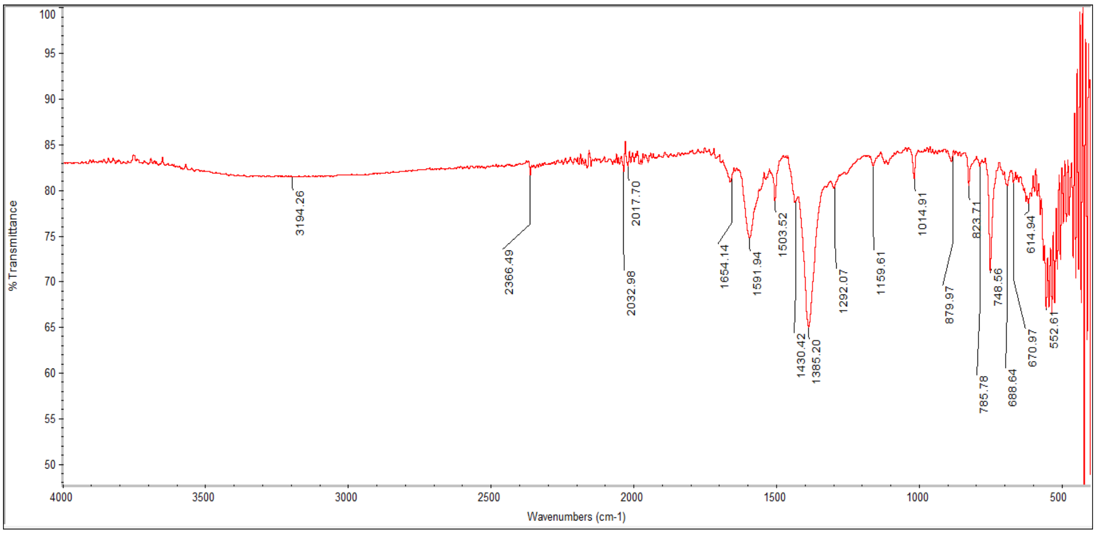


Figure 4.2.3(a) FTIR Spectra of MOF-235

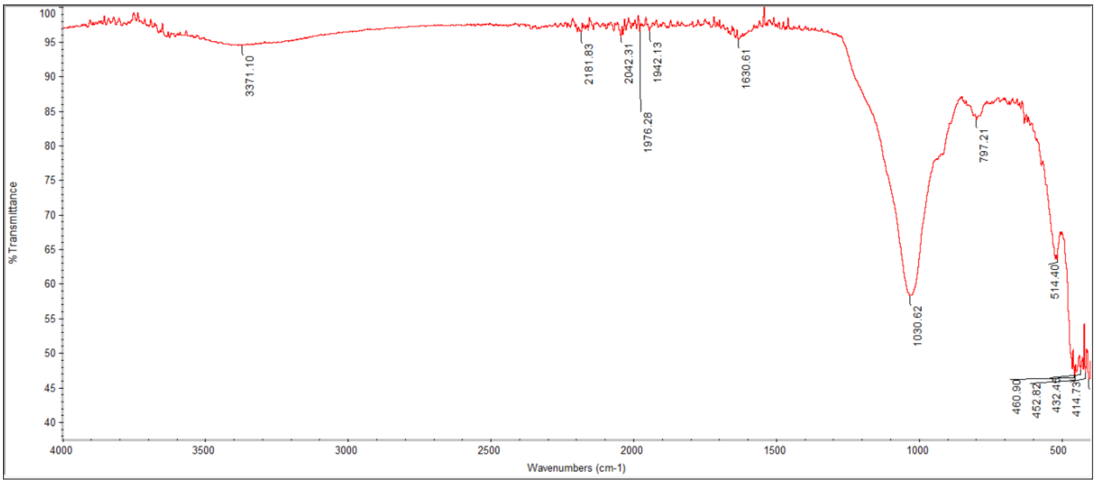


Figure 4.2.3(b) FTIR Spectra of MK-10

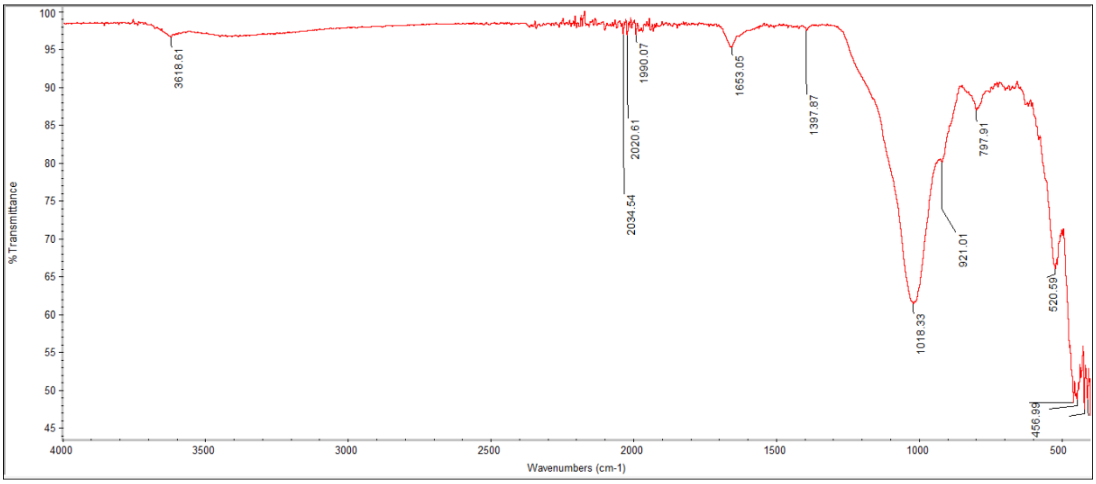


Figure 4.2.3(c) FTIR Spectra of 5% MOF-235/MK-10

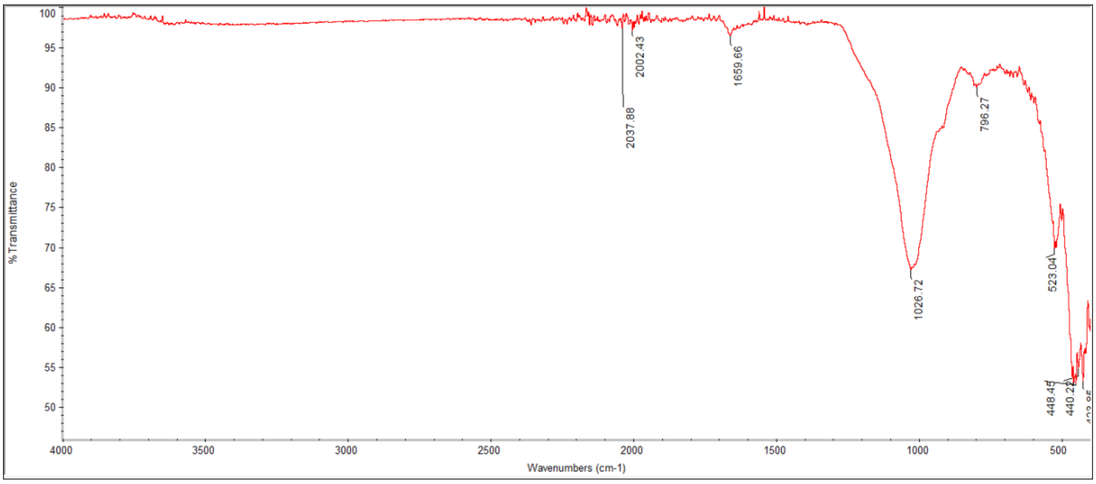


Figure 4.2.3(d) FTIR Spectra of 10% MOF-235/MK-10

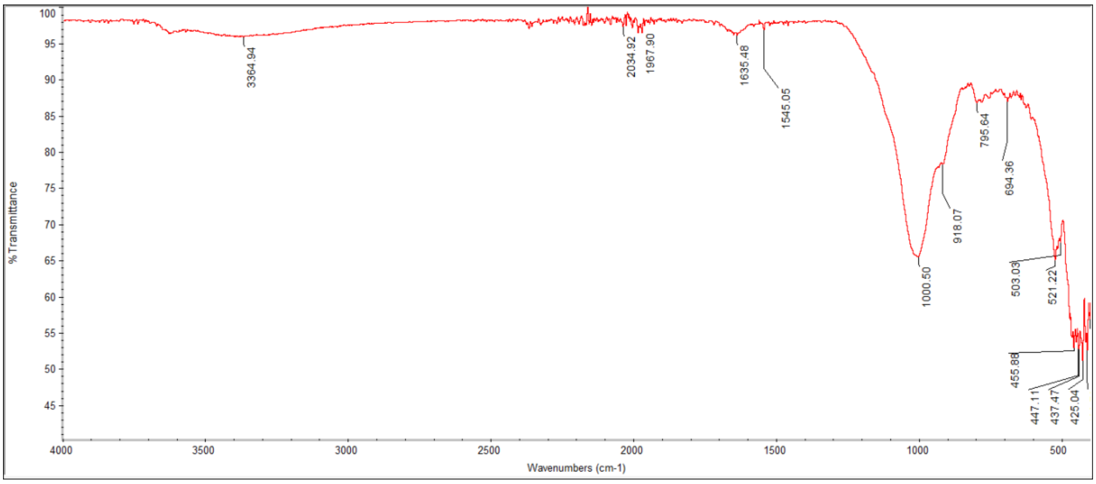


Figure 4.2.3(e) FTIR Spectra of 15% MOF-235/MK-10

The Figure 4.2.3 (a), Figure 4.2.3 (b), Figure 4.2.3 (c), Figure 4.2.3 (d) and Figure 4.2.3 (e) shows the FTIR spectra for MOF-235, MK-10, 5% MOF-235/MK-10, 10% MOF-235/MK-10 and 15% MOF-235/MK-10 respectively. The FTIR spectra are obtained in between range 400-4000 cm^{-1} of wave number.

The peak that obtained from the MOF-235 mostly comes from the carboxylate groups' vibration. These result also identical to the report from literature. The wave numbers that