The Synthesis and Characterization of Metal Organic Framework/Graphite Oxide Composites for Hydrogen Capturing

By

ARSLAN MUNIR

School of Chemical and Materials Engineering

National University of Sciences and Technology

2017

The Synthesis and Characterization of Metal Organic Framework/Graphite Oxide Composites for Hydrogen Capturing

This thesis is submitted as a partial fulfillment of the requirements for the degree of

(MS in Chemical Engineering)

Submitted By: Arslan Munir

Supervisor Name: Dr. Habib Nasir

School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)
H-12 Islamabad, Pakistan
September, 2017

Dedication

Dedicated to my Beloved Parents, Respected Teachers and Friends

Acknowledgments

All praise and glory is to **"ALMIGHTY ALLAH''** the ultimate creator of this universe: from particles to the stars, who blessed us with the ability to think and an eager to explore this whole universe. Countless salutations upon the **"HOLY PROPHET HAZRAT MUHAMMAD (S.A.W)":** the source of knowledge and blessings for entire mankind.

I wish to express my sincere thanks to, Principal of SCME **Dr. Arshad Hussain** and H.o.D Chemical Engineering **Dr. Abdul Qadeer Malik** for providing me with all the necessary facilities for the research.

I am extremely thankful to my supervisor, **Dr. Habib Nasir** who provided me an opportunity to have research work with him and it is his constant guidance that enabled me to accomplish this work timely. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my MS study. He has been a source of inspiration for me.

I would like to thank my guidance and examination committee member **Dr. Tayyaba Noor** and **Dr. Sarah Farrukh** for their valuable guidance.

Besides my advisor, I am also thankful to **Dr. Muhammad Rafique**, NESCOM for the constant cooperation, valuable guidance and suggestions in the technical and experimental work. He helped me a lot in my whole research work.

My sincere thanks also go to Muhammad Zeeshan, Khurram Shahzad and Shams ur Rehman from SCME who helped a lot for laboratory analysis. Without their precious support, it would not be possible to conduct the experimental work.

Last but not the least my appreciation also goes to my family and friends for their encouragement, love and support throughout my life.

Abstract

Hydrogen being the cleanest fuel has one of the highest energy densities. The cleanliness of hydrogen provides an attractive alternative to fossil fuels. Greenhouse emissions can be reduced by using the less fossil fuel. Those industries which use hydrogen as a fuel have the advantage of emitting water as waste product. But the main problem is of the hydrogen storage. These days a lot of work is being done on metal organic frameworks for better hydrogen storage. Metal organic frameworks have great tendency for hydrogen storage because of their simple preparation, tunable chemical functionality and structure toughness. In this work various composites of copper based metal organic framework and graphite oxide with different ratios have been synthesized. The composite materials have been studied for their hydrogen adsorption capacities. These compounds are characterized by X-ray diffraction, FT-IR spectroscopy, thermal analysis, scanning electron microscopy and BET. The new composites formed have the increased porosity and the surface area as compared to the parent materials. The crystalline structure of the composites has been confirmed by X-ray diffraction. MOF/GO 20% composite has the best surface area of $380 m^2 g^{-1}$. Hydrogen uptake study shows that this composite can store 6.12% of H_2 at -40 $^{\circ}$C.

Keywords: Metal organic frameworks, Graphene oxide, MOF/GO composites, Hydrogen.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

BDC   Benzene-1, 4-dicarboxylic acid

BTB   1, 3, 5-tris (4-carboxalicyphenyl) benzene

BTC   Benzene-1, 3, 5 tricarboxylic acid

BET   Brunauer, Emmett and Teller

DEF   Diethylformamide

DMF   Dimethylformamide

FTIR   Fourier Transform Infrared

GO   Graphene Oxide

IRMOF   Isoreticular Metal Organic Framework

MOF   Metal Organic Framework

SBU   Secondary building Unit

SEM   Scanning Electron Microscopy

XRD   X-ray Diffraction

Chapter -1

Introduction

Hydrogen is known as future fuel in perspective of human fuel evolution. The fuel evolution history starts from coal to natural gas that leads to the use of hydrogen. Greenhouse gases are responsible for environmental pollution leading to global warming. These emissions can be reduced by using less fossil fuel. Hydrogen can be used as an alternative fuel. Hydrogen is an ideal energy carrier for various applications producing zero emissions. Hydrogen is the cleanest gas, having the heating value greater than other fuels. The only bottleneck is the storage of hydrogen. The major techniques used for hydrogen storage are compressed gas and liquefied hydrogen. However both of these techniques have major stumbling block for mobile application, because for this purpose high pressure and extensive cooling is required. These days, stupendous efforts are being made to store hydrogen in solid materials [1] [2]. Hydrogen is stored in safer and compact manner in solid materials. Solid materials involve hydrogen bonding through weak van der Waals forces (physisorption) or stronger binding of atomic hydrogen (chemisorption) forming a new compound for hydrogen storage. These solid materials are generally classified in the following groups:

* Adsorbents (zeolites, metal organic frameworks)
* Conventional metal hydrides ($LaNi_5H_6,$ Mg_2NiH_4)
* Complex metal hydrides ($NaAlH_4$)
* Chemical hydrogen storage (NH_3BH_3)

Depending on the pores size, porous materials can be classified in three types:

(1) Micro pores, which have diameters smaller than 2 nm (< 20 Å). These are sometimes called Nano pores.

(2) Mesopores, which have diameters between 2 and 50 nm (20-500 Å)

(3) Macro pores, which have diameters larger than 50 nm (>500 Å)

1.1 Metal Organic Framework

Metal organic framework (MOFs) or porous coordination networks are advanced materials which are designed by engaging metal ions and organic linkers. They are crystalline, extremely porous having large surface area with low density. Metal organic frameworks (MOFs) have great tendency for hydrogen storage which is based on physisorption because of their simple preparation, tunable chemical functionality and structural toughness [3]. MOFs structure has two important building units including metal ions and organic ligands in three dimensional lattices.

organic linkers   metal ions or clusters   metal organic frameworks
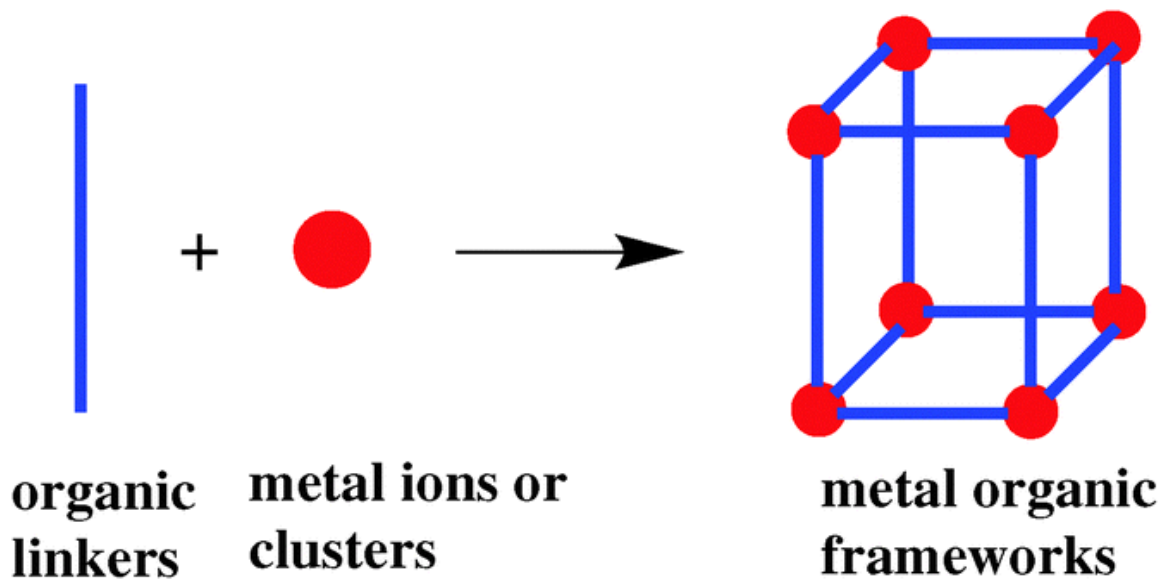
Figure 1: General scheme of building Metal Organic Frameworks

This coordination polymer or metal organic framework (MOF) that consists of metal ions and organic linkers produces the 1, 2 and 3 dimensional framework. The representation of these 1D, 2D and 3D MOFs are shown below in the figure 2.
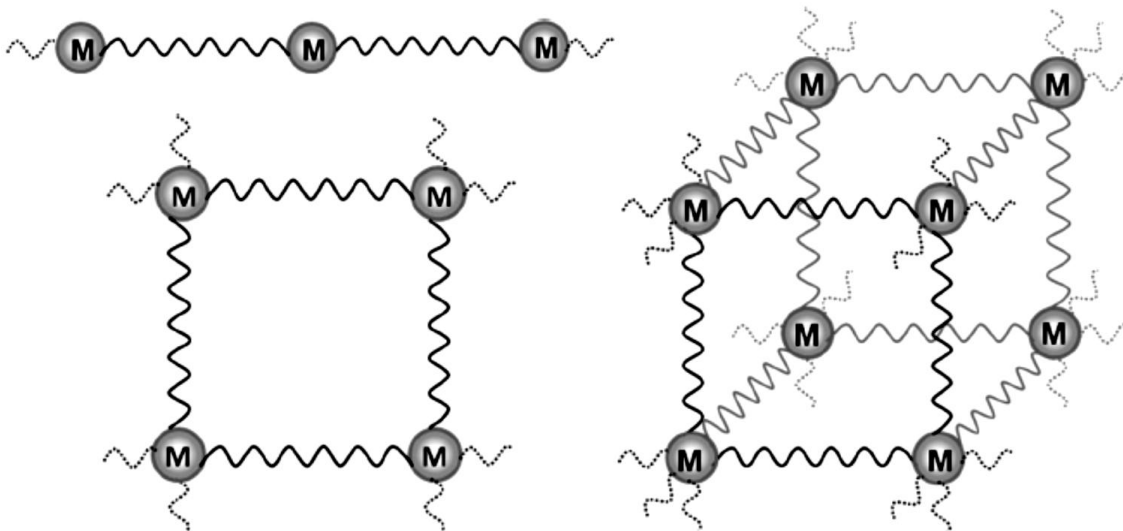
Figure 2: Representation of 1D, 2D and 3D MOFs

Metal organic frameworks (MOFs) have been studied for many applications including gas storage, gas separation, and heterogeneous catalysis and so on. MOFs are produced by combining metal containing cluster which is referred to as secondary building unit or SBU with multidentate organic ligand with the help of coordination bonds [4]. Examples of metal carboxylate clusters and organic units are shown in the below given figure 3. Many organic ligands and metal ions have the tendency to produce networks of required structure and properties. Mostly, MOFs have 3-D structures including regular pores and matrix of channels for the guest species to be trapped here during synthesis. The porosity can be varied by the appropriate removal of confined guest molecules. MOFs have high surface area as compared to other porous materials because of the open scaffolds having pores without walls. As the topography of this scaffold is elucidated by molecular building blocks, the pore size of the framework is very small which results in well-built interactions among guest molecules and frameworks [3].
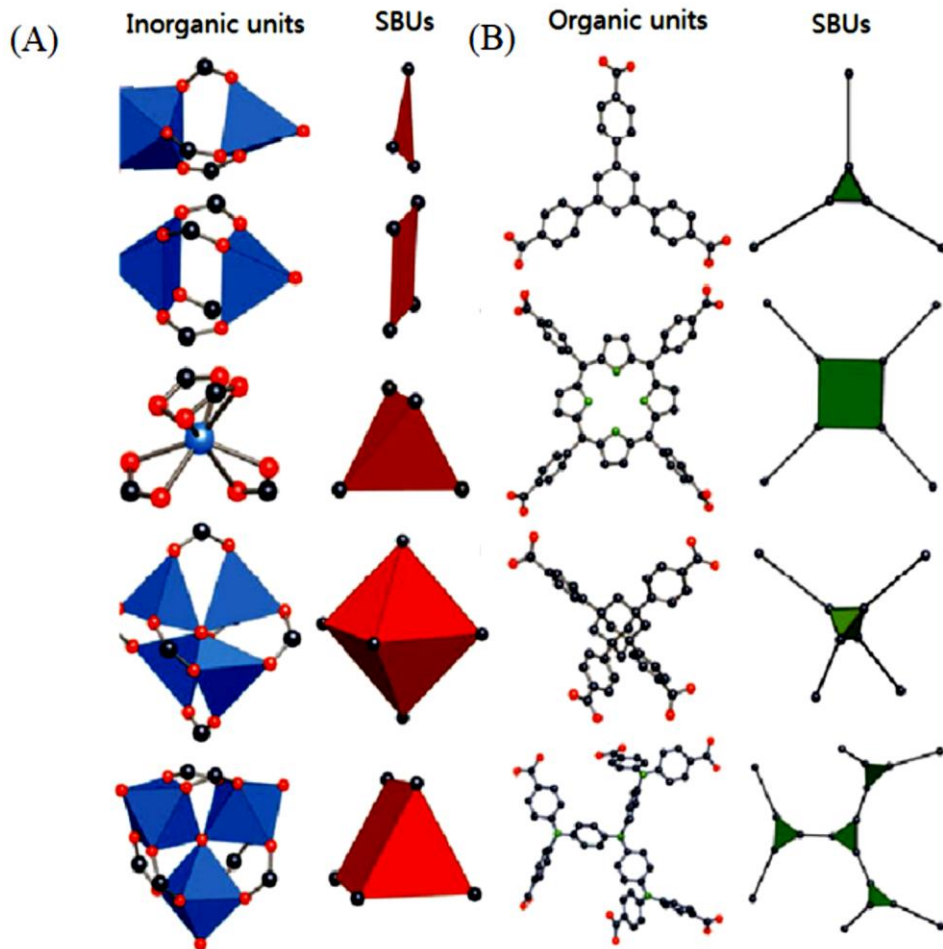
Figure 3: Examples of inorganic metal carboxylate clusters and their corresponding secondary building unit (SBU) geometry (A) and organic units and their corresponding secondary building unit (SBU) geometry.

1.2   Correlation between MOF structure and hydrogen storage capacity

These days lot of work is being done on the hydrogen uptake capacities of MOFs. Tremendous efforts have been made in order to understand the factors that influence the hydrogen adsorption capacity for developing suitable hydrogen storage materials. These factors consist of specific surface area, pore size, pore volume and hydrogen binding sites. Recently, at 77 K excessive hydrogen uptake has been disclosed with specific surface area [5] [6]. MOF-177 shows the highest hydrogen uptake with an absolute value of 0.112 kg kg^{-1} of hydrogen adsorption [7]. This reveals the high surface area of MOF-177, that is 5600 m^{2}g^{-1} [7]. Furukawa and coworkers revealed that MOF-210 has

the record BET surface area of 6240 m^2g^{-1}. MOF-210 showed 8.6wt % of hydrogen uptake and estimated total hydrogen uptake of 0.176 kg kg^{-1} [8]. Mostly, if the crystal density is low, the surface area is high. Most of the times due to low density of MOFs low volumetric hydrogen uptake capacities are obtained. So, a compromise is necessary between surface area and crystal density for porous MOFs with high hydrogen uptake capabilities.

1.3   Synthetic Considerations

MOFs can be prepared by using many methods including solvothermal, hydrothermal, vapor diffusion, direct mixing, sonochemical, microwave heating etc. The solvothermal method is the most commonly used that involves heating a mixture of organic linker and metal cluster in a solvent system. The solvents used for this purpose are water, ethanol, dimethylformamide and diethylformamide. Most commonly used solvents are formamides because of their tendency to not only dissolve the reactants but also deprotonate the carboxylic acids. Moreover, the important parameters in the reaction conditions are time, temperature and reagent concentration. The main disadvantage of solvothermal method is that, it takes long reaction time, high temperature and high cost of solvent. So alternative methods have been developed for MOF synthesis including microwave heating and electrochemical methods [9] [10].

