Metal Organic Frameworks: Synthesis and Applications

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Metal Organic Frameworks: Synthesis And Applications

Major Project

Submitted in partial fulfillment of the requirements

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Master of Technology in Chemical Engineering

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Guided By
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Certificate

This is to certify that the Major Project Report entitled “**”Metal Organic Frameworks: Synthesis And Applications”** submitted by **Ketul Shah (Roll No:12MCHC24)**, towards the partial fulfillment of the requirements for the degree of Master of Technology in Chemical Engineering (Chemical Process And Plant Design) of Nirma University, Ahmedabad is the record of work carried out by him under my supervision and guidance. In my opinion, the submitted work has reached a level required for being accepted for examination. The results embodied in this major project, to the best of my knowledge, haven’t been submitted to any other university or institution for award of any degree or diploma.

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Abstract

Metal organic frameworks (MOFs) are a recently identified new class of hybrid porous material, consisting of metal ions or cluster linked together by organic bridging ligands. MOFs have been shown tremendous potential in adsorptive separation application and gas storage owing to some of their extraordinary features in terms of specific area, pore volume, low to moderate heat of adsorption and fairly uniform pore size distribution. This project work is focused on the synthesis and characterization of different MOFs and their application in adsorptive separations.

MOFs are crystalline compound consisting of metal ions/cluster coordinated to often rigid organic molecules to form one, two, three dimensional structures that can be porous. The pore size and surface properties of these materials can be tuned to a great extent with relative ease by choosing appropriate metal centers and organic ligands. MOFs have got advantages over existing porous materials and zeolite. They possess a wide array of potential applications including materials for gas storage, gas/vapor separation, catalysis, etc.

As an explorative study of various MOFs using different metal precursor and ligand have done based on solvothermal methods. Mostly 1,4-benzenedicarboxylic acid(BDC) and 1,3,5-benzenetricarboxylic acid(BTC) based MOFs were synthesized. Various characterization techniques were applied to study the properties of these MOFs. And then after catalytic studiesusing MOF materials, as heterogeneous catalysts in organic transformation reactions were performed. Also adsorption studies were carried out for sulfur containing compound. The adsorbent was found to be dependent on concentration of adsorbate by keeping adsorbent constant.

Key words: metal-organic frameworks, heterogeneous catalysis, adsorptive separation, alkylation, adsorbent, adsorbate

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Chapter 1

Introduction

Since the global trend is toward green technology and green engineering there are so many researchers undergoing for developing environment friendly processes, products, catalysts etc. Catalysis is the one of such area where vast number of researchers are working aiming towards cleaner and greener processes. The main problem with catalysts is toxicity, difficulty in separation from product, presence of costly metals which results in high cost of the catalysts. Development of selective and stable heterogeneous catalysts that can be efficiently and easily recovered from the reaction media and reused in subsequent cycles, is an active research area.[1] Conventional acids such as H_2SO_4,HF,$AlCl_3$, BF_3, Sb_5, $H_3PO_4$and hydro chloric acid used in organic reactions introduce significant risks in handling, containment and disposal due to their poisonous and corrosive nature. As catalysts, solid acids have some additional features such as ease of separation from reaction mixture, no corrosion for the reactor, and pollution free etc. So they are indeed of attention in theoretical research and in practical application.[2] Because of high reactivity, ease of handling, recovery, low waste generation and environmental friendliness; heterogeneous solid acid catalysts are evolving as very potential alternative to the conventional homogeneous acidic reactants. Among various acidic catalysts such as zeolites, clays, and heteropoly acids, the sulfated metal oxides, based on iron oxide have emerged as strong catalysts due to their super acidity, high reactivity at low temperatures and frequent usability. The activity, selectivity, and stability of sulfated iron oxide catalysts can also improved by the addition of noble inert metals and transition metal oxides such as Cu and Co.[3][4]

Acid-catalyzed organic reactions are numerous and the usage of solid acid catalysts are very unrestrained in several industrial and environmental processes.[5].Solid acids are the most important heterogeneous catalysts used today, considering in terms of both the total amounts used and the final economic impact. As per recent review of industrial acid based catalysis of the 127 processes identified, over 115 are solid acid-catalyzed [6,7] It clearly shows the significance of their materials and the scope of their commercial exploitation. These are extremely useful in many applications, especially in petroleum industry for alkylation and isomerization reactions.[7]

Porous materials are very useful in gas storage, adsorption, catalysis, drug storage and delivery, and as templates in the preparation of low dimensional materials. Inorganic porous frameworks possess highly ordered structures.To get the advantage of the properties of both organic and inorganic porous materials, porous hybrids, known as metal organic frameworks (MOFs), can be generated that are stable,ordered and possess high surface areas.[8]

Among the classes of porous materials, metal-organic frameworks (MOFs) are unparalleled in their extent of tenability and structural diversity as well as their range of chemical and physical properties. MOFs are one of the fastest growing classes of novel inorganic materials. Their ordered porous construction with high surface areas and porosities, together with the possibility to functionalize the hybrid frameworks are the main reasons why MOFs have gained a tremendous interest during the last decade. MOFs are analogous to zeolites for their large internal surface areas, extensive porosity, and high degree of crystallinity. And hence, MOFs and zeolites have been utilized for many of the similar applications including gas storage and separation as well as heterogeneous catalysis. Technological advancement and requirement for more environmental friendly, economical material results in emergence of this attractive class of porous solids. MOFs offer promising qualities in general for such industrial applications. It is a hybrid of inorganic metal part and organic linker. The variety of metal ions, organic linkers, and structural motifs affords an essentially numerous possible combinations.[9] Moreover, the possibility for post synthetic modification adds an additional dimension to the synthetic variability. The metallic parts mainly correspond to divalent and trivalent ions of 3d transition metals (Zn, Cu, Fe, Ni etc), 3p metals, or lanthanides and multi organic acids as ligands.[10]

Also adsorption to high surface area materials like MOFs has attracted great attention in recent era. They are proved as adsorbents owing to their high surface area, low densities, high porosity, thermal stability and adjustable chemical functionalities.

1.1 Objective of study

Objective of this study is defined as synthesis of different MOFs using different metal precursors and observe the all possible applications of synthesized MOFs. It has wide scope in the field of catalysis since it is a novel class of porous materials. More importance is given to synthesis, application, and characterization in the field of catalysis and adsorption separation with focus on petrochemicals industry.