indicate carboxylate group are come from the peak at 748.56, 1385.20, 1503.52, 1591.94 and 1654.14 cm^{-1}. A peak appears at 3194.26 cm^{-1} indicates that there is a presence of O-H stretching vibration group and also represent the alcohol functional group. The aromatic ring of C-C bond also existed at the peak of 1591.94cm-1. Besides that, there are two peaks that indicate asymmetric and symmetric vibration of carboxyl group. These two peak appear at 1503.52cm^{-1} and 1385.20cm^{-1} which confirming the existing of dicarboxylate linker. The bending at 748.56cm^{-1} indicates the presence of C-H bending vibration of benzene. Hence, the result of FTIR confirms the formation of MOF-235 structure.

In addition, the MK-10 mainly consist of Al^{3+} with some $Fe^{2+/3+}$ and Mg^{2+} as octahedral cations and Na^+, K^+ and $C2^+$ as exchangeable interlayer cations. The results of FTIR show that there are huge different between the MOF-235 and MK-10. However, there is slightly change in the Modified MOF-235 from the MK-10 this is due to the high percentage of MK-10 in the Modified MOF-235. For MK-10, the band at 1030.62cm^{-1} is attributed to Si-O in-plane stretching while at 514.40cm^{-1} is indicated to Si-O bending vibration. The broad band that appeared at 337.10 and 1630.61cm^{-1} are indicated to the stretching and bending vibration of the hydroxyl group of water molecule.

In the meanwhile, a slightly different occurs in the FTIR spectra for the Modified MOF-235. It shows that the spectrum of Modified MOF-235 is shifted from the parent MK-10. The band that appears at 1030cm-1 in MK-10 had shifted to the 1018.33, 1026.72 and 1000.50 cm^{-1} for 5%, 10% and 15% MOF-235/MK-10. Also, there are a new peak appeared in the Modified MOF-235 that indicated the C-O stretching at 921.01cm^{-1}.