The key factors for the hydrogen uptake studies are the sample activation and good hydrogen uptake. Normally, MOF samples are immersed into low boiling solvents such as, dichloromethane, chloroform and methanol in order to remove high boiling solvent such as *N, N*-dimethylformamide (DMF) which normally occupies pores in synthesized MOFs. The lower boiling point solvents are removed by moderate heating. Although, due to this process MOFs structure may collapse because of surface tension. Freeze drying and supercritical drying are introduced for activation which results in better pore quality. These techniques have provided a path for MOFs that were unreachable before [11] [12]. By using one of these activation methods, solvent is replaced under moderate conditions and the problem of surface tension is removed. Better gas-attainable specific surface areas of four MOFs have been revealed by Nelson and Co-workers using supercritical carbon dioxide (sc-CO_2) drying process. For example, IRMOF-16 shows a

400% increase in the specific surface area compared to the conventional solvent exchanged sample [12].

1.4   Graphite Oxide

In recent times, great interest has ascended in graphene and graphene based materials in the scientific community because of its unique structure, mechanical and electronic properties [13] [14]. Graphene is a single layer of pure carbon, tightly packed carbon atoms which are held togather in a hexagonal honeycomb lattice. In another way you can say that graphene is a form of carbon which is in a shape of sp^2 bounded atoms having a bond length of 0.142 nanometers. The most usual source of graphene is graphite, which can be reckoned as 3D crystals having graphene layers. The separation of graphene layers from graphite is not a minor task and many attempts have been made of graphite oxide (GO). GO is synthesized by reacting graphite with a strong oxidizing agent having layered structure with non-stoichiometric chemical composition [15]. In recent times, GO is used to build many nanocomposites exhibiting improved electronic and adsorption properties [16] [17] [18]. Depending on the level of hydration graphene layers of GO are assembled together with an interlayer distance of 6 to 12 A^o [19]. When graphite is oxidized, there is an introduction of epoxy and hydroxyl groups into the graphene layers, as well as the carboxylic groups present on the edges of the layers [20] [21]. However, that strong oxidation causes the defects in the graphene layers which are in the form of assimilated oxygen atoms or vacancies [22] [23]. In this way hydrophilicity is increased and it causes GO to be easily scattered in water [24]. Afterwards, the graphite layers can be restacked and their degree of orientation depends on the method of drying.

1.5   Why MOF/GO composite?

Although MOFs have high porosities yet their open framework is not able to provide enough adsorption forces to retain small molecules at ambient conditions. A surface of dense and porous network is needed for this type of separation. The most suitable condition is present, when this dense surface produces a convenient porous framework that has pores similar to the required molecules. But it is a very difficult task and, for

years, many synthesis and modifications have been studied to achieve the best suitable surface characteristics.

Keeping in view of the above conditions, MOF/GO composites have been synthesized in the laboratory. As, the ratios of MOF and GO is known in the composites, it is contemplated that deformed graphene layers will improve the dispersive interactions; while MOF will help in the expansion of pore space, in which gas can be stored. Furthermore, many transition and noble metals can be used in MOF synthesis; these materials have the tendency to create active sites for heterogeneous catalysis.

1.6   Scope and outline of the thesis.

The main aim of my work was to synthesize the MOF/GO composite for hydrogen storage. For this purpose GO and MOF were synthesized by two different methods. Afterwards, keeping in view of MOF and GO ratios MOF/GO composites are prepared. These composites as well as the parental materials are characterized by different techniques and are studied for hydrogen adsorption.

1st chapter includes the overview of metal organic frameworks and graphite oxide. Correlations between MOF structure and hydrogen storage capacity are discussed. Synthetic considerations of MOF are highlighted. The challenges in MOF/GO composites synthesis are discussed.

2nd chapter comprises of summery of the research work already carried out on MOFs and GO for hydrogen adsorption applications. Synthesis techniques of MOFs have also been discussed. Moreover, different applications and properties of MOF materials are also highlighted in this chapter.

3rd chapter includes the materials and methodology endorsed for preparation of MOF, GO and their composites. Characterization techniques are also included in this chapter.

4th chapter encompasses the discussion of the results obtained from the characterization techniques. It also involves the study of the hydrogen uptake capacity.

5th chapter concludes the whole research and future recommendations.

Chapter-2

Literature review

2.1   Background

Metal organic frameworks (MOFs) are porous solids that have high crystallinity which are made up of metal ions and organic linkers giving high porosity to MOF structure. The option of metal ions and organic linkers depend on the way, how they are connected in a framework and their pore properties. Over the past few decades, MOF materials have been under great observation because of their easy tune up pore properties. Since their development in 1998 by Yaghi et al [25]. Many MOFs have been synthesized and developed through different combinations of metal clusters and ligands for various applications.

Usually, MOFs can be differentiated as rigid or flexible depending on their framework structure. It also depends on, how it behaves by adjusting different temperature and pressure and the inclusion/removal of guest molecules. MOF-5 is a rigid MOF that has permanent porosity having stable and strong framework which means MOF structure will remain intact even after the removal of guest molecules from the pores. Cu (bpy) $_2(BF_4)_2$ is a flexible MOF which shows structural flexibility even on the addition or removal of guest molecules.

HKUST-1 which is also called Cu-BTC is a copper based MOF which is under extensive study from last few years. Its structure is composed of Cu^{2+} paddlewheel clusters embedded to 1, 3, 5 benzene tricarboxylate in a twisted boracite (TBO) topology. The framework structure synthesis involve two Cu^{2+} from metal precursor and eight oxygen atoms from BTC react together and water molecule bounded to copper atom.

HKUST-1 can be characterized by 3D system showing void spaces of 9 A^o diameters which nearby smaller ones of 5 A^o diameter [26]. Water molecules attached on the Cu^{2+} sites can be removed by vacuum heating without disturbing the cystallinity and porosity

of the structure. Hence, producing the Cu Lewis acid centers convenient to guest molecules thus providing applications in gas adsorption and storage.
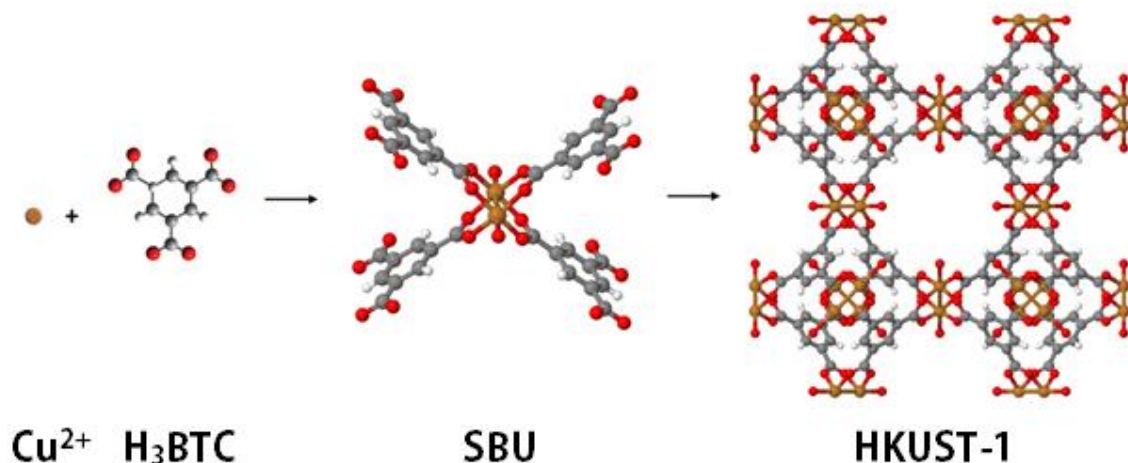
Figure 4: Combination of Cu^{2+} ions and BTC ligand to form HKUST-1(Orange-Cu, red-O, grey-C and white-H)

2.2   MOF/GO composites

Although MOFs have high porosities yet their open framework is not able to provide enough adsorption forces to retain small molecules at ambient conditions [27]. Keeping in view of this issue and to widen the MOF applications, MOF based composites idea has been revealed. Zhang et al suggested that by combining the inert and active components in composites a novel material with improved gas adsorption efficiency can be produced [28]. MOFs based composites can be prepared by the combination of MOFs with graphene oxide (GO). GO having 2D layered structure can carry a number of hydroxyl and epoxy functional groups. These functional groups help in the preparation of MOF/GO composites with encouraging adsorption properties [27] [29]. These MOF/GO composites exhibits enhanced adsorptive properties then that of the parental elements [30] [31]. The graphene layers in GO potentially enhance the nonspecific adsorption and the GOs acidic character enhances a strong specific adsorption, whereas the presence of MOF can lead to better adsorption kinetics owing to its framework structure while it can also enhance specific interactions and reactivity

9

owing to its chemical composition. The oxygen groups from GO coordinate with the metallic centers of the MOF resulting in materials with enhanced porosity resulting from the origin of new pores at the MOF/GO interface leading to increased dispersive interactions [32].

Petit and Bandosz contrived ammonia adsorption in MOF/GO composite, which manifest enhanced ammonia adsorption [30] [33]. It was revealed that addition of GO in MOF did not muddle the crystallization of MOF. Rao and co-workers synthesized ZIF-8/GO showing better CO_2 uptake capacity [34]. Chen et al also prepared ZIF-8/GO composites with adjustable morphology and porosity showing excellent uptake capacity of methylene chloride [35]. Li and workers used facile coordination- induced growth approach to synthesize a composite of SO_3H and functionalized GO and ZIF-8 particles which showed enhanced catalytic activity [36].

2.3   Synthesis of MOFs

MOFs are usually prepared by self-assembly reaction of metal precursor and organic linker to produce crystalline product. The structure of framework depends on metal ions and organic linkers, temperature, solvent used, ratio of metal ions to organic linkers thus by changing these conditions we can synthesize a framework with desirable properties [37]. The different methods used for MOFs synthesis are solvent evaporation, mechano-chemical, diffusion, microwave assisted method and solvothermal method [37]. The solvothermal method is most suitable method for MOFs synthesis in which metal ions and organic linkers are dissolved in polar solvents and heated to about 100 °C. The nature of this method can be reckoned as Lewis acid-base reaction where Lewis bases are the deprotonated ligands whereas the metal ions behave as the Lewis acids. The organic linkers are usually multidendate in carboxylates such as benzene tricarboxylate (BTC), benzene dicarboxylate (BDC) with two or more donor atoms. Mostly divalent transition metal ions such as $Cu^{2+,}$ $Zn^{2+,}$ $Zr^{2+,}$ Ni^{2+} are used as the metal precursors in polar solvents like water, methanol, ethanol, dimethylformamide (DMF), diethylformamide (DEF) and others [37].

2.4   Organic ligands

The primary need of organic ligands is that it can form coordinate bonds with central atoms. The pore volume and surface area can be adjusted by applying different organic linkers for a particular application [38]. Due to their rigidity and ability to form rigid metal carboxylate cluster benzene carboxylate group is the main source until now.
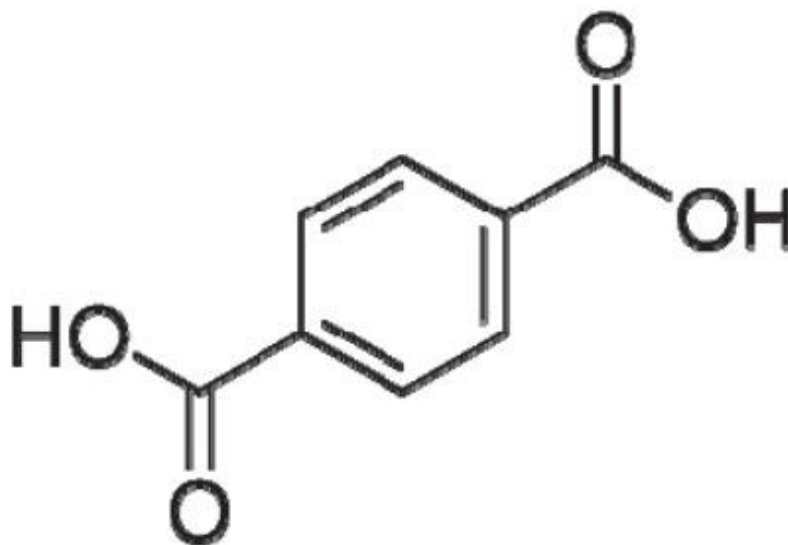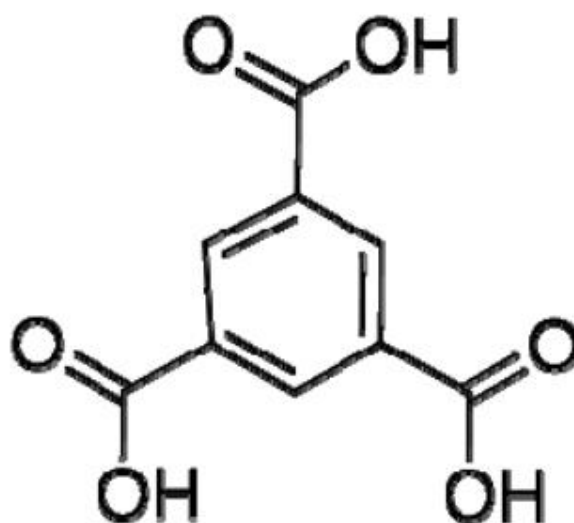
Figure 5: Benzene-1, 4-dicarboxylic acid

Figure 6: Benzene-1, 3, 5 tricarboxylic acid

2.5   Synthesis method

Solvothermal method is most commonly used for MOFs synthesis because the process is simple and easily controlled. But there are few drawbacks as well such as; it is time taking process and large size particles are commonly produced by this method.

2.5.1   Conventional synthesis

Solvothermal method is most popular for MOFs synthesis. In this process reactants and solvents are mixed together, and then close them in a Teflon reactor, and $100 - 200\ ^{\circ}C$ is provided to the reactor. Above the boiling point of the solvent, mixture will react under autogenously pressure. Reactants are slowly dissolved with the increasing temperature and react to produce crystalline product. Less time is required for this technique and very simple equipment is used which can utilize various reactants that are insolvable at or below the room temperature. Furthermore, products produced are perfectly crystals which can be characterized by XRD technique [39].

Product formation is usually determined by reaction temperature. At higher temperatures more condensed structures are examined [40]. Most of the MOFs require an increasing reaction temperature in order to get perfect crystals, mainly if more inert ions are used. This technique is used for the preparation of many MOFs especially MOF-5, MOF-74, MOF-177, Cu-BTC (HKUST-1) [41].

2.5.2   Microwave assisted method

Zeolites have already been synthesized by microwave assisted method [42]. Yeonshick developed microwave induced thermal method for the preparation of MOF-5 [43]. In this process first of all precursor solution was prepared, then put the substrates which are nanoporous anodized alumina discs coated with various conductive thin films into the container containing the precursor solution. 500W power microwave is provided for 5 to 30 seconds to produce MOF-5 in the container. The main advantage of this technique is that, it is a rapid process and nanoporous films with high kinetics are produced.

2.5.3 Centrifugal separation

ZIF-8 production has been reported by this method [44]. The mixture was stirred for two hours after adding a methanolic solution of Zn $(NO_3)_2 \cdot 6H_2O$ into a methanolic solution of 2-methylimidazole. The product was then centrifuged many times and washed with ethanol. ZIF-8 nanocrystals were produced after drying the product in an oven.