Chapter 2

Literature Review

2.1 Porous solid materials

Solids that have pores or channels permeating their structures that are large enough to permit diffusion of guest molecules, and that persist when guests are removed are referred to as porous solids. These solids usually have a porosity (fraction of void volume to the total volume occupied by the solid material) of 0.2-0.95. Porous materials find their way into a number of domestic, commercial and industrial applications that range from simple water purification by porous ceramics or activated carbon to energy storage, molecular storage and separation, and heterogeneous catalysis among many others.[11] Some porous materials have penetrating open pores that connect throughout the material forming channels through which molecular guests can diffuse. Such open porous solids are of particular interest because of their utility in continuous flow and batch processes where the flow of guest molecules through channel is desirable to achieve separation or carry out reactions. The high surface area provided by the walls of the channel is known to facilitate the uptake of molecules, thereby promoting chemical reactions and other processes that rely on adsorption of molecules. Haphazardly arranged pores that cannot be reproduced in a repeating pattern generally result in disordered porous solids such as gels organic polymers. Such materials have no defined structures and therefore the exact pore and void volume cannot be characterized easily. Although the porosity (void fraction) in disordered porous materials can be modified synthetically, the dimensions and patterns of microscopic pores generally are difficult to reproduce.[12]

2.2 Zeolites

Inorganic zeolites are one of the more ubiquitous ordered micro porous materials that consist of hydrated, crystalline tectoaluminosilicates, composed of TO_4 (T = Si, Al) tetrahedral bridged by oxygen atoms. To neutralize the charges resulting from trivalent aluminum coordinated tetrahedral by oxygen, captions of alkali and earth alkali metals are present within the channels of zeolites. Consequently, zeolites frequently are used in applications involving ion-exchange. Zeolites exhibit a broad range of crystalline structures with different channel topologies resulting from variation in the arrangements of the sodalite cage, which is the repeating unit in zeolites. Zeolites can be synthesized by hydrothermal reaction and subsequently crystallization of reactive alkali-based aluminosilicates. The sol gel method also can be utilized to prepare zeolites. Surface properties such as the hydrophobicity of the channels can be controlled by varying the ratio of silicon to aluminum, which also determines the crystalline structure and pore dimensions present in the resulting zeolite. The resulting channels of zeolites are constricted by narrow openings with a maximum diameter of 4 to 12 that restricts the utility of zeolites as porous hosts to guests consisting of ions and small organic molecules. Thus, zeolites offer a somewhat limited number of combinations of channel topology and porous properties. Nevertheless, zeolites are still used widely as porous hosts for applications that involve sorption of smaller guests (e.g., heterogeneous catalysis, molecular separation, ion exchange, etc) [13]. Also temperature stability aspects in case of zeolite are very much satisfactory which is advantageous in the high temperature catalytic processes like cracking.

2.3 Metal Organic Framework

Metal organic frameworks belong to class of crystalline compounds consisting metal ions or clusters coordinated to often rigid organic molecules to form one, two or three dimensional structures that can beorderedly porous. A metal organic framework is composed of two major components: a metal ion or cluster of metal ions and organic molecules called a linker. The choice of metals and linkers has significant effects on the structures and properties of the MOFs. This collection of compounds has been variously termed metal organic frameworks, coordination polymers, hybrid organic inorganic materials and organic zeolites analogous with unavoidable overlap. Over the past decade, a novel class inorganic-organic porous material known as MOFs has emerged as a new field in solid state research. The strong chemical bonds that hold MOFs together allow their structures to remain consistent yet empty inside.[14]

The first MOF was produced in the last decade of twentith century and since then, their potential for commerciall applications has drawn a lot of interest. One gram of a MOF can have a large surface area equivalent to a football pitch. One of the major applications for MOFs is for storage of gases. The porous material can catch,hold and store carbon, exploring a technology for carbon capture and storage. Apart from carbon storage, MOFs may be potent enough to play a part in industrial separation processes for gases, vapors and liquids as well as catalysis.[15] They utilize low cost, simple building blocks, such as Zn, Ni,Fe or Al, and can be prepared in high yield and purity. MOFs also offer proven merits over conventional porous solids, such as zeolites. With a diversity of metal oxide joints that can be linked by a large variety of organic struts, there are a virtually infinite number of MOFs to be made. A lots of MOFs have been described so till date, but only a few of them are porous and stable. With a virtually infinite number of possible MOFs structures, the challenge faced is to and efficiently produce MOFs with adsorptive as well as catalytic properties. One material already exhibiting potentially useful qualities is MIL-53, that is part of the Materials from Institute of Lavoisier (MIL) family of MOFs. It is chemically stable and yet retains flexible structures with the ability to absorb various gases. The characterization team applied time resolved diffraction tests to MIL-53,to analyze its reversible ability to adsorb gases, or breathing behavior in the presence of various foreign molecules. MOF does not given a proper IUPAC naming till date.[15,16]

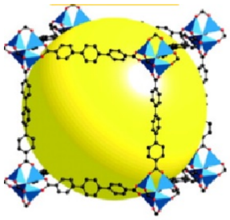

Figure 2.1: Graphical representation of MOF

2.4 Synthesis of MOFs

MOFs can be synthesized by self-assembly of organic ligands and metal ions. There are two ways to tune the pore size and provide desired surface chemistry: direct assembly of new MOFs from particular metal nodes and organic linkers and the pre-constructed robust precursor MOFs are modified by the post synthesis. The flexible ways of making MOFs have led to synthesis of thousands of MOFs during recent years. MOFs can be built from two types of building units: metal ions and organic ligands. The pore volume and surface area of MOFs can be controlled by modifying organic ligands which act as spacers and create an open porous structure. In order to make a coordination polymer it is, in principle, only necessary to react a potentially bridging ligand with a metal ion which has more than one vacant or labile site. MOFs are produced almost exclusively by

- Hydrothermal
- Solvothermal(reflux method or using high pressure reactor)
- Microwave synthesis

MOFs are synthesized by combining organic linkers and metal salts as a precursor in solvothermal reactions at relatively low temperatures ($<300°C$). The characteristics of the ligand (bond angles, bond length, bulkiness, chirality etc.) play a vital role in predicting the resultant framework. Several factors must be borne in mind when approaching the synthesis of a new metal organic framework, aside from the geometric principles that are considered during its design. By far the most important aspect is the maintenance of desired integrity of building blocks. The reactants are mixed in, polar solvents having such as water, dialkylformamide, dimethyl sulfideor acetonitrile. The most important parameters of solvothermal MOF synthesis are temperature, concentrations of metal salt and ligand,the degree of solubility of the reactants in the solvent, and the pH of the solution.Though experience often dictates the best conditions for growing these crystalline frameworks, experimentation and permutation and combination of methods are still often necessary[17].Here is one example of synthesis of $Cu_4(BTC)_2(H_2O)_3XH_2O$.

In a typical synthesis,0.875 g(3.6 mmol) copper nitrate(hydrated) were dissolved in 12ml de-ionized water and mixed with 0.42g(2.0 mmol) of trimesic acid(BTC) dissolved in 12ml ethyle alcohol. The solution was poured into a 50 ml Teflon(PTFE) liner, placed in an autoclave, and heated to 120°C for 12h. Physisorption measurements using Nitrogen were carried out using micrometrics ASAP-2000 instruments. PXRD patterns were recorded on a STOE diffractometer, equipped with a place sensitive detector and primary beam monochromator of Ge in the transmission mode using CuKal radiation. For the XRD measurements, the dried powder was filled into capillaries (0.5 mm diameter) and sealed under Ar if required. The entire structures of MOFs depend upon the solvent used for the synthesis that is if the organic solvent is changed, the topology of MOFs is going to be change.