4.2.4 Carbon Dioxide Adsorption Capacity

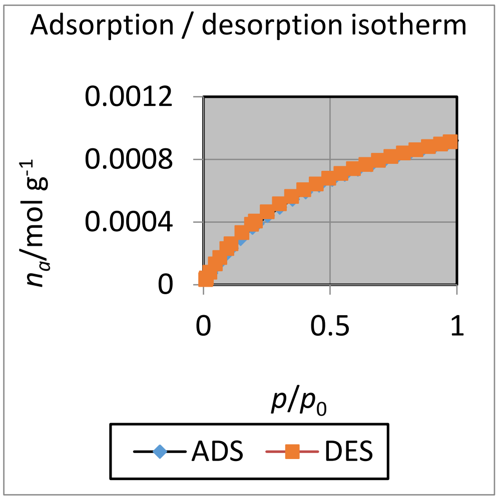


Figure 4.2.4(a) MOF-235 Adsorption Capacity

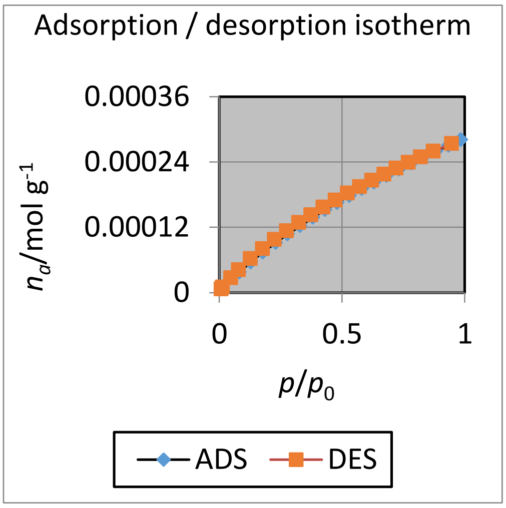


Figure 4.2.4(b) MK-10 Adsorption capacity

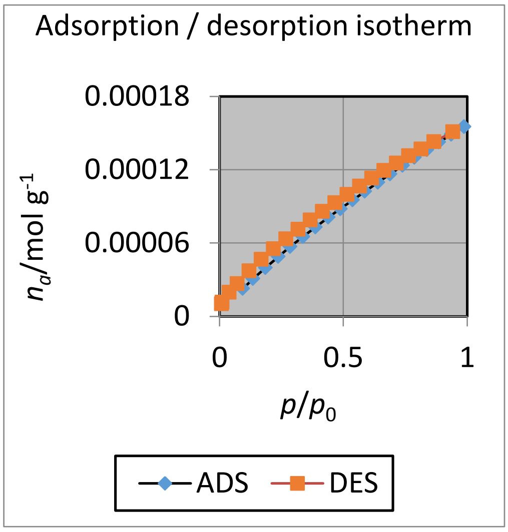


Figure 4.2.4(c) 5% MOF-235/MK-10 Adsorption Capacity

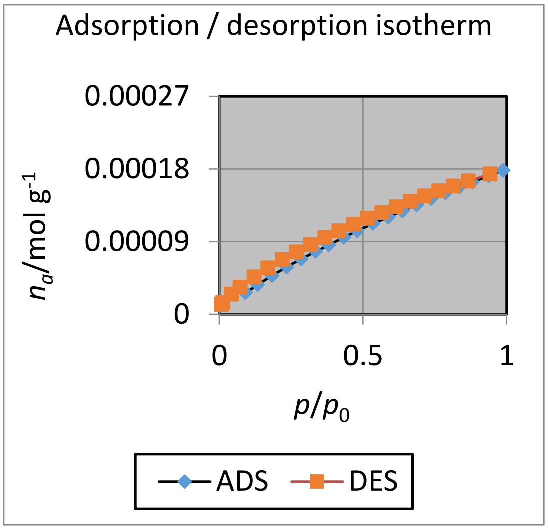


Figure 4.2.4(d) 10% MOF-235/MK-10 Adsorption Capacity

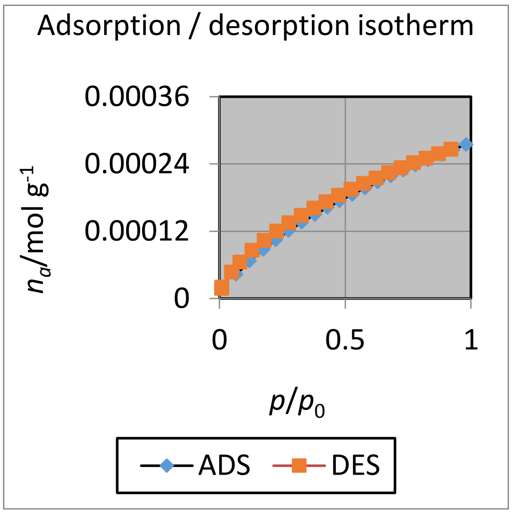


Figure 4.2.4(e) 15% MOF-235/MK-10 Adsorption Capacity

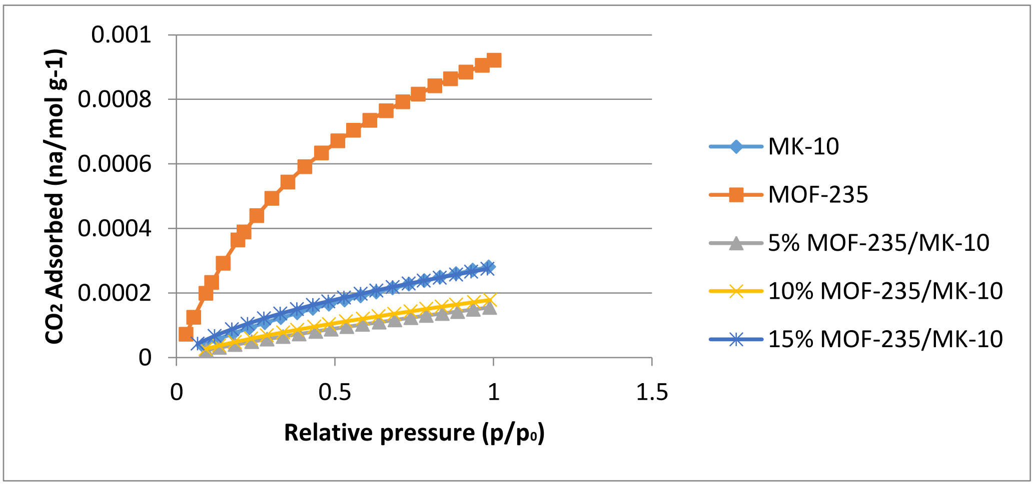


Figure 4.2.4(f) Summary Adsorption Capacity for MOF-235, MK-10 and Modified MOF-235

The CO_2 adsorption was conducted by using Belsorp Mini II. When comparing the graph the adsorption capacity of Modified MOF-235 is below the MOF-235 adsorption capacity. Meanwhile, by increasing the percentage of MOF-235 into MK-10, the adsorption capacity towards CO_2 had increase. From Figure 4.2.4 (f), the adsorption capacity of 15% MOF-235/MK-10 is similar to the adsorption capacity of MK-10. We believe that the adsorption capacity will be higher when we increase the percentage of MOF-235 beyond 15%.

The project is continued by increasing the percentage of MOF-235. The optimization of adsorption capacity will be achieved by increasing the percentage MOF-235 to 20%, 40% and 50%. This project still continues in order to investigate the capability of Modified MOF-235 towards CO_2 adsorption by increasing the percentage ofMOF-235.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

For the past decade, thousands of MOF materials have been synthesized and characterized structurally. Yet, only a small part has been checked for CO_2 adsorption, storage, and related gas separation. As a conclusion, this project is important as it deals with overcoming the major CO_2 problem around the world. We believe that the synthesis of MOF-235 by montmorillonite-K10 will become one of the high efficiency and cost effectively for the CO_2 removal.

The following is some recommendation for the future study:

- The study of modified MOF-235 and parent MOF-235 need to carry out with and without the presence of humidity. This is necessary in order to know the performance of the parent MOF-235 and modified MOF-235 towards humidity.
- Furthermore, the MOF-235 is also can be modified by using others material that have same characteristic with montmorillonite-K10. For example, the MOF-235 can be modified by using graphite instead of montmorillonite. The effects for both materials may be different.
- Future work may be done for methane and hydrogen adsorption isotherm analysis of MOF-235 impregnated Aluminum Pillared Clay.
- The different technique of modified MOF-235 may be used like heat treatment, ion exchange and dry impregnation. This is because different method of synthesis will give us the different results. The most important is the integration of MOF-235 applications in various industries.