2.5.4 Slow evaporation method

It is a commonly used method for the synthesis of MOF and this method does not require any external energy source. Although this method is more preferable because it is performed at room temperature, yet its major problem is that it takes much more time than the other known conventional methods. In this method at room temperature starting material is concentrated by slow evaporation of the solvent. This process involves mixture of solvents many times, which increases the solubility of reagents and can make the process time saving by rapid evaporation of low-boiling solvents [45].

2.6 Applications of MOF

MOF has been widely studied as heterogeneous catalyst due to their thermal stability and ease of reuse. MOF allows the faster transport through the large pores and it prevents the self-degradation of active sites. MOF has also been studied for biomedical applications, drug delivery, chemical sensors and bio-image applications. Although the main application is in gas storage, separation and adsorption. MOFs have been studied for the uptake capacity of hydrogen and methane and capturing of carbon dioxide. MOFs are also being studied for gas separation as filler in polymer membranes. Different composites formation for MOFs are also being attempted to generate desired properties for various applications [46].

2.6.1 Gas storage

MOFs are porous materials therefore the applications of MOF on gas are of highly important. Various MOFs have been prepared for CO_2 capturing from flue gases [47]. The main problem for technology these days for gas absorption is that equipment sizes are too big due to which high energy is consumed [48]. On the other hand, MOFs are

cheap and easily produceable with other benefits as well [49]. MOFs are also a promising storage material for H_2 and CH_4. MOFs have already shown promising results for gas storage. For example, MOF-519 exhibits high methane volumetric storage capacity of $279cm^3cm^{-3}$ at 298K and 80bar has been reported [50].
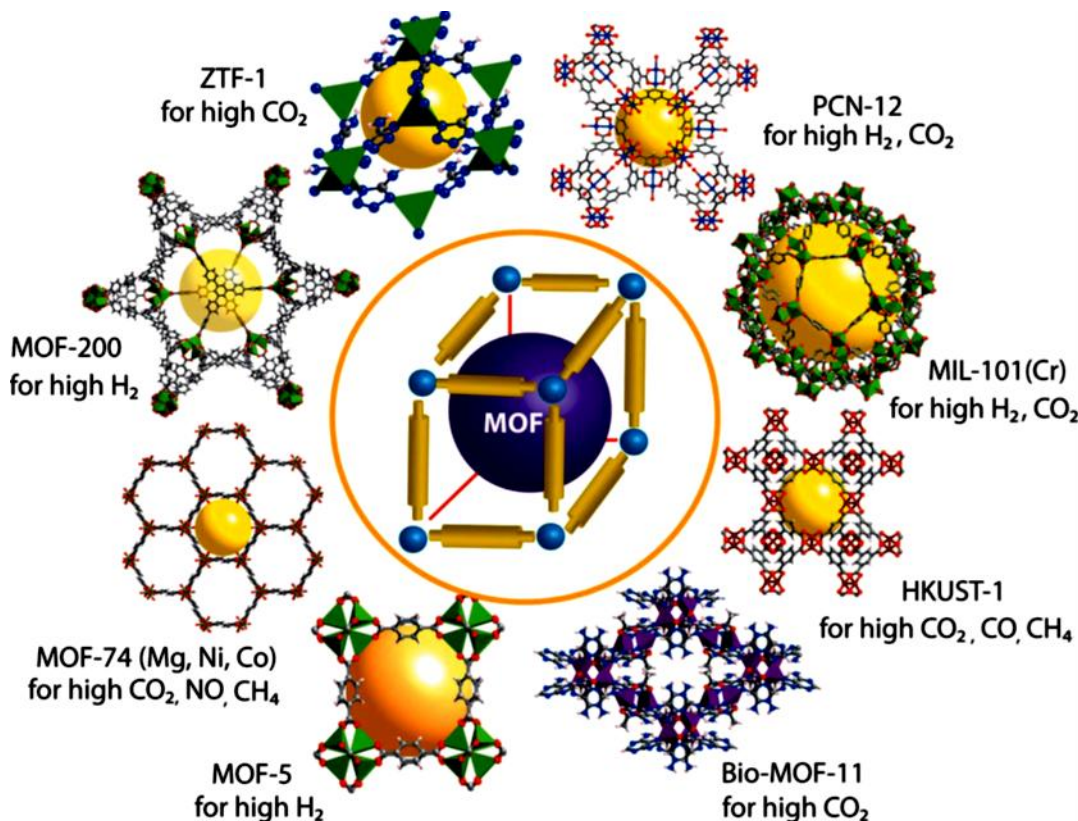
Figure 7: Schematic illustration of important testified MOFs known for high gas storage capacity

2.6.2 Adsorptive separation

Gas separation by MOF depends on the difference in the adsorption/desorption behavior of components of a mixture [51]. Pore size and other properties of MOF results in unique interaction with guest molecules than others and thus obtained excellent chemicophysical adsorption. For example, homochiral MOFs have the potential on enantio-separation which is still a challenge [51].

2.6.3 Biomedical/drug deliver

Due to high surface area and excellent bio-compatibility, some MOFs have remarkable ability of drug loading. Some MOFs on nanometer scale provides a path to design novel theranostic Nano medical devices. On the mesoporous scale some MOFs have the tendency to load biological molecules such as anticancer drug into their pores [52]. Patricia et al. for the first time revealed the excellent capacity of Ibuprofen hosting and delivery by MIL-100 and MIL-101. They also explained that there are many possibilities for the design of new MOFs including their benefits to adapt to the structure of the drugs and their dosage requirements [53].

2.7 Adsorption in MOFs

MOFs are strong crystalline materials with robust coordination bonds having well-defined framework structure. When the guest species are removed only solvent molecules coordinated to the metal ions creating the open metal sites which can be used for the adsorption of desired gas molecules [54]. This process of removing solvent from the MOF under vacuum heating is called activation. In HKUST-1 bimetallic tricarboxylate are exposed after activation which provides the inclusion of gas molecules. The MOF framework is electrically neutral with copper atoms and the polymeric crystal lattice having partial positive charges and carboxylate units present with partial negative charges. A type of ion pair is produced by the coordinately unsaturated Cu^{2+} cations and negatively charged carboxylate units which help in the adsorption of molecules. This recommends that along with Van der Waals interactions, Cu^{2+} species related specific interactions also govern the adsorption properties of HKUST-1. The combined effect of the presence of these sites and the framework topology are key points towards the promising adsorption properties.

2.8 CO_2 adsorption on MOFs

The presence of open metal sites and the large surface area of MOFs are the key factors for huge amount of CO_2 adsorption. These open metal sites play very important role in binding CO_2 molecules onto the pore surface. The binding energy between the MOF surface and adsorbed CO_2 molecules are provide by the result of dipole-quadrupole

interactions between them. Materials having large surface areas show huge amount of CO_2 adsorption at high pressures. However, at low pressure and room temperature the adsorption of gas depend on the nature of the pore surfaces with highly functionalized surfaces showing high adsorption capacities. The adsorption equilibrium can be calculated by using volumetric or gravimetric methods. The gravimetric method provides the data on the amount of CO_2 adsorbed per unit mass of the MOF thus providing the mass of MOF required for assembling the adsorbent bed however the volumetric method provides information on how densely the CO_2 can be captured within the adsorbent thus providing idea on the volume of the adsorbent bed [55].

A large amount of work has been done on MOFs for storing of H_2, CO_2, methane gas and toxic gas adsorption. Liu et al analyze the adsorption of CO_2 in various MOFs at different pressures [56]. Various MOFs can selectively adsorb CO_2 over CH_4 owing to a substantial quadrupole moment of CO_2. Keeping in view of the experimental results and molecular simulations, Snurr and coworkers carbon dioxide adsorption over methane in a carborane based MOF [57]. The adsorption of CO_2 was also tested in Cu_3 (BTC) $_2$, which revealed CO_2 uptake capacity of 6.6kmol/kg at 2.5 bar and 303 K and selectivity of 4-6 for CO_2/CH_4 at 00.1-3 bar pressure. ZIF-68, 69, and 70 have also manifested high affinity for CO_2 at 273 K in CO_2/CO mixtures[58]. The CO_2 uptake capacities of various MOFs measured at different temperatures and pressures are shown in the table 2-1.

Table 1: CO_2 Adsorption capacities at different pressures

Name	BET Surface Area (m²/g)	Capacity (wt. %)	Pressure (bar)	Temp (K)	Qst (kj/mol)
UiO(bpdc)	2646	72.5	20	303	-
		8	1		
$Cu_3(H_2L_2)(bipy)_2.11H_2O$	-	6.5	8.5	298	-
		2.3	1		
ZIF-7	312	20.9	10	298	33

		9.1	1		
IRMOF-8	1599	7.8	1	298	21.1
		51.2	30		
HKUST-1	1326	13.2	1	303	-
		26.3	30		
CuBTTri	1700	10.8	1	293	
Mg/DOBDC	1415	25	1	298	47
Ni/DOBDC	1017	20.5	1	298	42

2.9   Graphite oxide

Graphene is a single layer of pure carbon, tightly packed carbon atoms which are held to gather in a hexagonal honeycomb lattice. In another way you can say that graphene is a form of carbon which is in a shape of sp^2 bounded atoms having a bond length of 0.142 nanometers. Graphene layers stacked on top of each other to form graphite having inter planar spacing of 0.335 nanometers. The term graphene was first introduced in 1987 to describe monolayer of graphite. Graphene is a two dimensional building material for all other carbon materials. Graphene can be halt to buckyballs, turn up to nanotubes and deformed into graphite. Andre Geim and Konstantin Novoselov were awarded with noble prize in 2010 for their work on graphene. The worldwide sales of graphene have become $9 million in 2014 with major sales in electronics.

Usually, graphene sheets can be obtained in different ways. The first method which is known as micromechanical cleavage was revealed by Geim in 2004 [59]. This method involves continuously splitting graphite crystals by scotch tape and dissolving the resulting product in acetone. After this the dispersion is deposited on silicon wafer and sheets having graphene layers were found under SEM.

Figure 8: Micromechanical cleavage of graphite to obtain graphene using Scotch tape

Graphite oxide or graphitic acid is usually prepared by two different processes: one in which sulphuric acid acts as an oxidizing agent known as Hummers–Offeman method and other one without using sulphur containing compound in oxidation process is known as Brodie method. In the past few decades GO has gained the attraction of many researchers because of its remarkable applications as adsorbents, conductive, electric properties and a part in composite materials. GO has many beneficial properties. It disperses very easily in different mediums such as aqueous solvents, organic solvents and various matrices. Due to the presence of both electron rich oxygen species and an electron rich graphene backbone provides further surface functionalization, which as a result gives adaptable material for multiple applications. Graphene oxide anyhow suffers from a low electrical conductivity and is an electrical insulator. Graphene oxide is also soluble in various solvents, both aqueous and organic.

Chapter-3

Experimental and Characterization Techniques

In the preparation of MOF and GO different methods are used which are discussed in this section. The characterization techniques and gas adsorption measurements are also highlighted in this chapter

3.1 Materials.

Graphite flakes, 97% sulphuric acid H_2SO_4, 35% hydrogen peroxide (H_2O_2), 99% potassium permanganate ($KMnO_4$) and distilled water are used in the preparation of graphite oxide (GO). Copper nitrate hemipentahydrate 98% Sigma Aldrich, 1,3,5 benzene tricarboxylic acid 95% (trimesic acid) Merck, N, N dimethylformamide (DMF), 99.8% ethanol, 99.9% dichloromethane and deionized water are used in the preparation of HKUST-1 (MOF-199).

Table 2: List of chemicals used in this research project.

Chemical name	Formula	Company name	Grade	Molecular weight g/mole	Boiling point ^{0}C	Melting point ^{o} C
Sulphuric acid	H_2SO_4	Merck	97%	98	337	10
Hydrogen peroxide	H_2O_2	Merck	35%	34	150.2	-0.43

Potassium permegnate	KMNO$_4$		99%	158		240
Copper nitrate hemipentahydrate	Cu(NO$_3$)$_2$ · 2.5H$_2$O	Sigma Aldrich	98%	232.59	170	115
Trimesic acid	C$_9$H$_6$O$_6$	Merck	purum	210.14	561	374
N,N dimethyformamide	C$_3$H$_7$NO	Sigma Aldrich	99%	73.09	153	-61
Ethanol	C$_2$H$_6$O		99%	46.06	78.37	-114.1
Dichloromethane	CH$_2$Cl$_2$		99%	84.93	39.6	-96.7

3.2   Synthesis of GO

First of all, 2g of graphite powder was oxidized in 46ml of cold concentrated sulphuric acid at 0 $^\circ$C. After that 6g of KMO$_4$ was added slowly and temperature was kept less than 20 $^\circ$C. Than it was cooled to 2 $^\circ$C. Ice bath was removed and mixture was stirred for 15 minutes at room temperature. 280ml of distilled water was then added to dilute it and stirred for 15 more minutes. After this 40ml of H$_2$O$_2$ was added to end the oxidation process. Mixture was then left for overnight. The solution was then centrifuged and decanted several times to attain the pH of 6-7. After that the centrifuged slurry was dried at 60 $^\circ$C in vacuum over for about 24 hours to obtain the graphite oxide.

3.3   Synthesis of MOF-199

HKUST-1 was prepared by mixing 2g of copper nitrate hemipentahydrate and 1g of trimesic acid in 17ml of N, N dimethylformamide. The solution was then stirred and

sonicated for 5 minutes. After this 17ml of ethanol was added to the mixture followed by 5 minutes of sonication and stirring. Deionized water 17ml was then added followed by the 30 minutes of stirring and sonication. All the crystals were dissolved at this point. The mixture was then poured to the 500ml round bottom flask kept in an oil bath and heated at 85 $^\circ$C. The mixture was kept in the oil bath at a temperature of 85 °C for 21 hours. The mixture was then cooled and filtered and the product was washed with dichloromethane and immersed in it for two to three days. The crystals were then dried in vacuum oven at 170 °C to attain the final product.
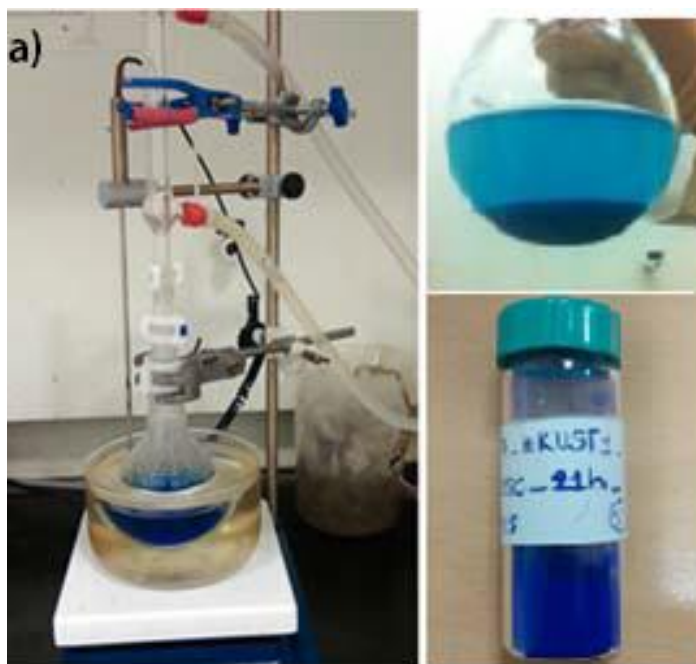

Figure 9: Synthesis of HKUST-1

3.4   MOF/GO composite synthesis.

The composite was prepared by mixing GO powder to well dissolved MOF precursors to obtain the solvent mixture in the same process as in the synthesis of MOF-199. After that the resulting mixture was stirred and sonicated for 30 minutes followed by the same synthesis process as that for MOF-199 was carried out. The added GO contains 10, 20 and 30 weight% of the final product. This proportionate to concentration of 0.961, 1.922 and 2.883mg_{GO}/ml_{DMF} respectively. The copper (from MOF) to oxygen (from GO) ratios

in the composites are 2.7, 1.6 and 0.71 respectively[60]. The composite were named as MG-n where n=1, 2 and 3for various GO contents 10, 20 and 30 weight% respectively.