One of the possible alternatives in microwave irradiation which allows access to a wide range of temperatures and can be used to shorten crystallization times, tendency is the general lack of formation of crystal large enough to shorten crystallization times while controlling face morphology and PSD.One of the limitation of this tendency is lack of formation of crystals large enough to obtain good structural data. On the other hand, a microwave irradiation method has been studied in the synthesis of not only organic molecules but also inorganic materials. More recently, microwave assisted synthesis of inorganic materials requiring several days for their crystallization has attracted much attention. This technique provides synthesis methods of porous materials with savings the reaction time within a few minutes and offering phase selectivity and facile morphology control. Very recently, some of us recently reported that microwave technique can be well applied to the rapid synthesis as well as phase selective crystallization of porous hybrid solids[18].

Metal ions as building units

Transitions-metal ions are often used as versatile connectors of MOFs. The first-row transition metal ions, such as $Cr^{+}3$,$Fe^{+}3$,$Cu^{+}2$,$Zn^{+}2$, are especially common used. Some alkali metal ions, alkaline-earth metal ions and rear earth metal ions have also been employed as metal nodes for constructing MOF structure. The important characteristics of metal connectors are the number and orientation of their binding sites. Depending on the metal and its oxidation state, coordination numbers can range from 2 to 7, giving rise to various geometries, such as T-or Y- shaped, square-planer, tetrahedral, square-pyramidal, octahedral etc, play important role in directing the MOF structure.

Organic ligands

The organic ligands, which are used for MOF construction, generally contain coordination functional group such as carboxylate, phosphate, sulfonate, amine or nitrile.

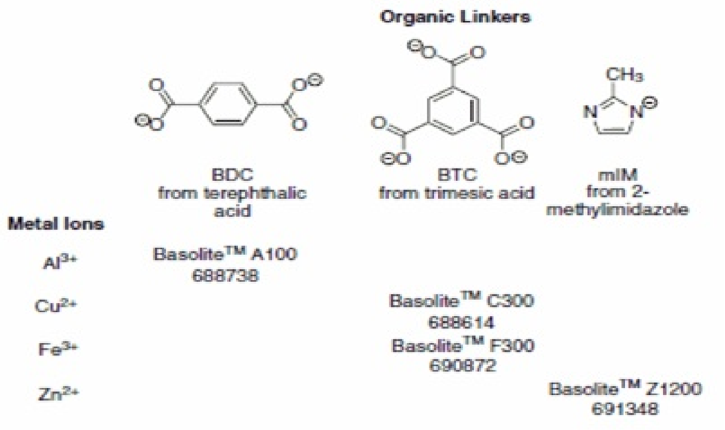

Figure 2.2: Organic ligands for the synthesis of MOFs[19]

2.4.1 Structure of MOFs

A metal organic framework (MOF) is combination of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. The organic units are basically mono, di, tri, or tetravalent ligands. The choice of metal and linker has remarkable effects on the structure and properties of the MOF. For example, the metals coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation. MOFs have basically have crystalline solid structure, formed by combination solution reaction of metal salt with organic linker. The bondage between these two is quite strong and hence extended network structures of MOFs are robust. The coordination complex between metal ions and donor atom of linker is known as secondary building unit(SBU).e.g. copper-carboxylate cluster in which two copper atoms are chelated by four carboxylates can be considered as square SBU, whereas zinc carboxylates have octahedral SBUs.[20]

Materials of this type are prepared using an approach known as reticular chemistry which involves linking of molecular building blocks into predetermined architectures that are held together by strong bonds. In MOF structures, organic linkers serve as rigid struts that bridge inorganic joint to form extended three-dimensional networks. Unlike other porous materials, MOFs are open scaffolds that have pores without walls, a feature that endows these materials with exceptionally large surface areas. In addition, since the topology of the scaffold is defined by molecular building blocks, the pore or aperture size within the framework is quite small, typically less than 20, leading to strong interactions between guest molecules and the framework. The porosity of MOFS is greater than that of any other porous material, including activated carbons, making MOFs ideal candidates for use as adsorbents. The objective of this report is to survey the vast number of MOF structures reported in the open literature to select candidate materials for use as specific proper applications. The reticular chemistry approach has been used with a wide variety of struts and joints, leading to over 4000 reported MOF structures [21].When considering the structure of Metal Organic Frameworks, it is helpful to recognize the secondary building units (SBUs), which dictate the final anatomy of a framework. While the organic linkers are also important SBUs, their structures do not change during MOF assembly. The following discussion will focus on metal-cluster-based SBUs, which evolve from the initial bonding between the metal ions and connecting ligands.

2.5 Salient Feature of MOFs

Some of the characteristic features of MOFs include:

- High surface area(c.a 800-5000 m^2/g) and pore volume (ca.0.5-2.5 ml/g)
- Highly crystalline and can be synthesized in pure form with less crystal imperfections
- Uniform pore size distribution akin to zeolites and hence good molecular sieving properties
- Low to moderate heat of adsorption and hence can act as a good gas storage medium
- Low bulk packing density i.e. lighter in weight

Although MOFs have shown remarkable features but still there are certain unresolved issues which hindered its application at the industrial level. Most importantly, the thermal and chemical stability of MOFs is a bottleneck which requires to be overcome. Out of an excess 2000 MOFs matrix synthesized and analyzed very few could withstand a temperatures in excess of 300°C. The frameworks collapse and show low robustness at moderate to high temperatures. Moreover frameworks also show less immunity under aqueous and organic mediums. Qualitatively as well as quantitatively speaking, same MOF synthesized at same conditions following same recipes at times tend to yield products with varying percentage purities. Since percentage yields and product purities of different batches vary, care must be taken during synthesis and post synthesis treatments. It is also observed that MOF undergoing adsorption mechanism in pressure swing adsorption (PSA) column undergo physical deformation after a few cycles or swings. The effect of high pressure is also a cause of concern before they can be approved to be industrially more viable. Another problem is that in most of known MOF structures the coordination sphere of the metal ion is completely blocked by the organic linkers so that they have no free positions to interact with the substrates. The two main limitations are responsible for the scarce number of catalytic applications.[1,22]