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APPENDICES

APPENDIX A

FTIR Spectra Table

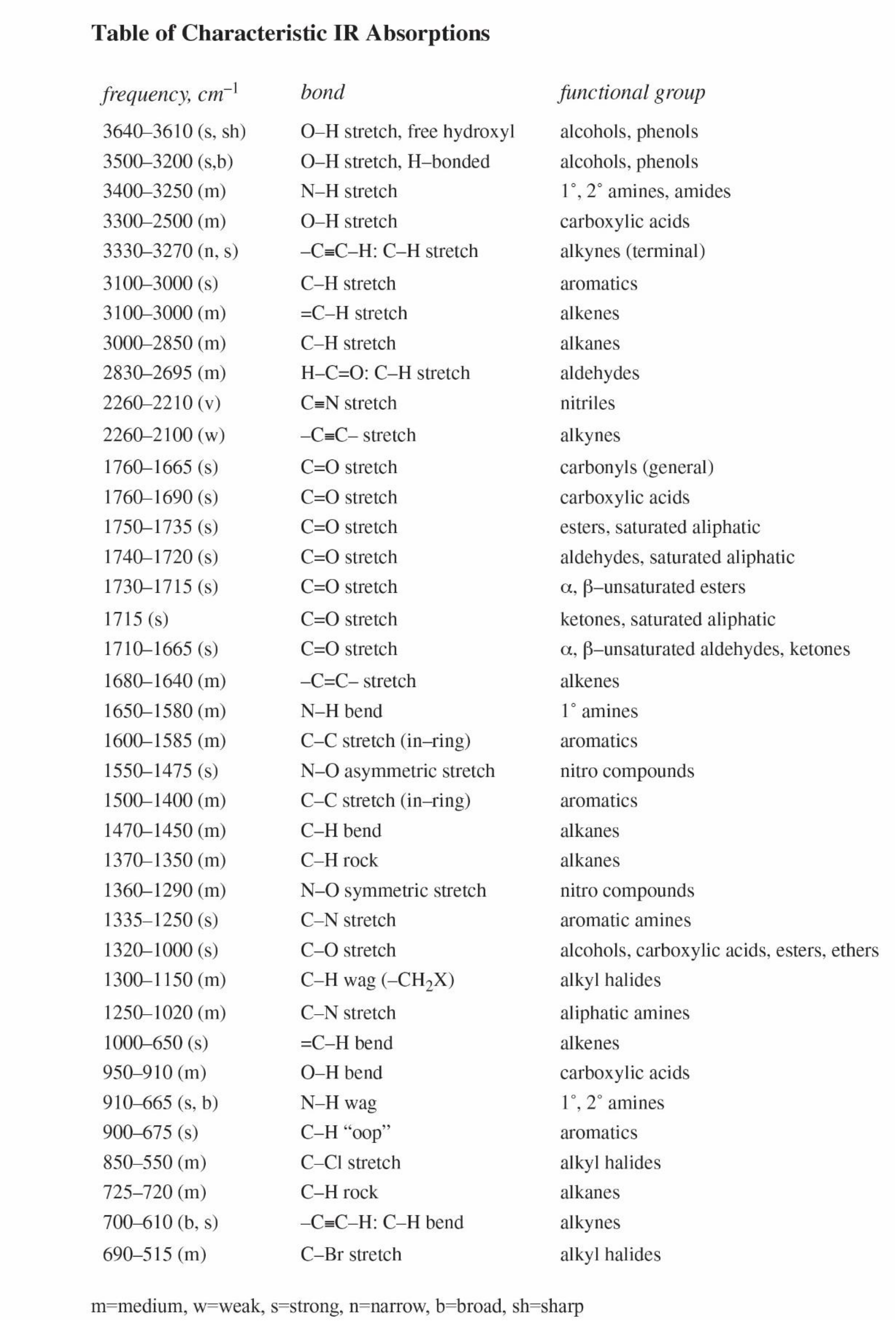

Table of Characteristic IR Absorptions

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_2X)	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