3.5   Characterization Techniques

The characterization of GO, MOF and their composites have been done by various techniques such as XRD, SEM, FTIR, TGA and BET. These techniques are discussed below;

3.5.1   X-ray diffraction (XRD)

XRD is emphasized on crystalline structures of solid samples. Valuable information regarding size of crystallites, lattice parameters etc. can be gained by interpreting the results. X-rays have a wavelength of ~1 $\overset{\circ}{A}$, shorter than ultraviolet but longer than gamma rays.

Figure 10: X-Ray Diffractometer

Working principle shows that X-rays are formed when high-energy charged electrons beam on a solid surface target copper or molybdenum. Due to interaction of electrons, the inner shell electrons can be evicted by ionization process. Outer orbital will fill the empty site immediately and due to release of energy in conversion an X-ray photon is discharged. The relationship between energy of radiation and wavelength is given in the following equation:

$$E = hc/\lambda$$

Where h represents the planks constant and c is for speed of light in vacuum.

Bragg's law is a common formula for understanding the process of diffraction and is widely used in crystal diffraction as well. We can calculate crystallite size of crystals by using Debye-Scherrer equation. Each crystalline material has its own unique X-ray pattern which is used as finger print for its identification.
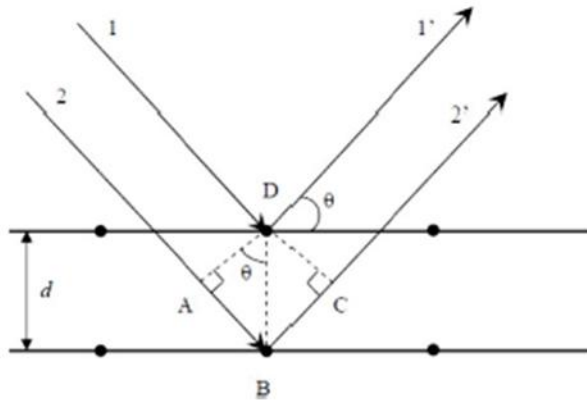

Figure 11: Description of Bragg's Law

3.5.2 Scanning electron microscopy (SEM)

SEM is routinely used electron microscope. High energy electrons ray is focused on the surface of materials and examines morphology of materials. Electron ray produces different signals at materials surface and delivers information about microscopic structure and chemical composition of sample. Information is obtained mainly over the selective area of the sample surface. Selected points on the sample surface can be analyzed by SEM. Function of SEM is similar to electron probe microscope.

Kinetic energy of electrons is scattered, when electrons with high-energy beam strikes on the solid surface. Mainly secondary electrons and backscattered electrons form the sample image. Back scattered electrons have more value in phase discrimination and secondary electrons are important for visualizing morphology and topography of the sample. When incident electrons and electrons present in shells of the sample atoms collide together X-rays are produced [61]. The working principle of SEM is shown in figure 12. SEM analysis gives information about the sample's morphology (size and appearance) and topography (surface and its characteristics related).
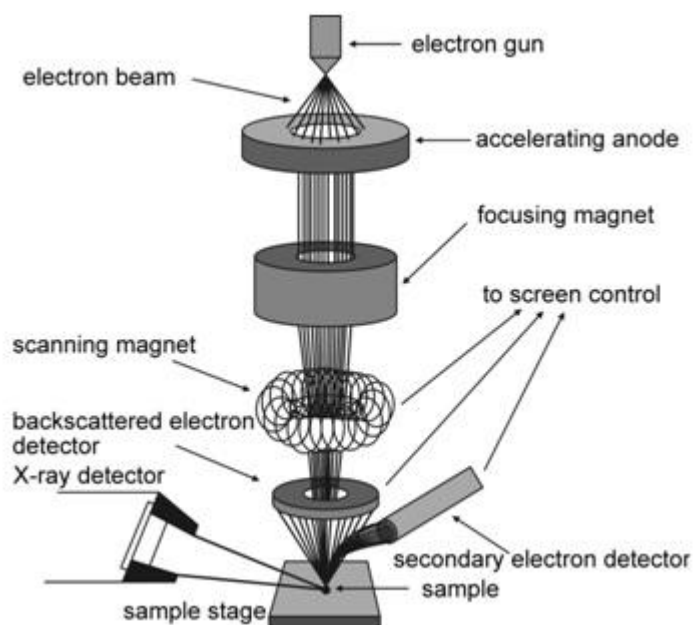

Figure 12: Working principle of SEM

3.5.3 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform is mathematical process required to obtain actual spectrum from raw data that is the reason Fourier transform is used for this type of spectroscopy. FTIR is used for quantitative and qualitative analysis of organic and inorganic samples. It is an efficient method for the detection of functional groups and for identification of type of chemical bonds present in the sample under test.

Infrared radiations interact with the sample in FTIR analysis. Sample absorbs some radiations while other radiations are transmitted through sample. FTIR spectrum is obtained on the bases of absorbed and transmitted radiations. The resulting spectrum generates finger print of the sample, used to identify the sample. The range of frequency is calculated in terms of wave number and varies from 4000 - 400 cm^{-1} [62]

Figure 13: FTIR spectrometer

The covalent bonds are flexible and always in a state of vibration unlike rigid bonds. Vibration could be bending or stretching. The vibrational motion of these molecules is characteristic of their respective atoms. All organic compounds have capability to absorb IR that matches to their vibration. IR spectrum is the graph presenting the variation of percentage transmittance with the frequency of the infrared variation drawn between percentage transmittance and wavenumber.
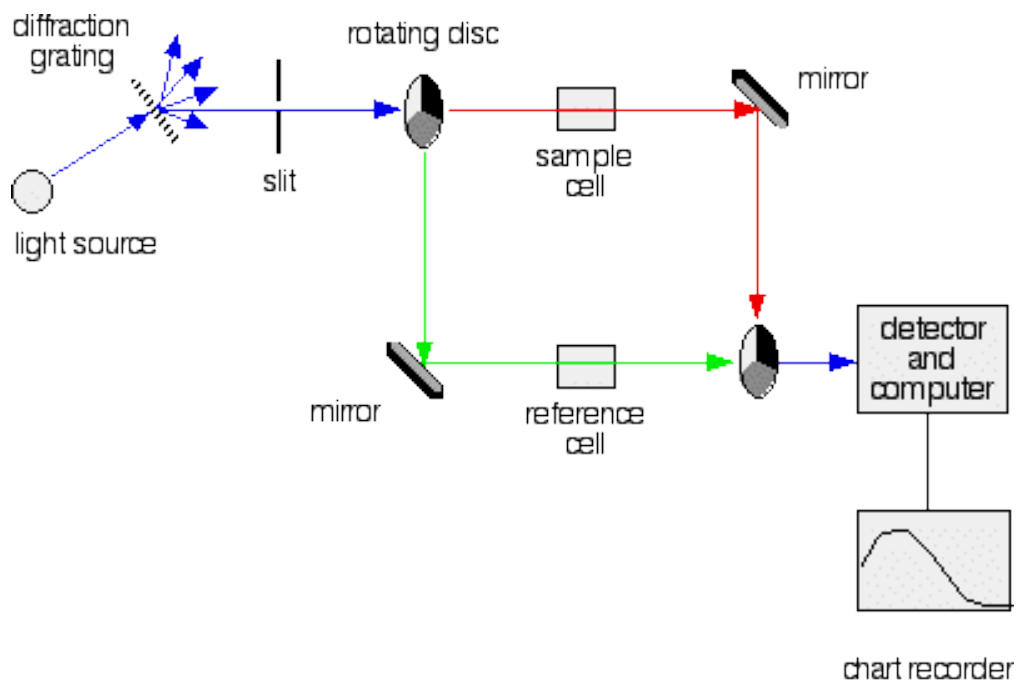
Figure 14: Working principle of FTIR

3.5.4 Thermogravimetric Analysis (TGA)

TGA is a thermal analysis technique which is used to observe weight gain or weight loss of the sample powder with time or increasing temperature. The alterations in chemicals like dehydration, solid gas reactions, chemisorption, decomposition etc. and physical properties like desorption, absorption, adsorption, vaporization, sublimation etc. are determined. Physical and chemical changes take place when materials are subjected to heat. Material weight is either increased or decreased. Thermogravimetric analyzer has pan placed in a programmable furnace.

Figure 15: Hi-Res TGA 2950 thermal gravimetric analyzer

This pan is supported by a sensitive precision balance. The specimen is placed onto pan and a heating rate and temperature range is given to the furnace. The furnace is first heated from lower limit of temperature range reaches the maximum point and then cooled. During heating and cooling process mass change is monitored. Inert or reactive gas controls the environment of furnace.

Interpretation of loss of volatile components of sample, its thermal stability and decomposition is enabled by the data obtained from TG analysis. The graph between increasing temperature (x-axis) and percentage in weight (y-axis) is plotted and indicates data obtained. If a graph shows a straight line (no temperature change) in a given temperature range, this means species is thermally stable. Sometimes an initial weight loss is shown in the graph and then line becomes straight, denotes species is thermally unstable at low temperature and then becomes stable. Information about maximum used temperature of the material beyond which material will degrade is provided by data from

TG analysis. It also gives information about reaction kinetics, degradation mechanism, the presence of inorganic content in material and decomposition patterns[63].
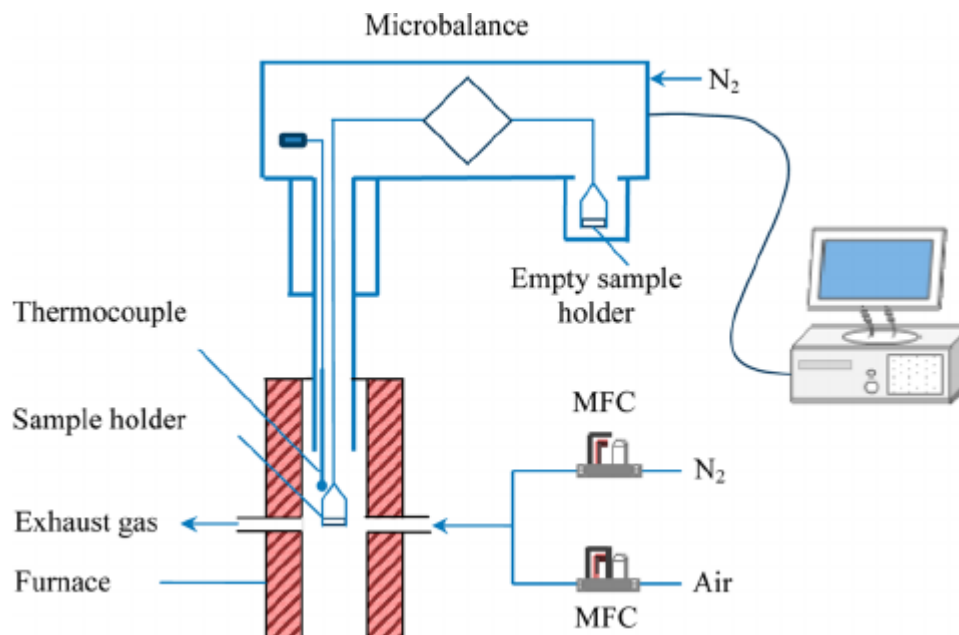

Figure 16: Schematic Diagram of TGA

3.5.5 Brunauer-Emmett-Teller (BET) Surface Area Analysis

Surface area and porosity are two key factors that affect the quality and utility of solid materials. The differences in surface area and porosity of materials have great impact on the performance characteristics of materials.

The Brunauer, Emmett and Teller (BET) characterization technique is most commonly used technique for analyzing the surface area of powders and porous materials. In BET analysis nitrogen multilayer adsorption is determined as a function of relative pressure with the help of a fully automated analyzer, which gives exact specific surface area evaluation of materials. Nitrogen gas is supplied as an investigating molecule exposed to material surface at liquid nitrogen condition i-e 77K. The surface area is measured in m^2/g which provides important information while investigating the effects of particle size and surface porosity. For spherical, non-porous particles, BET surface area is related to particle diameter or radius and skeletal density. Skeletal density (ρS) is the

mass of the solid divided by the volume of the solid excluding open and closed pores. In case of non-porous solids, skeletal and geometric or envelope densities are similar. Using particle density and diameter BET surface area can be determined. Same way for a known BET surface area and material density, particle diameter can be measured. In case of porous materials or for those which have unsmooth surface, BET surface area is generally quite large.

It is primarily needed to prepare sample before the BET analysis. Adsorbed gases or vapors present on the material surface must be removed. This is done to keep the material surface unaffected. Pretreatment can be done under vacuum heating or by degasing with an inert gas to remove the adsorbed materials from the surface. Sample preparation can highly affect the BET analysis and pore size distribution results. Too severe activation or less cleaning can cause the collapse of pore structure.

Typical Application includes determination of specific area, calculating the open pores and external surface area of mesoporous and micro porous materials. It is also used for analysis of catalysts, metal organic frameworks, zeolites and reactivity studies of materials and various other applications.

Figure 17: BET surface area analyzer

Chapter-4

Results and Discussion

The results obtained from the above mentioned characterization techniques are elaborated in this chapter.

4.1   X-ray diffraction analysis (XRD)

X-ray diffraction calculations were performed by using standard diffraction procedures. Crystal structure and phase analysis of the lab prepared samples were characterized by XRD patterns using CuKα (λ =1.54060Å) at room temperature and operated at 20KV and 5 mA over 2θ range of 5 to 50°.