2.6 Applications of MOFs

With the advent of a large body of synthetic protocols for preparing MOFs, researchers are now exploring the host-guest behavior of MOFs in many areas of chemistry, with the vast majority of applications focusing on the porous properties of isoreticular MOFs. For example, Yaghi and others are developing IRMOFs as host materials for energy storage. It has been shown that MOFs can be used to store high densities of hydrogen under relatively moderate pressures in steel cylinders packed with those materials. The high accessible void volumes MOFs provide make them one of the more promising materials to meet hydrogen storage standards set by the DOE. Similar to zeolites, the utility of MOFs in heterogeneous catalysis has also been explored. MOFs offer the added advantage of having an organic component that can be tailored to accommodate a range of reactive groups that can actively or passively participate in catalysis.MOFs can also serve as nonreactors that provide unique phases in which to carry out organic reactions where the large cavities of MOFs server as Nano scale containers for reactants and transition states that are too satirically demanding to fit within zeolite channels.Furthermore, MOFs with chiral framework architectures can catalyze reactions enantioselectively. Molecular sorption is an additional area where the large surface areas pore dimensions and high porosities of MOFs provide unique opportunities. The ability of MOFs to act as sorbents is invaluable for environmental remediation and purification. Other applications that have been explored include molecular separation, molecular sensing and nanofabrication. Hence because of having properties like high surface area, uniform porosity, inter-connected pore/channel system, accessible pore volume, high adsorption capacity, ion-exchange ability, enhanced catalytic activity and shape/size selectivity, MOFs have wide range of applications. Some potential application of MOFs is described here.

2.6.1 Gas Detection

MOFs can serve as effective recognition chemistries for a variety of gases and might be useful in a breath analysis or humidity sensing application. Homeland security and defense application such as portal monitoring, chemical weapon detection, radiation detection, and water quality monitoring have long been priorities.[23]

2.6.2 Selective Adsorption

Recently, industrial methods for gas adsorption rely mostly on cryogenics as well as membrane-and adsorption-based techniques. The principal mechanisms based on which selective gas adsorption is achieved in MOFs are adsorbate-surface interactions and size-exclusion (molecular sieving effect). Adsorption based process involves the chemical as well as physical interaction between the adsorbent and the adsorbate while the MOFs depends on the dimension and shape of the framework pores.[23]

In petroleum industry removal of sulfur (desulfurization) from crude or any other fuel or petroleum stream is called sweetening. It is listed as the one of the oldest methods that is being followed till the date. Various mineral clays and synthetic adsorbents are the listed materials for this treatment. Asphalt and resins are adsorbed on this clay. It is mainly done for decolorizing and stabilizing cracked gasoline and also for desulfurizing virgin gasoline and kerosene. Removal of resins improves colour of the oil. Clays (adsorbents) having tendency to adsorb some sulfur compounds. Material loss is very much because of wetting the whole quantity of the clay and retention of some in pores. The material adsorbed is governed by Freundlich equation and is the useful for decolorizing operations and is given by

$$log\frac{x}{m} = log\mathrm{a}+\frac{1}{n}logc$$

Where,
x = units of impurities adsorbed
m = quantity of adsorbent
c = concentration of impurities in equilibrium at surface

In the treatment of light fractions the clay acts as catalysts for light fractions and for heavy oils it is an adsorbent purifier. Gasoline is also clay treated to eliminate materials inclined to give colours or form gums. A comprehensive study regarding removal of sulfur compounds from naphtha cuts using different adsorbents was presented.[24,25]. Most of the clay treatment is conducted in two ways, namely contact filtration and percolation technique. Various adsorbents used for this study was conducted.[26,27]. To utilize these materials as sorbents, the MOF structure must first be activated. This process involves removal of solvent molecules from the pores of the MOF to open the void space in crystal lattice. Typically majority of the solvent included can be removed from the structure through evaporation. More rigorous techniques, however, are often required to evacuate solvent or guest molecules that have stronger interactions with organic struts or inorganic clusters. Therefore, most of the MOFs have to be activated under vacuum at elevated temperatures to eliminate the strongly bound solvent molecules. In addition, these materials are quite stable to a variety of chemical environments. MOFs are soluble in water, most organic solvents and can even retain their crystalline structure after treatment in strongly basic solutions. In certain MOFs, the organic linker of framework can be modified through solution based techniques without destruction of crystal lattice. Many MOF structures, however, are digested when treated with mild acid, especially those constructed from carboxylate SBUs. This digestion process may be useful in the recovery of guest analytes that adsorb strongly to the MOF framework.[16]

2.6.3 Catalytic Application

The catalytic properties of MOFs have created much attention, for the separated metal cluster and porous structure. The active catalytic sites can be introduced during the construction of the framework, in the metal sites or organic link. However,as a catalyst, the application is limited by their chemical and thermal stability. Most of the catalytic reactions are conducted under relatively mild conditions to prevent the break down of frameworks. There are so many researchers undergoing to study catalytic application. Several MOFs have been used as solids catalyst or supports for a variety of organic transformations such as aldol condensation, oxidation, epoxidation, hydrogenation, Suzuki cross-coupling, trans esterification, friedel crafts acylation, epoxide ring-opening reaction, methylation of aromatic amines, activation of alkynes,and cyclization reactions, and alkene cyclopropanation.[14]

Ammonia borane(NH_3BH_3,AB) is a hydrogen storage material with a theoretical hydrogen capacity up to 20 wt%. AB can release hydrogen through hydrolysis, methanolysis, and thermolysis. A number of noble (Pt, Ru, Rh, Pd, Au) and non-noble (Co,Ni,Fe,Cu) transition metal catalysts have been developed to promote the hydrolytic dehydrogenation of AB. The catalysts with low cost metals, such as Cobalt, are predominant for economic reasons. The Co-MOF based catalyst demonstrates a highly efficient catalytic activity to hydrolysis of AB. The Co based catalyst is synthesized from the MOFs precursor $Co_2(bdc)_2(dabco)$[1,4-benzenedicarboxylate;1,4-diazabicyclo octane[14]

Friedel crafts alkylation reactions of aromatic compounds with acid chlorides are accepted as fundamentals and important processes in organic synthesis as well as in industrial chemistry traditionally, these reactions require excessive stoichiometric amounts of anhydrous strong Lewis acids such as $AlCl_3$,$TiCl_3$, $FeCl_3$ or etc. These methods are influenced by toxicity and corrosion of the catalysts, generation of a huge amount of waste, byproducts and difficult purification of products. Moreover, these catalysts are prone to moisture and hence moisture free reaction condition is required to achieve the balanced yields of the desired aromatic ketones. Several solid acid catalysts have been investigated for the friedel crafts acylation and alkylation reactions, such as metal triflate loaded SBA-15, mesoporous superacid catalyst, zeolite, hybrid zeolites, modified clay, silica composite materials, mesoporoussulphated zirconium based compound, and meso-porous sieve ALKIT-5. Literature gives IRMOF8 have shown high activity for liquid phase friedel craft alkylation in absence of anhydrous compared to Lewis acids and solid catalysts.[28]

Iron and copper metal organic frameworks of 1,3,5-benzenetricarboxylate [Fe(BTC) and $Cu_3(BTC)_2$] are effective and reusable solid catalysts for the oxidation of benzylic compounds with t-butylhydroperoxide as oxidant in acetonitrile with moderate to good yields.Work done by Amarajothi Dhakshinamoorthy & Co. shows the utility of inexpensive Fe and Cu MOFs as effective catalysts for the aerobic oxidation of xanthene and other benzylic compounds with t-butylhydroperoxide in acetonitrile. Studies also show the MOFs were stable under the reaction conditions as confirmed by comparison of the powder XRD of the fresh and reused catalysts.[29]

In case of alkylation reaction we have to add stoichiometric amounts of lewis acids like $FeCl_3$,$AlCl_3$ etc. and which cannot be reused after from the reaction mixture, also it require large quantity of water to neutralize the lewis acid. But metal organic framework can be recovered and reuse after regenerating from the reaction mixture. This is the big advantage of metal organic framework over lewis acid catalysts.