The X-ray diffraction patterns of the composites and the parental materials are disused in the following figures 18,19,20,21. It has be clarified here that peak at 2θ less than 7° are experimental antiquity which relates to the slide used to run the test and that is why they are not considered in the analysis of the material pattern. For GO, a single peak around 2θ=10^{0} is observed which indicates the distance between carbon layers of 9.7 A^{o} and it is calculated with the help of Braggs law. In case of HKUST-1, the patterns show a good crystalline behavior showing all the representing peaks in accordance with the reported literature [64] [65]. The MOF/GO composites also exhibit the same diffraction pattern similar to MOF-199 which shows that there is well defined MOF present in the prepared composites. Hence, it can be presumed that GO did not obstruct the formation of linkage among Cu dimers and organic linkers. Another interesting fact is that the broad GO peak is not appeared in the composites pattern. This can be due to the dispersion of GO during the synthesis of MOF/GO composites. As the synthesis process of composites involves polar solvents like DMF which is famous for GO dispersion [66].
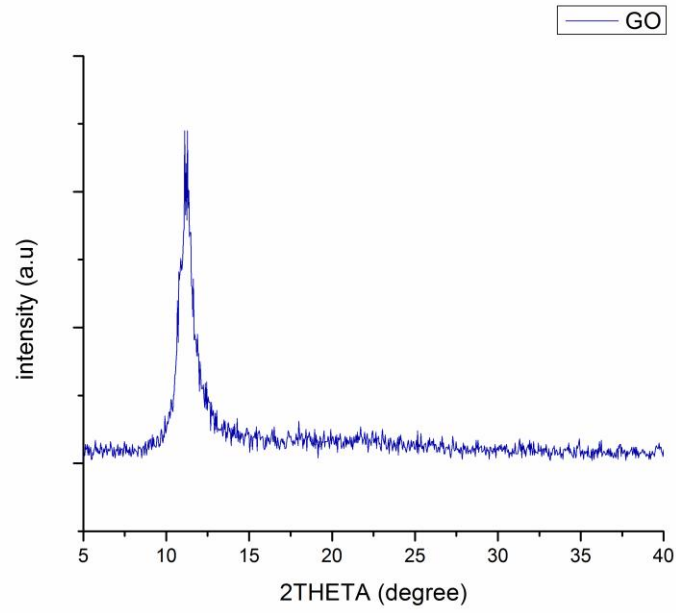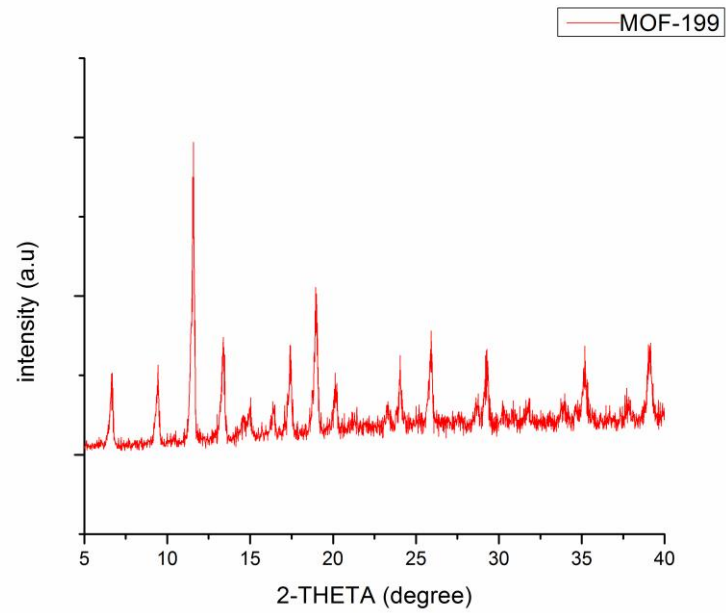
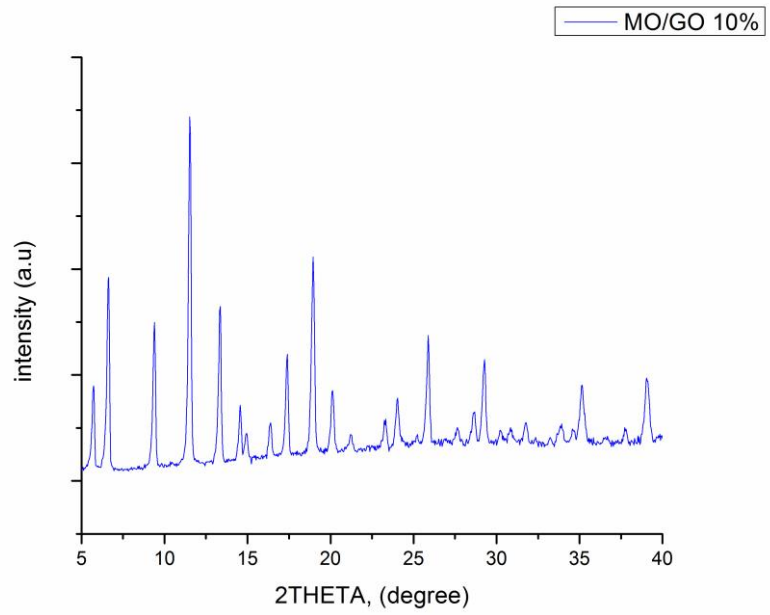Figure 17: XRD PATTERN OF GO

Figure 18: XRD PATTERN OF MOF-199
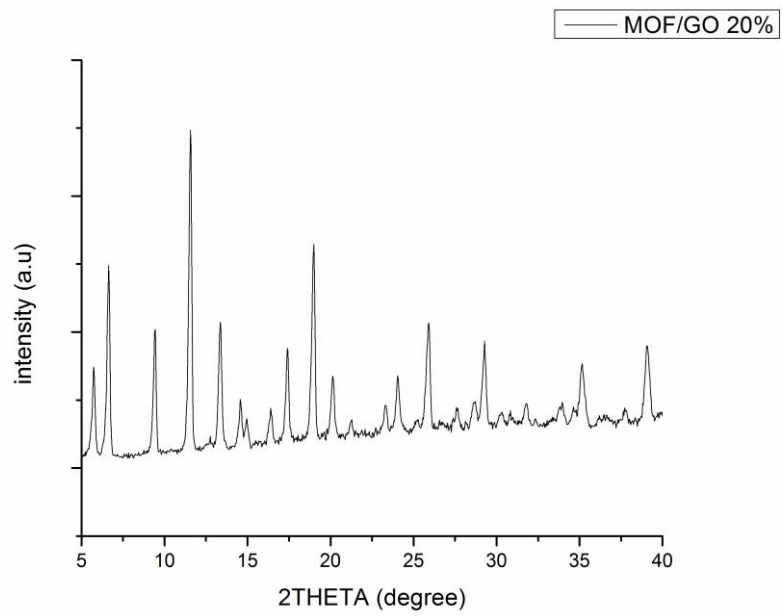
Figure 19: XRD pattern of MOF/GO 10% composite

Figure 20: XRD pattern of MOF/GO 20% composite

4.2 Scanning Electron Microscopy Analysis

The shape and morphology of the composites as well as the parental materials are verified by SEM. As the materials and their composites are non-conductors, so before SEM analysis these materials are thin coated with gold with the help of ion sputtering device.

The parental elements as well as the composites synthesized in the laboratory are characterized by SEM to get information about the materials at low and high magnification. The SEM images of GO at different magnifications are shown below which shows the dense flakes graphene layers assembled together by dispersive forces.
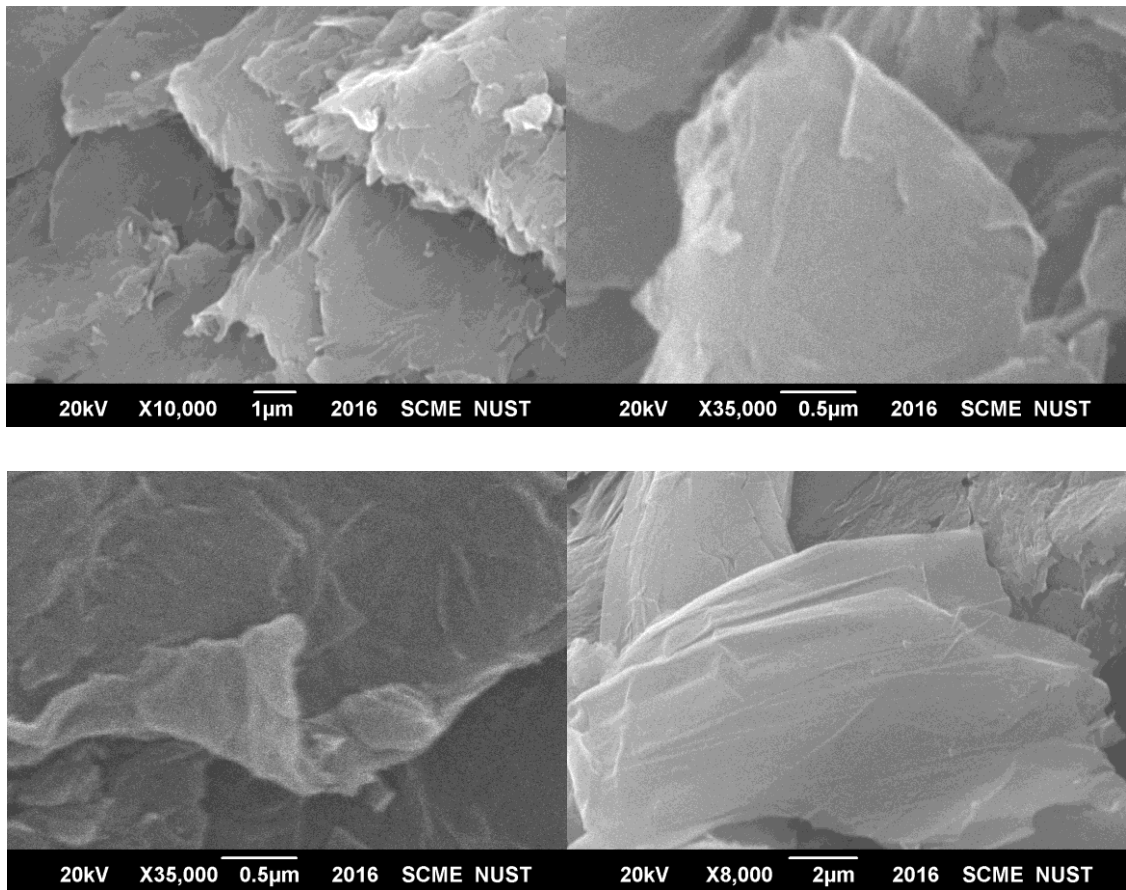

Figure 21: SEM images of GO at different magnifications

In case of HKUST-1, octahedral structure can be seen with average diameter of approximately 15-20 μm. Synthesis of MOF-199 at low temperature usually provides

crystals of cubic shape with sharp edges; though at high temperature produces spherical-shaped particles [67]. The rough structure of MOF confirms the synthesized MOF is favorable for hydrogen uptake. SEM images of HKUST-1 at different magnifications are given below.
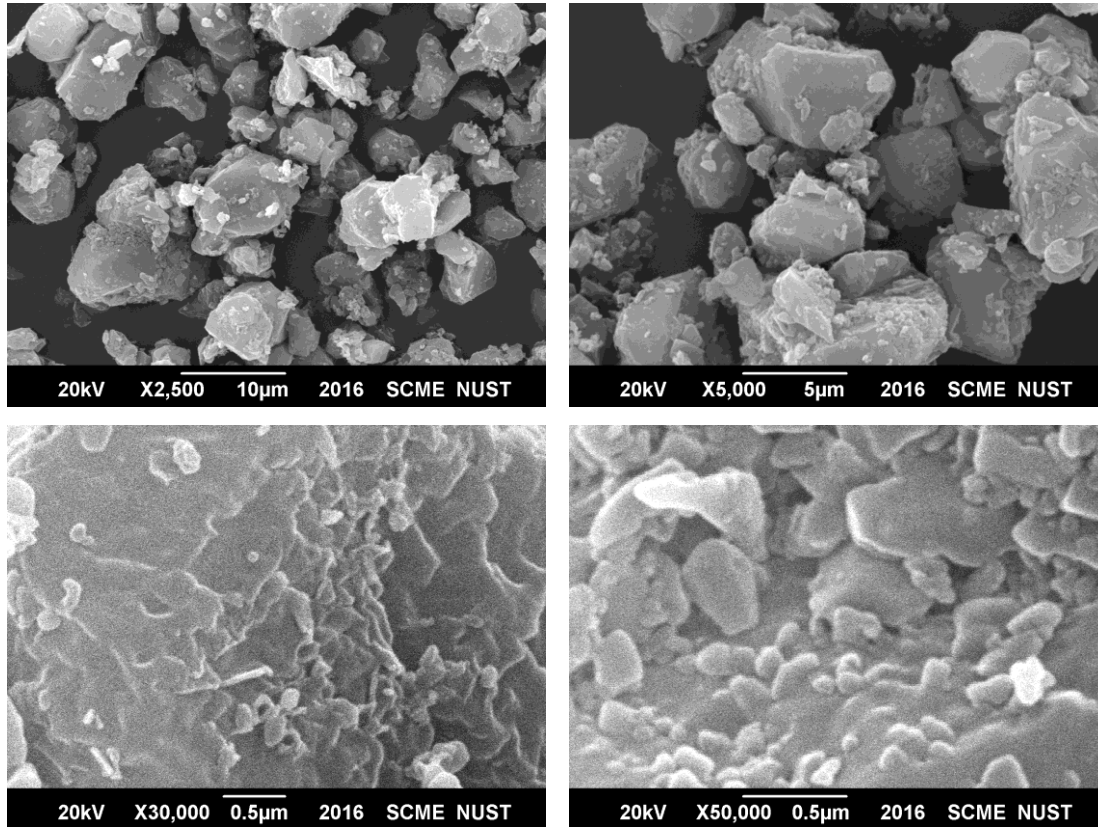
Figure 22: SEM images of HKUST-1

SEM images of composites are shown below. The composite with 10% of GO/MOF showed the presence of graphene layers with submerged MOF. In case of 20% of GO/MOF composite more graphene layers are observed showing a legible lattice image within GO layers. It is a known fact that electron beams can be a reason of the collapse of HKUST-1 and can hence it prevents any visualization of its lattice structure[68]. Although, the patterns investigated showed the lattice image of MOF-199. GO deformed graphene layers in MOF/GO composite assisted MOF in retaining its crystallinity by dissipation of electrostatic charges. Yang et al. also observed this phenomenon with

their MOF 5/CNTs composites [69]. It is clear that as percentage of GO increases in the composite GO dominate the composite. These results showed that the GO and MOF are well mixed within our composite. This assists the result of thermal analysis and the concept that chemical reactions are carried out for the synthesis of the composites. It can also be seen that GO deformed graphene layers are well scattered and do not form lumps which is assisted by XRD results.
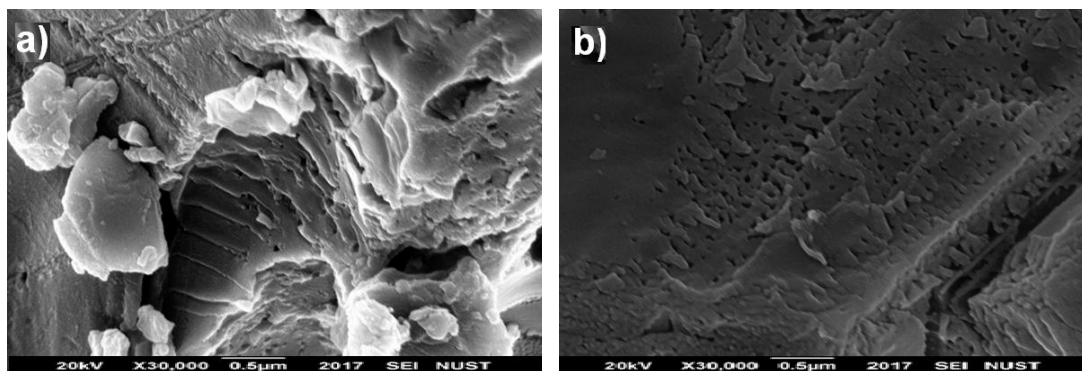

Figure 23: SEM images of MOF/GO composites

4.3   Thermogravimetric Analysis

Weight loss of new composites as well as parental materials is observed by thermogravimetric analysis. 3 to 5 mg of each sample was used for the analysis. TGA is used to investigate the thermal stability of the materials. The DTG curves of synthesized samples are given below between the temperature ranges of 30 °C to 450 °C because there was no significance weight loss measured above 450 °C. Three important curves are observed in case of GO. The first curve which is at100 °C shows the removal of adsorbed water. The second one which is near about at 200 °C correspond the breakdown of epoxy groups. There is a hump between 250 °C and 400 °C which indicate the decomposition of carboxylic and sulphonic groups. For HKUST-1, there is a small peak at 100 °C that indicates the removal of adsorbed water. The extra molecules of water are emancipated at about 300 °C. The complete breakdown of MOF-199 is revealed at about 350 °C. As a result of this CO_2 is produced which in result helps in the formation of copper oxide. The decomposition of HKUST-1 at this temperature is

related with the literature. The curves for MOF/GO composites look similar to the parental HKUST-1 element. The absence of the additional dehydration step from MOF-199 reveals that few copper centers in MOF/GO composites are involved into a more hydrophobic environment. They are perhaps present in the region of GO deformed graphene layers. The important thing is the absence of the curve showing the breakdown of GO epoxy groups from the composites. This is due to the participation of groups in the synthesis of composites and more accurately one can say that, this is due to the binding of copper ions to the oxygen of epoxy groups. The following curves show the exact weight loss in composites as well as parental materials.
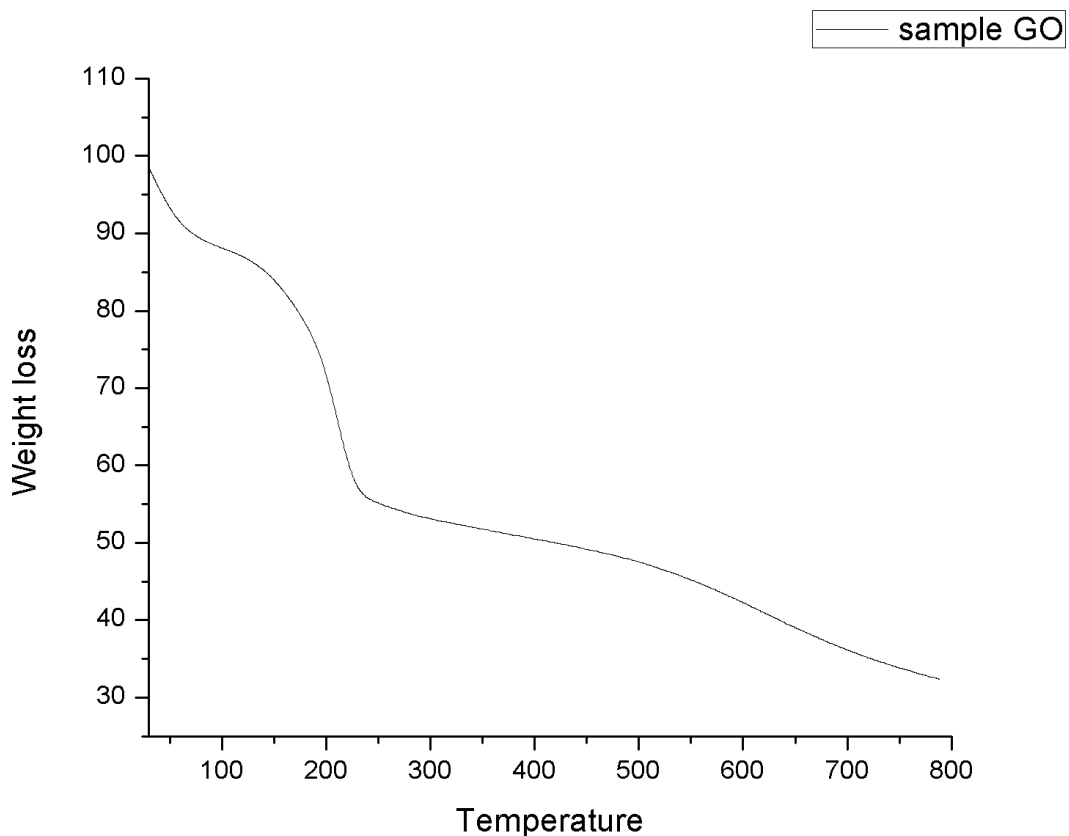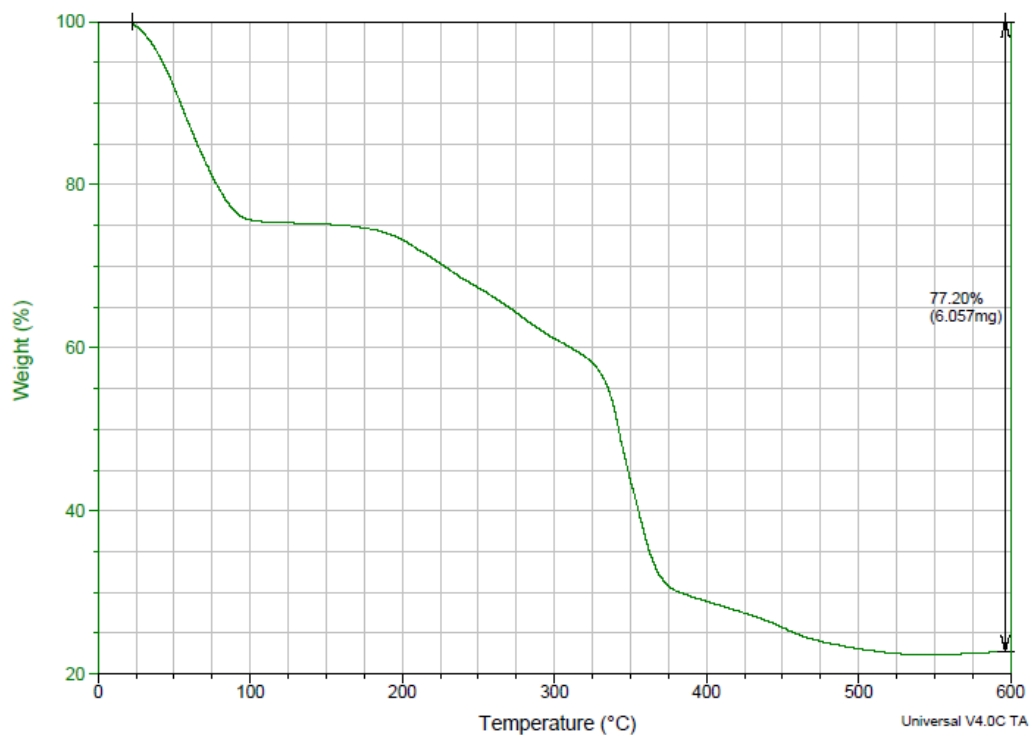

Figure 24: TGA OF GO
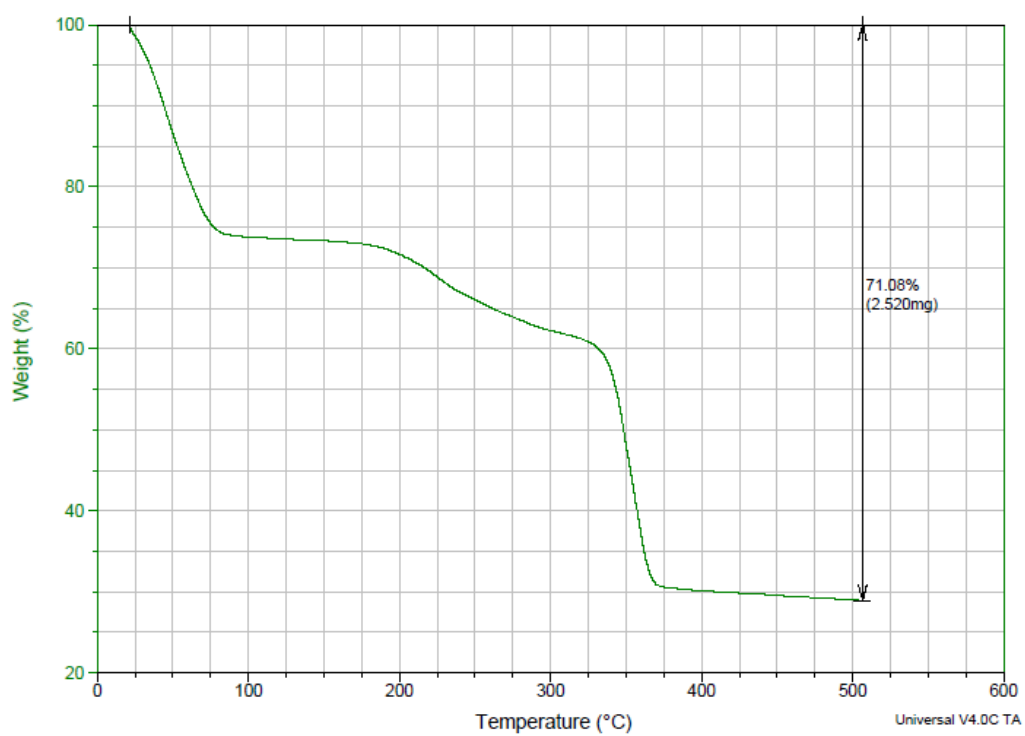
Figure 25: TGA of MOF-199

Figure 26: TGA OF MOF/GO 10%
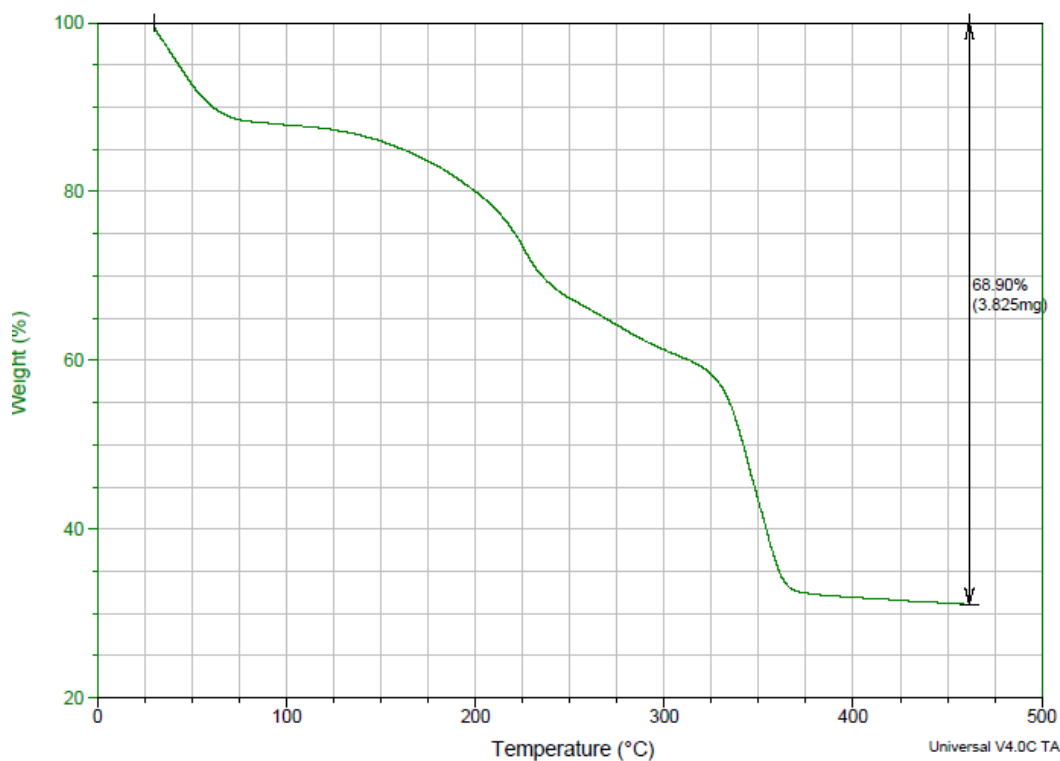
Figure 27: TGA OF MOF/20%

4.4   Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is used to analyze quantitative and qualitative analysis of organic and inorganic samples. It is an excellent method for the detection of functional groups and to identify the type of chemical bonds present in the samples.

The IR spectrum of composites as well as parent materials is given below. The IR spectrum of GO was reported in the literature. The vibrations of C–O appear at 1031 cm^{-1} and the vibrations of O–H bond in water and/or oxygen surface groups are investigated at 1613 cm^{-1}. C=O vibrations from carboxyl and/or carbonyl groups are observed at 1713 cm^{-1}. Two other spectra are revealed at 990 and 1228 cm^{-1}. The first spectrum can be related to epoxy/peroxide groups and the second to S=O asymmetric stretching vibration in sulfonic groups and/or vibration of C–O in epoxides [70]. The spectrum of MOF-199 is very quiet near to those present in literature for the same network [71]. Two zones can be made from this spectrum. The first zone, which is below 1400 cm^{-1}, showed various bands assign to the vibrations of the BTC linker. The zone between