Also voidage of Metal Organic Frameworks can be designed in a proper manner for allowing it to be applicable for specific application. Because of its crystalline nature, they are having rarely different active sites. Zinc containing frameworks were used for the addition of alcohol or carboxylic acids to acetylene and propylene.[30]

Friedel-Crafts alkylation and acylation reactions are a special class of electrophilic aromatic substitution reaction(EAS) in which the electrophile is a carbocation or acylium ion. These reactions are highly useful in that they involve carbon-carbon bond formation and allow alkyl and acyl groups to be substituted onto aromatic rings. The Friedel-Crafts alkylation reaction is a very important for the synthesis of aklylaromatic compounds both in the laboratory and on an industrial scale. The reaction is carried out with alkylating reagents as alkenes, alkyl chlorides and alcohols by using a stoichiometric amount of Lewis and Bronsted acids. The alkylation of benzene with ethylene and propylene to produce ethyl-benzene and cummene respectively widely used in petrochemical industry.[31]

Liquid phase alkylation of aromatic compounds, using homogeneous acid catalysts, is a commonly practiced FriedelCrafts type reaction in organic synthesis. But commonly used acid homogeneous acid catalysts ($AlCl_3$, BF_3, and H_2SO_4) pose several problems, such as difficulty in separation and recovery, disposal of spent catalysts, corrosion, high toxicity, etc. development of reusable solid acid catalysts having high activity for the FriedelCrafts reaction is therefore great practical importance. Worldwide efforts have been made to achieve this goal using different catalysts, such as heteropoly acid salts, sulfated ZrO_2 or Fe_2O_3, Fe containing MCM-41, ion exchanged clays and clayzic for benzylation of benzene and HY, H-beta and H-ZSM-5 zeolites for benzylation of toluene. However, the zeolite catalysts showed a poor activity in the benzylation reactions. The alkylation of an aromatic compound containing an electron-donating group (e.g.,alkyl, alkoxy, OH, etc.) can be accomplished with ease but of that without such aromatic-ring-activating group(e.g, benzene) is difficult.[32]

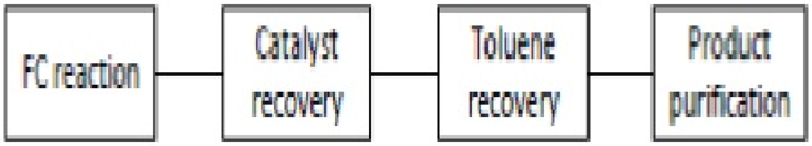

Figure 2.3: Block diagram for FriedelCrafts alkylation reaction of Toluene

FriedelCrafts alkylation reaction of toluene with benzyle chloride produces mixture of products containing o-methyl diphenyl methane and p-methyl diphenyl methane, simultaneously evolution of HCl as well. Both of these ortho and pera liquid mixture isomers are sent to distillation column for the final product recovery. And simultaneously in this reaction, toluene(solvent) and catalyst recovery is carried out.

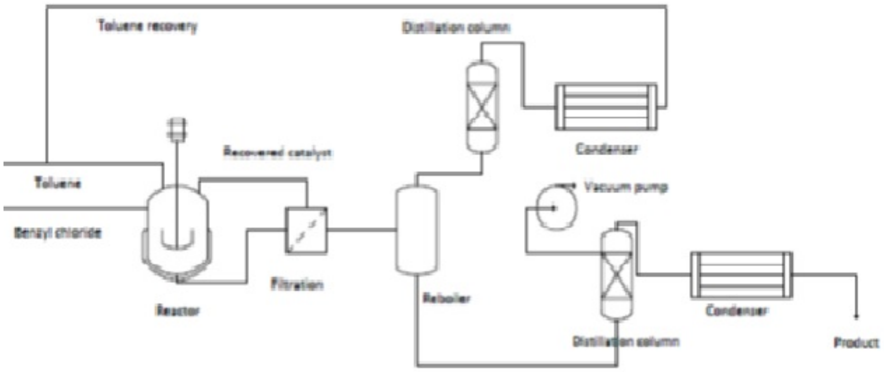

Figure 2.4: PFD for FC alkylation reaction of toluene

For the aromatic alkylation accounting the largest productions, new solid catalysts and new processes confirming the environmental and safety concerns are currently available. Various solid catalysts based on different zeolites have been developed for the production of ethyle benzene and cumene up to the commercial scale. The new technologies operate in the liquid-phase and showed to be very promising as far as the productivity and stability are concerned, so that a complete submission of $AlCl_3$, HF and H_3PO_4 with solid acid catalysts can be possible.[33]

Chapter 3

Synthesis Methodology and Experiments

3.1 Introduction

This chapter illustrates MOF synthesis methods, characterization techniques and instruments used. The solvothermal method was used for the synthesis of new compounds in this project. These new compounds can be characterized using following techniques: X-ray diffraction (XRD), thermo gravimetric analysis (TGA), Infrared spectroscopy, uv-visiblespectroscopy, and differential scanning calorimetry (DSC).

3.2 Hydrothermal/solvothermal methods

Hydrothermal reaction is the most common synthesis method to produce MOFs material. A hydrothermal reactor is used which consists of a special stainless autoclave with a Teflon internal cup. Two different precursors are prepared individually and are mixed into the reaction vessel. The mixtures need to be well mixed for at least 10 minutes. The vessel is closed and placed into a furnace for 18 to 24 hours at desired reaction temperatures [34]. After reaction time is completed, decrease the temperature to room temperature and collect MOF particles by separating the liquid solution from particle. The liquid solution contains the left over precursor and byproducts. For particles, perform a three cycle centrifugal and disperse process. Finally ultrapure MOF crystal can be achieved.The characteristics of ligand play a crucial role in resultant framework. Normally reactants are mixed in high boiling solvents like water, dialkylformamaides, dimethylesulfoxides or acetonitrile. Also important parameters are temperature, concentration of metal salt and ligand, the degree of solubility of reactants in solvent.[35,36]

3.3 Reflux Method

The sound procedure is by refluxing the reaction mixture, without H_2O_2, using heat to accelerate the precipitation. The solid formed precipitates from the solution in hours. Solvothermal reaction method can provide a higher reaction temperature to allow crystal grow gradually to achieve more uniformly. It is required to use an autoclave to maintain a pressurized condition to enhance a homogeneous reaction. The drawback of the autoclave is not easy to sample without releasing pressure which drop the solution temperature. To apply a reflux synthesis method, a condenser-three neck flask design would be an easy way to test the reaction mechanism while maintaining ambient conditions. The reflux system is consisted of a three neck flask, condenser, heating bath, stir function build-in hot plate, k-type thermal couple, and PID temperature controller. The two different precursors were poured into the three neck flask and mixed by a magnetic stir bar. A k-type thermal couple was placed into the flask to read the temperature from the mixture solution. The PID temperature controller used to receive the temperature signal and provide the thermal energy to the bottom of the flask as the flask as the feedback controller. The maximum reaction temperature would be limited by the exact boiling point of the solvent. The reaction can be run as long as needed since the reactant solvent would not escape from the system.