38

1400 and 1700 cm^{-1} corresponds to the carboxylate linkers and hence shows binding of BTC ligand to the copper sites. More accurately, the bands at 1643 and 1589 cm^{-1} and at 1447 and 1370 cm^{-1} represent the asymmetric and symmetric stretching vibration of the carboxylate groups in BTC linkers, duly [72]. In agreement with the data of X-ray diffraction and thermal analyses, the FT-IR spectra of the composites show characteristics near to the MOF-199 spectrum. The changes in the ratios of the spectrums at 1643/1580 cm^{-1} and 1447/1370 cm^{-1} must be assigned to variations in the atmosphere of the carboxylate linkers. This is due to the interactions between the organic linkers with functional group from graphene oxide as well as the disturbance in the structure of MOF-199 due to the inclusion of GO. The gradual reduction in the intensity of the spectra can be seen as the amount of GO increases. This reduction can be corresponded to the less amount of MOF in the composites.
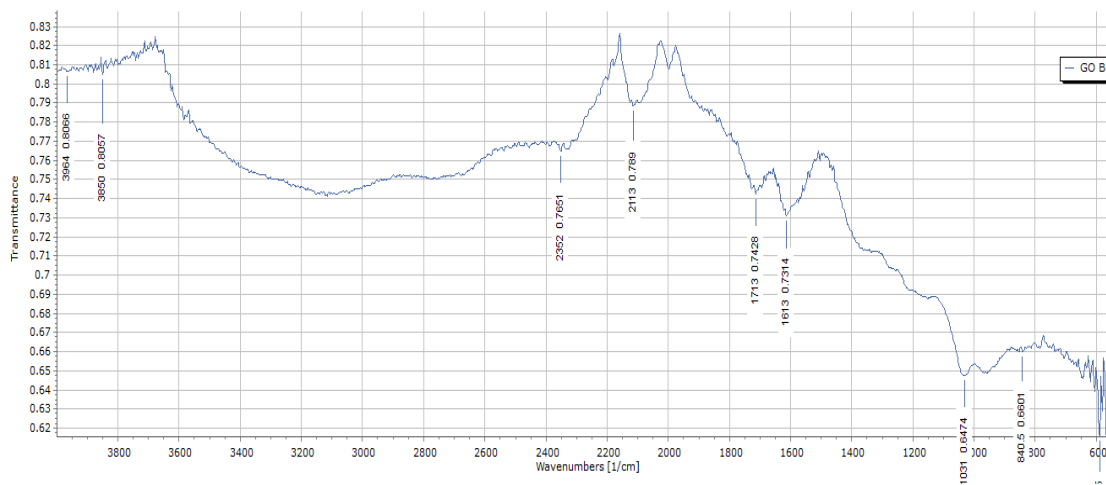
Figure 28: FTIR OF GO
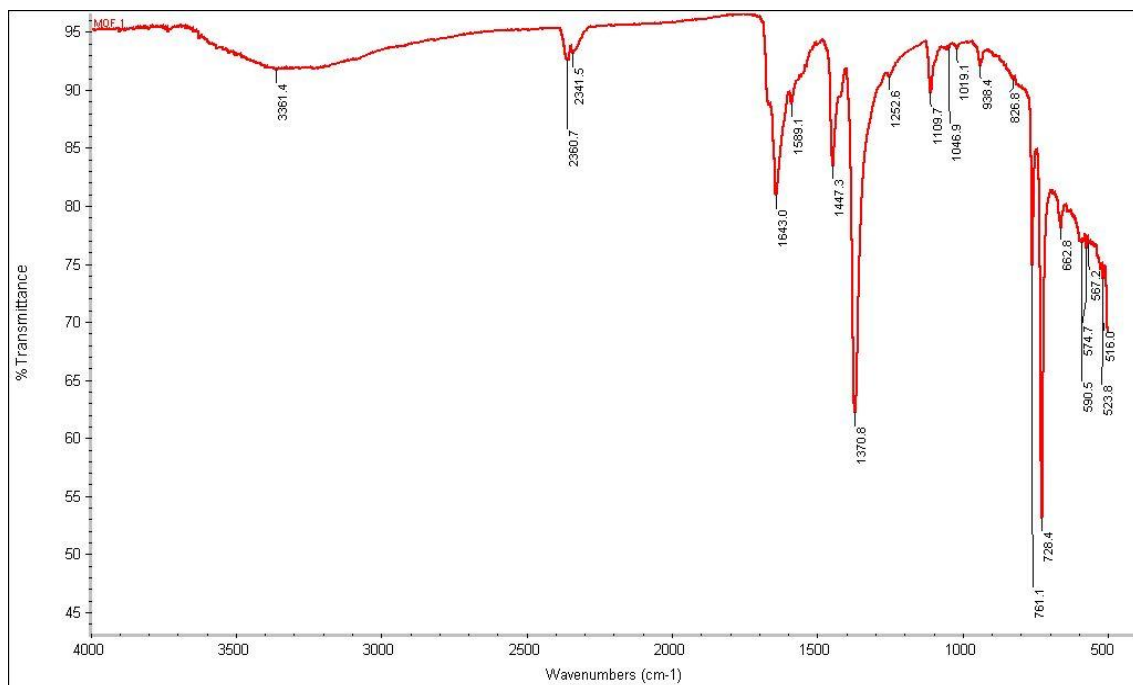
Figure 29: FTIR OF HKUST-1
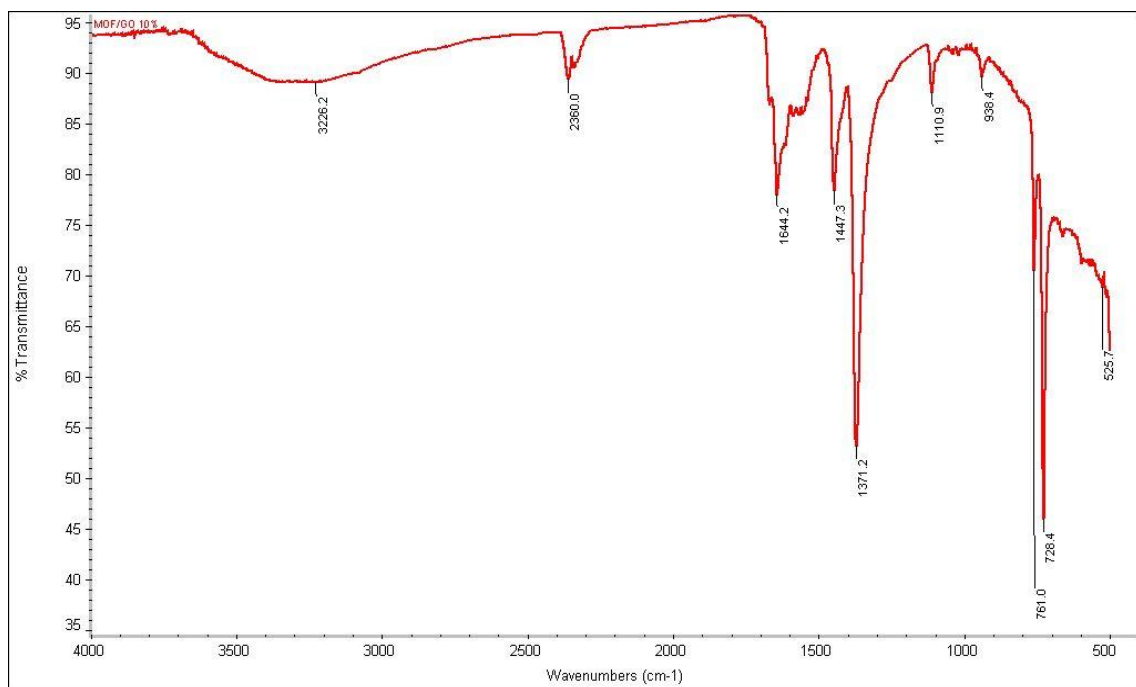
Figure 30:FTIR OF MOF/GO 10%
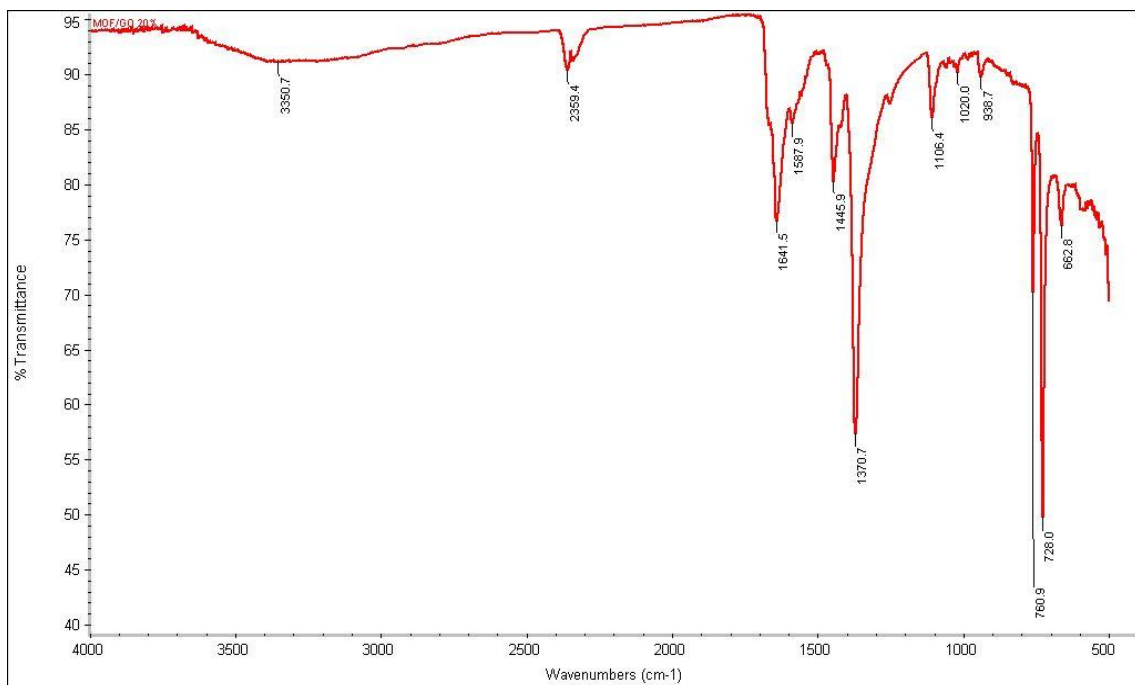
Figure 31: FTIR OF MOF/GO 20%

4.5   Brunauer-Emmett-Teller (BET) Surface Area Analysis

BET is used for the investigation of surface area of the samples. BET surface area of the MOF as well as the composites are given in the below table. The results suggest that surface area of MOF/GO composites with lowest GO contents is higher than the parental MOF, however as the GO content increases the surface area decreases. This is due to the increasing amount of GO which causes deformation in the structures of the material. Another clarification is that as the GO content increases, number of functional group on GO surpasses the number of approachable sites on MOF which interact with each other. At this point some amount of the GO acts as if there was no other component present in composites except solvent. Hence, when the sample was dried the GO layers reassembled together in irregular way as they usually do causing agglomeration which in result decreases the porosity as well as the surface area. BET surface areas of the samples are given in the following table.

41

Table 3: Surface areas of sample

Sample	S_{BET} [m²/g]
HKUST-1	310
MOF/GO 10%	340
MOF/GO 20%	380
MOF/GO 30%	290

4.6   Adsorption Experiments

Adsorption experiments are performed to investigate the uptake capacity of hydrogen. Samples were dried at 150 °C under vacuum for 4 hours. The sample after drying was sealed in polythene bag and stored in desiccator. Samples were conditioned at -40 °C for 8hours in constant cooling chamber.

4.6.1   Equipment/Apparatus

Quartz tube (Model: PYI-2018) Frontier labs japan.

Analytical balance (Model: AT-400) Mettler Toledo Switzerland.

Pyrolyzer (Model: PY2020Id) Frontier labs japan

Hydrogen gas generator (Model: PH-200) peak scientific USA.

4.6.2   Procedure

An accurately weighed quantity of sample (5-6 ± 0.02mg) was packed in a pre-weighed quartz tube used as sample holding device. The sample was inserted in pyrolyzer and connected to hydrogen gas source. The hydrogen gas was passed continuously for ~20 minutes at the flow rate of 5ml/min. After that the samples tube was reweighed precisely and quantity of hydrogen gas adsorbed was calculated by difference in weight method. The results of our samples are discussed below.

4.7   MOF-199

The sample was treated in the same procedure as described above. We took 5.6435 mg of HKUST-1 and packed it in quartz tube. The hydrogen gas was passed for 20 minutes at a flow rate of 5ml/min. Then we reweighed the sample and the hydrogen gas adsorbed was calculated by weight difference method.

$$\% \ adsorbed = \frac{final \ weight - initial \ weight}{initial \ weight} \times 100$$

Initial weight = 5.6435mg

Final weight = 5.9539mg

By using difference method % of hydrogen adsorbed

(final-initial/initial) 100 = (5.9539-5.6435/5.6435)100

$$= 5.50\%$$

4.8   MOF/GO 10%

MOF/GO 10% composite was dried at150 $^{\circ}$C under vacuum for 4 hours. The sample after drying was sealed in polythene bag and stored in desiccator. Sample was conditioned at -40 $^{\circ}$C for 8hours in constant cooling chamber. Then it is packed in the quartz tube and hydrogen gas was passed for 20 minutes at a flow rate of 5ml/min. The results obtained are given below.

Initial weight = 5.5436mg

Final weight = 5.8682mg

By using difference method % of hydrogen adsorbed

(final-initial/initial) 100 = (5.8682-5.5436/5.5436)100

$$= 5.86\%$$

4.9   MOF/GO 20%

The sample was treated in a similar way as explained above. All the conditions are same and the following results were obtained.

Initial weight = 5.0198mg

Final weight = 5.3270mg

By using difference method % of hydrogen adsorbed

(final-initial/initial) 100 = (5.3270-5.0198/5.0198)100

$$= 6.12\%$$

4.10   MOF/GO 30%

Sample was treated in same way as explained above and the following results are produced.

Initial weight = 5.1069mg

Final weight = 5.3779mg

By using difference method % of hydrogen adsorbed

(final-initial/initial) 100 = (5.3779-5.1069/5.1069)100

$$= 5.31\%$$

Table 4: % of hydrogen adsorbed

Sample	Initial weight (mg)	Final weight (mg)	% hydrogen adsorbed
HKUST-1	5.6435	5.9539	5.50
MOF/GO 10%	5.5436	5.8682	5.86
MOF/GO 20%	5.0198	5.3270	6.12
MOF/GO 30%	5.1069	5.3779	5.31

These results depict that the hydrogen uptake first increases when the amount of GO content increases up to 20% and then decreases. This is because of the increase in GO content that causes disturbance in the structures of the material. Another elucidation is that as the GO amount increases in the sample, number of functional group on GO transcends the number of available sites on MOF which react with each other. At this point some amount of the GO behaves like as if there was no other compound present in composites except solvents. Therefore, when the sample was dried the GO layers reassembled together in irregular way as they usually do causing agglomeration which in result decreases the porosity as well as the surface area.

Chapter-5

Conclusion

To conclude, MOF/GO composites are synthesized with different ratios. New composites as well as the parental elements are characterized by SEM, XRD, FTIR, TGA and BET. The properties of MOF-199 in MOF/GO composites are assertive while the porosity is higher as compared to the parental elements. It is considered that the interaction MOF-199 with functional groups of GO (epoxy, hydroxylic, carboxylic and sulfonic groups) assists the formation of new pores. The increment in the porosity of the composites is well observed up to 20% of GO and then declines. This is due to the fact that when the higher contents of GO are present, functional groups on the deformed graphene layer surpasses the number of available sites on MOF which react with each other. Hence, GO deformed graphene layers form agglomerates which decreases the porosity. The enhanced porosity of the composites is responsible for better uptake of hydrogen as compared to the parental elements.

5.1   Future Recommendations

- The prepared MOF/GO composites can be assimilated in polymeric membranes to manufacture mix-MOF-membrane to increase gas separation capacity.

- The manufactured composites can be investigated for their adsorption capacity for   heavy metal removal from waste water.

References

[1]   van den Berg, Annemieke WC, and Carlos Otero Areán. "Materials for hydrogen storage: current research trends and perspectives." *Chemical Communications* 6 (2008): 668-681

[2]   Yang, Jun, Andrea Sudik, Christopher Wolverton, and Donald J. Siegel. "High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery." *Chemical Society Reviews* 39, no. 2 (2010): 656-675.

[3]   Suh, Myunghyun Paik, Hye Jeong Park, Thazhe Kootteri Prasad, and Dae-Woon Lim. "Hydrogen storage in metal–organic frameworks." *Chemical reviews* 112, no. 2 (2011): 782-835.

[4]   Wang, Xiao-Feng, Yue-Biao Zhang, Xiao-Ning Cheng, and Xiao-Ming Chen. "Two microporous metal–organic frameworks with different topologies constructed from linear trinuclear M 3 (COO) n secondary building units." *CrystEngComm* 10, no. 6 (2008): 753-758.

[5]   Putkham, Apipong. "Synthesis, characterisation and gas absorption studies for metal organic framework materials." (2010).

[6]   Panella, Barbara, Katja Hönes, Ulrich Müller, Natalia Trukhan, Markus Schubert, Hermann Pütter, and Michael Hirscher. "Desorption studies of hydrogen in metal–organic frameworks." *Angewandte Chemie International Edition* 47, no. 11 (2008): 2138-2142.

[7]   Jhung, Sung Hwa, J. Lee, and J. Chang. "Microwave synthesis of a nanoporous hybrid material, chromium trimesate." *BULLETIN-KOREAN CHEMICAL SOCIETY* 26, no. 6 (2005): 880.

[8]   Furukawa, Hiroyasu, Nakeun Ko, Yong Bok Go, Naoki Aratani, Sang Beom Choi, Eunwoo Choi, A. Özgür Yazaydin et al. "Ultrahigh porosity in metal-organic frameworks." *Science* 329, no. 5990 (2010): 424-428.

[9]   Pichon, Anne, Ana Lazuen-Garay, and Stuart L. James. "Solvent-free synthesis of a microporous metal–organic framework." *CrystEngComm* 8, no. 3 (2006): 211-214.

[10]   Ni, Zheng, and Richard I. Masel. "Rapid production of metal− organic frameworks via microwave-assisted solvothermal synthesis." *Journal of the American Chemical Society* 128, no. 38 (2006): 12394-12395.

[11]   Nelson, Andrew P., Omar K. Farha, Karen L. Mulfort, and Joseph T. Hupp. "Supercritical processing as a route to high internal surface areas and permanent microporosity in metal− organic framework materials." *Journal of the American Chemical Society* 131, no. 2 (2008): 458-460.

[12]   Ma, Liqing, Athena Jin, Zhigang Xie, and Wenbin Lin. "Freeze Drying Significantly Increases Permanent Porosity and Hydrogen Uptake in 4, 4-Connected Metal–Organic Frameworks." *Angewandte Chemie International Edition* 48, no. 52 (2009): 9905-9908.

[13]   Stankovich, Sasha, Dmitriy A. Dikin, Richard D. Piner, Kevin A. Kohlhaas, Alfred Kleinhammes, Yuanyuan Jia, Yue Wu, SonBinh T. Nguyen, and Rodney S. Ruoff. "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide." *carbon* 45, no. 7 (2007): 1558-1565.

[14]   Dikin, Dmitriy A., Sasha Stankovich, Eric J. Zimney, Richard D. Piner, Geoffrey HB Dommett, Guennadi Evmenenko, SonBinh T. Nguyen, and Rodney S. Ruoff. "Preparation and characterization of graphene oxide paper." *Nature* 448, no. 7152 (2007): 457-460.