Figure 3.1: Synthesis experimental setup (Reflux method)

3.4 Crystallization

Crystallization is the (natural or artificial) process of formation of solid crystal precipitating from a solution. Crystallization is also a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. The crystallization process is considered to occur in two steps: nucleation and growth. Nucleation is the step where the solute molecules are loosely distributed in the solvent, start to gather into clusters, on the nano scale. The growth of crystal is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur parallely while the super saturation exists. Super saturation is the driving force of the crystallization; hence the rate of nucleation and growth is govern by the existing super saturation in the solution. Based on the conditions, either nucleation or growth may be predominant over the other, and ultimately, crystals with different sizes and shapes are obtained.

3.5 Equipments used for Experimental studies

3.5.1 Powder X-ray diffraction (PXRD)

X-ray diffraction is a non-destructive analytical technique which reveals information about the crystal structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. Each crystalline solid has its unique characteristics X-ray powder pattern which may be used as a fingerprint for its identification. Once the material has been identified, X-ray crystallography may be used to determine its structure. X-ray powder diffraction is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit celldimensions. The analyzed material is finely ground, homogenized and average bulk composition is determined. It is an important technique to obtain structural information on an atomic scale from both crystalline and amorphous materials. It is widely used to derive information such as crystallite size, lattice strain, surface and interface roughness, crystal orientation etc.Bruker AXSD8 advance was used for phase and structural analysis, purity and stability of powder samples. The sample was swept from 1.5° to 60°. The X-ray generator was set to 20 kV and 20 mA. After the samples were analyzed the purity and the stability can be determined by comparing sample pattern with simulated pattern. The system includes:

- Vertical Theta-theta Goniometer with -1100 $< \theta <$ 1680 goniometer control with stepper motors and optical encoders providing smallest selectable step size 0.0001°
- New short ceramic Cu X-Ray tube with fine long focus
- Two exchangeable detectors of scattered X-rays: NaI scintillator type detector with low background (0.4 cps) and high dynamic range and Braun position-sensitive detector.

Figure 3.2: Bruker D 8 advanced [37]

3.5.2 Thermogravimetric Analysis(TGA)

Thermo gravimetric analysis (TGA) is a technique performed on samples to determine changes in weight in relation to change in temperature or time under a controlled atmosphere. It provides a quantitative measurement of the mass changes in a material associated with both material and thermal degradation and thus can be used in determination of the thermal stability and decomposition products of a material. Its principal uses include measurement of a materials thermal stability and composition. TGA instruments are routinely used in quality control and production operations.

Figure 3.3: TGA instrument [38]

3.5.3 Differential scanning Calorimetry(DSC):

Differential scanning calorimetry (DSC) is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature and time. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperature to be scanned. DSC is especially useful for thermal characterization of polymers, such as glass transition temperature, crystalline temperature, and melting point, heat capacity, thermal stability and transformation temperatures.

Figure 3.4: DSC instrument [39]

3.5.4 BET Surface Area:(BET)

BET surface area is ananalytical technique performed on sample to determine surface area, pore size and pore volume. It is based on BET theory. BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. This analysis aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.

Figure 3.5: BET instrument[40]

3.5.5 Vacuum Oven:

Vacuum oven was used for heating synthesized MOFs before sent to characterizations. Operating feature of vacuum oven

- 5°C above room temperature to 250°C
- Vacuum range: 0 to 0.1MPa, analog gauge
- Microprocess PID control/ Auto-tuning/ Calibration
- Digital timer: 1 min to 99hr 59min, display ON/OFF
- Digital LED display (1°C resolution) with touch sensitive keypads

Figure 3.6: Vacuum Oven[41]

3.5.6 Gas Chromatogram Analyzer:(GC)

Gas chromatographic(GC) analyses of liquid mixture performed using Thermo Scientific Trace GC Ultra equipped with a flame ionization detector(FID) and HP-1 capillary column(length=30m, inner diameter=0.25 mm, and film thickness=0.25m)

Figure 3.7: Shimadzu 2010 GC instrument[42]

3.5.7 PAAR Reactor:

High pressure 4605 series vessels are available in volumes of 1000 and 1200 ml. Using the teflon Gasket, these vessels can obtain temperature up to 350°C with maximum pressure of 5000 psi (350 bar). They come standard with a Split Ring closure with 8 cap screws, and the choice of two different head styles: a 1/8 NPT w/plug, or a VGR(Valve, Gage, and Rupture Disc) with Thermo well. A maximum of 5 to 7 openings are allowed on the heads of these vessels. These vessels are as either a movable or fixed head design.

Figure 3.8: PAAR Reactor[43]

3.5.8 Radleys carousel Reactor:

The patented Carousel 6 simultaneously heats, stirs and refluxes multiple samples under an inert atmosphere. Radleys carousel reactor is used for kinetic study of alkylation reaction using Fe-MOF Features of carousel reactor are

- Powerful, even stirring-fits on to a Carousel stirring hotplate.
- Rapid heating to 180°C.
- Quick to setup and easy to use
- Water cooled reflux head.
- Perform reactions under an inert atmosphere.
- Easy viewing of flask contents during experiments.
- 250ml Azeotropic(Dean & Stark) flask option.