[15]   Brodie, B. C. "Sur le poids atomique du graphite." *Ann. Chim. Phys* 59, no. 466 (1860): e472.

[16]   Liu, Zong-huai, Zheng-Ming Wang, Xiaojing Yang, and Kenta Ooi. "Intercalation of organic ammonium ions into layered graphite oxide." *Langmuir* 18, no. 12 (2002): 4926-4932.

[17]   Yang, Xiaojing, Yoji Makita, Zong-huai Liu, and Kenta Ooi. "Novel Synthesis of Layered Graphite Oxide− Birnessite Manganese Oxide Nanocomposite." *Chemistry of materials*15, no. 6 (2003): 1228-1231.

[18]   Li, Jing, Linda Vaisman, Gad Marom, and Jang-Kyo Kim. "Br treated graphite nanoplatelets for improved electrical conductivity of polymer composites." *Carbon* 45, no. 4 (2007): 744-750.

[19]   Buchsteiner, Alexandra, Anton Lerf, and Jörg Pieper. "Water dynamics in graphite oxide investigated with neutron scattering." *The Journal of Physical Chemistry B* 110, no. 45 (2006): 22328-22338.

[20]   Szabó, Tamás, Etelka Tombácz, Erzsébet Illés, and Imre Dékány. "Enhanced acidity and pH-dependent surface charge characterization of successively oxidized graphite oxides." *Carbon* 44, no. 3 (2006): 537-545.

[21]   Lerf, Anton, Heyong He, Michael Forster, and Jacek Klinowski. "Structure of graphite oxide revisited‖." *The Journal of Physical Chemistry B* 102, no. 23 (1998): 4477-4482.

[22]   Li, Je-Luen, Konstantin N. Kudin, Michael J. McAllister, Robert K. Prud'homme, Ilhan A. Aksay, and Roberto Car. "Oxygen-driven unzipping of graphitic materials." *Physical review letters*96, no. 17 (2006): 176101.

[23]   Hashimoto, Ayako, Kazu Suenaga, Alexandre Gloter, Koki Urita, and Sumio Iijima. "Direct evidence for atomic defects in graphene layers." *Nature* 430, no. 7002 (2004): 870-873.

[24]   Hirata, Masukazu, Takuya Gotou, Shigeo Horiuchi, Masahiro Fujiwara, and Michio Ohba. "Thin-film particles of graphite oxide 1:: High-yield synthesis and flexibility of the particles." *Carbon* 42, no. 14 (2004): 2929-2937.

[25]   Millward, Andrew R., and Omar M. Yaghi. "Metal− organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature." *Journal of the American Chemical Society* 127, no. 51 (2005):

17998-17999.

[26]   Bordiga, S., L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. S. Wheatley, R. E. Morris, and A. Zecchina. "Adsorption properties of HKUST-1 toward hydrogen and other small molecules monitored by IR." *Physical Chemistry Chemical Physics* 9, no. 21 (2007): 2676-2685.

[27]   Petit, Camille, and Teresa J. Bandosz. "MOF–graphite oxide composites: combining the uniqueness of graphene layers and metal–organic frameworks." *Advanced Materials* 21, no. 46 (2009): 4753-4757.

[28]   Liu, Dingxin, Jiajun Gu, Qinglei Liu, Yongwen Tan, Zhuo Li, Wang Zhang, Yishi Su et al. "Metal-Organic Frameworks Reactivate Deceased Diatoms to be Efficient CO2 Absorbents." *Advanced Materials* 26, no. 8 (2014): 1229-1234.

[29]   Zhou, Yang, Lin Zhou, Xinghua Zhang, and Yunlin Chen. "Preparation of zeolitic imidazolate framework-8/graphene oxide composites with enhanced VOCs adsorption capacity." *Microporous and Mesoporous Materials* 225 (2016): 488-493.

[30]   Petit, Camille, Barbara Mendoza, and Teresa J. Bandosz. "Hydrogen sulfide adsorption on MOFs and MOF/graphite oxide composites." *ChemPhysChem* 11, no. 17 (2010): 3678-3684.

[31]   Petit, Camille, and Teresa J. Bandosz. "Synthesis, characterization, and ammonia adsorption properties of mesoporous metal–organic framework (MIL (Fe))–graphite oxide composites: exploring the limits of materials fabrication." *Advanced Functional Materials* 21, no. 11 (2011): 2108-2117.

[32]   Petit, Camille, and Teresa J. Bandosz. "MOF–graphite oxide nanocomposites: surface characterization and evaluation as adsorbents of ammonia." *Journal of Materials Chemistry* 19, no. 36 (2009): 6521-6528.

[33]   Petit, Camille, and Teresa J. Bandosz. "Enhanced Adsorption of Ammonia on Metal-Organic Framework/Graphite Oxide Composites: Analysis of Surface

Interactions." *Advanced Functional Materials* 20, no. 1 (2010): 111-118.

[34] Kumar, Ram, Kolleboyina Jayaramulu, Tapas Kumar Maji, and C. N. R. Rao. "Hybrid nanocomposites of ZIF-8 with graphene oxide exhibiting tunable morphology, significant CO 2 uptake and other novel properties." *Chemical Communications* 49, no. 43 (2013): 4947-4949.

[35] Chen, Binling, Yanqiu Zhu, and Yongde Xia. "Controlled in situ synthesis of graphene oxide/zeolitic imidazolate framework composites with enhanced CO 2 uptake capacity." *RSC Advances* 5, no. 39 (2015): 30464-30471.

[36] Wei, Yongyi, Zhongkai Hao, Fang Zhang, and Hexing Li. "A functionalized graphene oxide and nano-zeolitic imidazolate framework composite as a highly active and reusable catalyst for [3+ 3] formal cycloaddition reactions." *Journal of Materials Chemistry A* 3, no. 28 (2015): 14779-14785.

[37] Ge, Jianping, Le He, and Yadong Yin. "Magnetically Tunable Colloidal Photonic Crystals." In *The Chemistry Of Nanostructured Materials: Volume II*, pp. 1-35. 2011.

[38] García-Pérez, Elena, Jorge Gascón, Víctor Morales-Flórez, Juan Manuel Castillo, Freek Kapteijn, and Sofía Calero. "Identification of adsorption sites in Cu-BTC by experimentation and molecular simulation." *Langmuir* 25, no. 3 (2009): 1725-1731.

[39] Pachfule, Pradip, Raja Das, Pankaj Poddar, and Rahul Banerjee. "Solvothermal synthesis, structure, and properties of metal organic framework isomers derived from a partially fluorinated link." *Crystal Growth & Design* 11, no. 4 (2011): 1215-1222.

[40] Forster, Paul M., Norbert Stock, and Anthony K. Cheetham. "A High-Throughput Investigation of the Role of pH, Temperature, Concentration, and Time on the Synthesis of Hybrid Inorganic–Organic Materials." *Angewandte Chemie International Edition* 44, no. 46 (2005): 7608-7611.

[41] Cravillon, Janosch, Simon Münzer, Sven-Jare Lohmeier, Armin Feldhoff, Klaus Huber, and Michael Wiebcke. "Rapid room-temperature synthesis and characterization of nanocrystals of a prototypical zeolitic imidazolate framework." *Chemistry of Materials* 21, no. 8 (2009): 1410-1412.

[42] Hasebe, Shinji. "Design and operation of micro-chemical plants—bridging the gap between nano, micro and macro technologies." *Computers & chemical engineering* 29, no. 1 (2004): 57-64.

[43] Yoo, Yeonshick, and Hae-Kwon Jeong. "Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition." *Chemical communications* 21 (2008): 2441-2443.

[44] Liu, Qi, Ze-Xian Low, Lunxi Li, Amir Razmjou, Kun Wang, Jianfeng Yao, and Huanting Wang. "ZIF-8/Zn 2 GeO 4 nanorods with an enhanced CO 2 adsorption property in an aqueous medium for photocatalytic synthesis of liquid fuel." *Journal of Materials Chemistry A* 1, no. 38 (2013): 11563-11569.

[45] MacGillivray, Leonard R., ed. *Metal-organic frameworks: design and application*. John Wiley & Sons, 2010.

[46] Tanabe, Kristine K., and Seth M. Cohen. "Postsynthetic modification of metal–organic frameworks—a progress report." *Chemical Society Reviews* 40, no. 2 (2011): 498-519.

[47] Xu, Feng, Shikai Xian, Qibin Xia, Yingwei Li, and Zhong Li. "Effect of textural properties on the adsorption and desorption of toluene on the metal-organic frameworks HKUST-1 and MIL-101." *Adsorption Science & Technology* 31, no. 4 (2013): 325-339.

[48] Pan, Long, Brett Parker, Xiaoying Huang, David H. Olson, JeongYong Lee, and Jing Li. "Zn (tbip)(H2tbip= 5-tert-butyl isophthalic acid): a highly stable guest-free microporous metal organic framework with unique gas separation capability." *Journal of the American Chemical Society* 128, no. 13 (2006): 4180-4181.

[49]   Pan, Long, David H. Olson, Lauren R. Ciemnolonski, Ryan Heddy, and Jing Li. "Separation of hydrocarbons with a microporous metal–organic framework." *Angewandte Chemie*118, no. 4 (2006): 632-635.

[50]   Gándara, Felipe, Hiroyasu Furukawa, Seungkyu Lee, and Omar M. Yaghi. "High methane storage capacity in aluminum metal–organic frameworks." *Journal of the American Chemical Society* 136, no. 14 (2014): 5271-5274.

[51]   Li, Jian-Rong, Julian Sculley, and Hong-Cai Zhou. "Metal–organic frameworks for separations." *Chemical reviews* 112, no. 2 (2011): 869-932.

[52]   Cui, Yuanjing, Yanfeng Yue, Guodong Qian, and Banglin Chen. "Luminescent functional metal–organic frameworks." *Chemical reviews* 112, no. 2 (2011): 1126-1162.

[53]   McKinlay, Alistair C., Russell E. Morris, Patricia Horcajada, Gérard Férey, Ruxandra Gref, Patrick Couvreur, and Christian Serre. "BioMOFs: metal–organic frameworks for biological and medical applications." *Angewandte Chemie International Edition* 49, no. 36 (2010): 6260-6266.

[54]   Liu, Yangyang, Zhiyong U. Wang, and Hong-Cai Zhou. "Recent advances in carbon dioxide capture with metal-organic frameworks." *Greenhouse Gases: Science and Technology* 2, no. 4 (2012): 239-259.

[55]   Sumida, Kenji, David L. Rogow, Jarad A. Mason, Thomas M. McDonald, Eric D. Bloch, Zoey R. Herm, Tae-Hyun Bae, and Jeffrey R. Long. "Carbon dioxide capture in metal–organic frameworks." *Chemical reviews* 112, no. 2 (2011): 724-781.

[56]   Liu, Jian, Praveen K. Thallapally, B. Peter McGrail, Daryl R. Brown, and Jun Liu. "Progress in adsorption-based CO 2 capture by metal–organic frameworks." *Chemical Society Reviews* 41, no. 6 (2012): 2308-2322.

[57]   Bae, Youn-Sang, Omar K. Farha, Alexander M. Spokoyny, Chad A. Mirkin, Joseph T. Hupp, and Randall Q. Snurr. "Carborane-based metal–organic

frameworks as highly selective sorbents for CO 2 over methane." *Chemical Communications* 35 (2008): 4135-4137.

[58] Banerjee, Rahul, Anh Phan, Bo Wang, Carolyn Knobler, Hiroyasu Furukawa, Michael O'keeffe, and Omar M. Yaghi. "High-throughput synthesis of zeolitic imidazolate frameworks and application to CO2 capture." *Science* 319, no. 5865 (2008): 939-943.

[59] Novoselov, Kostya S., Andre K. Geim, Sergei V. Morozov, D. Jiang, Y_ Zhang, Sergey V. Dubonos, Irina V. Grigorieva, and Alexandr A. Firsov. "Electric field effect in atomically thin carbon films." *science* 306, no. 5696 (2004): 666-669.

[60] Petit, Camille, Mykola Seredych, and Teresa J. Bandosz. "Revisiting the chemistry of graphite oxides and its effect on ammonia adsorption." *Journal of Materials Chemistry* 19, no. 48 (2009): 9176-9185.

[61] Poweleit, Nicole Lynn. "Using advances in electron microscopy to study microbial interactions." PhD diss., University of California, Los Angeles, 2016.

[62] Nicolet, Thermo, and C. All. "Introduction to fourier transform infrared spectrometry." *Thermo Nicolet Corporation* (2001).

[63] Menezes, Prashanth W., Arindam Indra, Diego González-Flores, Nastaran Ranjbar Sahraie, Ivelina Zaharieva, Michael Schwarze, Peter Strasser, Holger Dau, and Matthias Driess. "High-performance oxygen redox catalysis with multifunctional cobalt oxide nanochains: morphology-dependent activity." *ACS Catalysis* 5, no. 4 (2015): 2017-2027.

[64] Prestipino, C., L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug, and S. Bordiga. "Local structure of framework Cu (II) in HKUST-1 metallorganic framework: spectroscopic characterization upon activation and interaction with adsorbates." *Chemistry of materials* 18, no. 5 (2006): 1337-1346.

[65] Biemmi, Enrica, Sandra Christian, Norbert Stock, and Thomas Bein. "High-

throughput screening of synthesis parameters in the formation of the metal-organic frameworks MOF-5 and HKUST-1." *Microporous and Mesoporous Materials* 117, no. 1 (2009): 111-117.

[66] Cai, Dongyu, and Mo Song. "Preparation of fully exfoliated graphite oxide nanoplatelets in organic solvents." *Journal of Materials Chemistry* 17, no. 35 (2007): 3678-3680.

[67] Wang, Qing Min, Dongmin Shen, Martin Bülow, Miu Ling Lau, Shuguang Deng, Frank R. Fitch, Norberto O. Lemcoff, and Jessica Semanscin. "Metallo-organic molecular sieve for gas separation and purification." *Microporous and mesoporous materials* 55, no. 2 (2002): 217-230.

[68] Houk, Ronald JT, Benjamin W. Jacobs, Farid El Gabaly, Noel N. Chang, A. Alec Talin, Dennis D. Graham, Stephen D. House, Ian M. Robertson, and Mark D. Allendorf. "Silver cluster formation, dynamics, and chemistry in metal− organic frameworks." *Nano letters* 9, no. 10 (2009): 3413-3418.

[69] Yang, Seung Jae, Jae Yong Choi, Hee K. Chae, Jung Hyun Cho, Kee Suk Nahm, and Chong Rae Park. "Preparation and enhanced hydrostability and hydrogen storage capacity of CNT@ MOF-5 hybrid composite." *Chemistry of Materials* 21, no. 9 (2009): 1893-1897.

[70] Petit, Camille, Mykola Seredych, and Teresa J. Bandosz. "Revisiting the chemistry of graphite oxides and its effect on ammonia adsorption." *Journal of Materials Chemistry* 19, no. 48 (2009): 9176-9185.

[71] Seo, You-Kyong, Geeta Hundal, In Tae Jang, Young Kyu Hwang, Chul-Ho Jun, and Jong-San Chang. "Microwave synthesis of hybrid inorganic–organic materials including porous Cu 3 (BTC) 2 from Cu (II)-trimesate mixture." *Microporous and Mesoporous Materials* 119, no. 1 (2009): 331-337.

[72] Vairam, S., and S. Govindarajan. "New hydrazinium salts of benzene tricarboxylic and tetracarboxylic acids—preparation and their thermal studies." *Thermochimica acta* 414, no. 2 (2004): 263-270.