Figure 3.9: RadleysReactor[44]

3.6 Materials for experiment synthesis

The different chemicals used in experiments are as follows with list

Table 3.1: Chemicals used for synthesis study

Sr No.	Name of Chemical	Formula	Company	Grade
1	Chromium Nitrate	$CrNO_3$	Sigma Aldrich	98%
2	Titanium Isopropoxide	$Ti(OC_3H_7)_4$	Johnson Matthey	98%
3	PTA(BDC)	$C_6H_4(COOH)_2$	Reliance Ind	98%
4	DMF	C_3H_7NO	S.D Fine Chem	99%
5	Methanol	CH_3OH	Labort Fine Chem	99.5%
6	Trimisic Acid(BTC)	$C_9H_6O_6$	Sigma Aldrich	99.4%
7	Cupric Nitrate	$Cu(NO_3)_2$	S.D Fine Chem	98%
8	Aluminium Nitrate	$Al(NO_3)_2$	Sigma Aldrich	98%
9	Zinc Nitrate	$Zn(NO_3)_26H_2O$	S.D Fine Chem	99%
10	Ferric Nitrate	$Fe(NO_3)_3$	Sigma Aldrich	99%
11	Acetone	CH_3COCH_3	Sigma Aldrich	99%

3.7 Synthesis Of MOFs

Various methods have been followed in the synthesis of MOFs. Here in this study mainly used solvothermal method of synthesis. The common steps in synthesis of MOF is given below

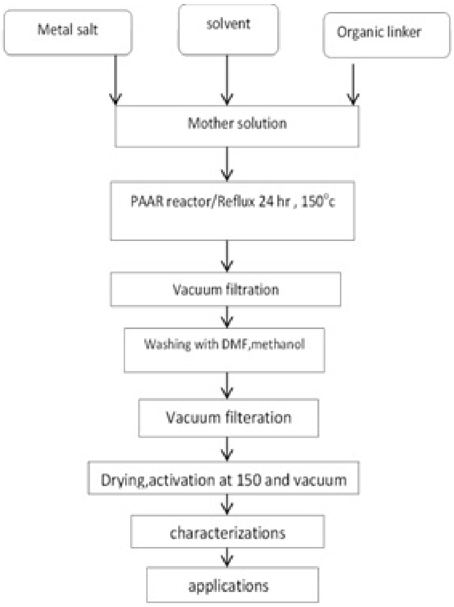

Figure 3.10: Synthesis flow chart

3.7.1 Synthesis of Cr-MOF

Cr MOF was prepared by adding 10 gm of $CrNO_3$ metal precursor, 12 gm PTA(organic ligand),(1:1 molar ratio) and 150 ml N-N DMF as a solvent, in a round bottom flask and temp set to around 180°C, it was kept for 24hrs. The resulting mixture was then filtered and washing was then done with acetone,180 ml DMF, and 200 ml methanol respectively. After that solid particles obtained were dried under vacuum at 70°C for 3 hrs. and final material was obtained.

Figure 3.11: Cr-MOF

3.7.2 Synthesis of Cu-MOF

Cu-BTC samples were obtained as powders using a procedure described in a literature[45].2.1 gm(11.42 mmol) of BTC or 1.66 gm of BDC were used as metal salts/precursor solution. Along with that 2.4 gm(11.42mmol) copper nitrate hydrate were dissolved in 100 ml DMF. The two solutions were then mixed at ambient temperature and aged for 30 min, after which the resulting mixture was heated at 150°C under solvothermal conditions for 24hr. using reflux method. The reaction vessel was allowed to reach ambient temperature and the resulting crystals were isolated by filtration and washed with acetone, DMF and Ethanol. The final product was then dried at 70°c vacuum for 4hr.

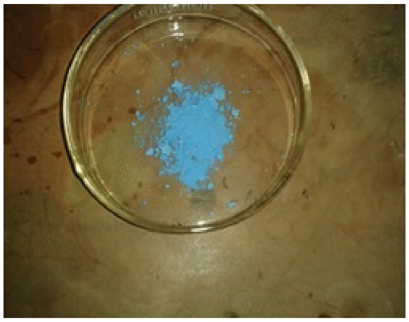

Figure 3.12: Cu-MOF

3.7.3 Synthesis of Ti-MOFs

$TiO_8(OH)_4[O_2C\text{-}C_6H_4\text{-}CO_2]_6$ was obtained from 10 gm of BDC, 12 ml of titanium isopropoxide $Ti(OiPr)_4$ (molar ratio 1:1.5) introduced in a solution of 180 ml dimethylformamide and 20 ml of dry methanol. The mixture was gently stirred during 5 minutes at room temperature and then put into a round bottom flask to heat 150°c during 15hrs. back to room temperature, the solid was recovered by vacuum filtration, washed twice with acetone after keeping in 150 ml of DMF and methanol respectively and dried under air at room temperature. The free solvent was removed by calcination.

3.7.4 Synthesis of Zn-MOFs

Zn-MOF was synthesized according to published procedure. It was obtained from 1.15 molar ratio of BTC/BDC to Zinc nitrate solution formed in 150 ml, 2 molar of dimethylformamide. The mixture was gently stirred during 5 minutes at room temperature and then undergone for reflux method of synthesis at the bubbling temperature of DMF (150°C) for a period of 15 hrs. Taken back to room temperature, the solid was recovered by vacuum filteration, washed twice with acetone after keeping in 150 ml of DMF and methanol respectively and dried under air at room temperature. The free solvent was removed by heating at 70°c in vacuum for a period of 12hrs.

3.7.5 Synthesis of Fe-MOFs

Fe-MOF or $Fe(OH)[O_2C\text{-}C_6H_4\text{-}CO_2]$ was synthesized according to the published literature procedure. $FeCl_35H_2O$(32gm) and benzene-1,4-dicarboxylic acid(20g)(1 mmol of each in 5 ml of DMF) were introduced in a solution of dimethylformamide and synthesized by reflux method of synthesis at a temperature 150°C for 24 hrs. The resulting solid was washed with DMF, acetone and dried in air. Product formed was kept in methanol at room temperature for DMF exchange.

Figure 3.13: Fe-MOF

Table 3.2: Synthesis summary

MOF	Metal Salt	Organic Ligand	Solvent	Method of Synthesis	Time and Temperature
Ti-MOF	$C_{12}H_{28}O_4Ti$	PTA	DMF, CH_3OH	Reflux	180°C& 24hrs
Fe-MOF	$FeCl_35H_2O$	PTA	H_2O	Solvothermal reflux	150°C& 24hrs
Al-MOF	$Al(NO_3)_36H_2O$	TMA	DMF	Reflux	150°C& 24hrs
Zn-MOF	$Zn(NO_3)_26H_2O$	PTA	DMF	Reflux	150°C& 24hrs
Zn-MOF	$Zn(NO_3)6H_2O$	TMA	DMF	Reflux	150°C& 24hrs
Cr-MOF	$CrNO_3$	PTA	DMF	Reflux	150°C& 24hrs
Co-MOF	$Co(NO_3)_26H_2O$	PTA	DMF	Reflux	150°C& 24hrs
Cu-MOF	$Cu(NO_3)_3$	PTA/TMA	DMF	Reflux	150°C& 24hrs

3.8 Catalytic study

Aim
To identify the catalytic applicability of synthesized and characterized RMOF's reactions like alkylation, acylation and oxidations.

3.8.1 Alkylation

Since literature shows Fe, Zn and Al based catalysts are widely used for alkylation reactions, Iron based, Zinc based and Aluminum based MOFs were used for alkylation studies.[31,33]

Figure 3.14: Reaction setup

Primary alkylation reaction using different MOFs were carried out and detailed studies have done, for which conversion was good. Fe-MOFs giving good conversion, whereas Zinc and Aluminium based MOFs no product identified. Anhydrous A.R grade chemicals used without subsequent purification for the liquid phase alkylation reaction obtained from Aldrich chemicals. The reaction was carried out with constant Fe-MOF concentration and molar ratio (1:1.5 of benzylechloride:toluene) at a toluene reflux temperature.(i.e 110°C) for 6 hrs by a reflux condenser system. The catalysts was activated at 70°C in vacuum for 4 hr and cooled to room temperature prior to its use in the reaction. Toluene was taken in excess quantity, as reactant and solvent. The reaction mixture was magnetically agitated and heated to the required temperature under atmospheric pressure using oil bath. Samples were withdrawn after 6 hrs and analyzed periodically on a gas chromatograph (HP-1) equipped with a FID detector and a capillary column. n-Decane was used as internal standard as an inert for calculating conversion. Kinetic studies were carried out.

3.8.2 Kinetic Study

As among all reported MOFs, alkylation reaction between benzyle chloride and toluene gives good result for Fe-MOFs, kinetic study of reaction between benzyl chloride and toluene were carried out at toluene reflux temperature with 1:1.5 weightratio (1:2 molar ratio) of benzyl chloride to toluene and constant catalyst concentration. Kinetics studies were conducted using Radleys reactor, so as to maintain same temperature throughout the reaction. in a typical reaction a mixture of toluene and benzyl chloride with respect to their molar ratio and n-Decane(1 ml) as an internal standard was added into a 250ml Radleys flask containing Fe-MOF. The resulting mixture was stirred at desired temperature(toluene refuxing temperature) for 4 hrs. Reaction conversion was monitored by withdrawing aliquots from the reaction mixture at different time intervals, and analyzed by GC with reference to n-Decane.

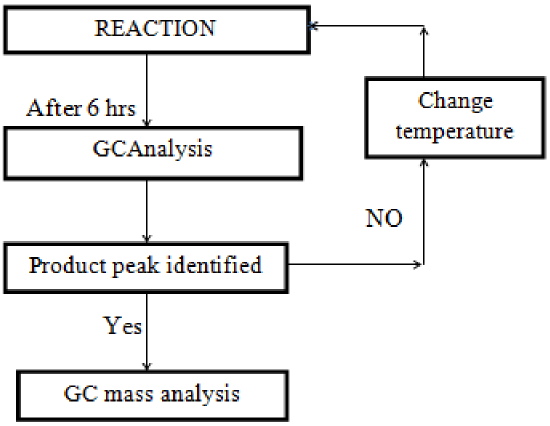

Figure 3.15: Flowchart for reaction study

3.9 Adsorption Study

The exceptional porous property of MOFs makes these materials promising host materials. As already discussed in first and second chapter of introduction and literature review, the loading of guest molecule into MOFs is an important area of research. Gas storage and separation in MOFs is well known science. Adsorption of liquid organic compounds currently is a rarely explored field, in this exploratory kind of project work separations of liquid adsorbates containing sulfur, (DMDS)-dimethyl disulfide using MOF as adsorbents was studied as this is one objective of present research work. Liquid phase batch experiments were based on literature procedure. Initially adsorption was carried out. For that 0.5gms of DMDS was taken in 100 ml n-Hexane and homogeneous solution was prepared. Eight well cleaned, dried reaction vials (25 ml) were taken and labeled. About 0.1 gm of the activated adsorbents was carefully weighed and transferred carefully into each vials. By means of pipette 5ml of previously made solution was added. Vials were sealed by para film and kept in beaker after thoroughly shaking by means of mechanical shaker. The supernatant liquid of each of the bottles were filtered through small cotton and the filtrate was collected in properly labeled vial for GC analysis. From gas chromatographic analysis equilibrium and initial concentration of compound was determined. The differences between these pairs of concentration values were used directly for the calculation of adsorbed amounts, expressed as weight percentages.

Chapter 4

Result and Discussion

4.1 Yield Calculation

4.1.1 Fe-MOF $Fe^{III}OH)[O_2C\text{-}C_6H_4\text{-}CO_2]$

Reactants used
Ferric chloride($FeCl_35H_2O$) = 32 gm
Molecular weight of ferric chloride = 252 gm/mol
1 Mole of ferric chloride = 252 g of ferric chloride
Then 32 gm of ferric chloride = (1/252)*32
Moles of ferric chloride used = 0.127 mole
Molecular weight of terephthalic acid =166gm
Terephthalic acid($C_8H_6O_4$) = 20 gm
1 Mole of terephthalic acid = 166 gm of terephthalic acid
Then 20 g of terephthalic acid = (1/166)*20
Moles of terephthalic acid used = 0.120 mole
Molecular weight of Fe-MOF = 239
Fe-MOF formed =17 g
239 g of Fe-mof = 1mol
17 g of Fe- mof=(1/239)*17=0.071 mole
Assuming 0.120 moles of terephthalic acid used, as limiting reactant
Yield = (moles of product formed/moles of reactant consumed)*100
=(0.071/0.120)*100=59.16%

4.1.2 Al-MOF Al(OH)[O_2C-C_6H_4-CO_2]

Reactants used
Aluminium nitrate($AlNO_36H_2O$) = 45g
PTA($C_6H_6O_4$) = 30g
Molecular weight of Aluminium nitrate = 197
1 mole of Aluminium nitrate = 197 g of ferric chloride
Then 32 g of ferric chloride = (1/197)*45
Moles of ferric chloride used = 0.23 mole
Molecular weight of terephthalic acid =166
Molecular weight of terephthalic acid =166
1 mole of terephthalic acid =166 g of terephthalic acid
Then 20 g of terephthalic acid = (1/166)*20
Moles of terephthalic acid used =0.18 mole
Molecular weight of MOF = 211 g
MOF formed = 21 g
1 g of Al-MOF =(1/210) mole
21 g of MOF =(1/210)*21=0.1 mole
Assuming 0.120 moles of terephthalic acid used as limiting reactant
Yield=(moles of product formed/moles of reactant consumed)*100
=(0.1/0.18)*100=55.55%

As per above calculation remaining MOFs yield is calculated and tabulated as shown below

Table 4.1: MOFs Yield Calculations

RMOF	Molecular Formula	Yield
Ti-MOF	$Ti_8O_8(OH)_4[O_2C\text{-}C_6H_4\text{-}CO_2]_6$	17.13
Fe-MOF	$Fe^3(OH)(O_2C\text{-}C_6H_4\text{-}CO_2]$	59.16
Al-MOF	$Al(OH)[O_2C\text{-}C_6H_4\text{-}CO_2]$	55.15
Zn-MOF	$Zn_4O[O_2C\text{-}C_6H_4\text{-}CO_2]_3$	68.5
Cu-MOF	$Cu_3[C_6H_3(COO)_3]_2$	43.57

4.2 Characterization of MOFs

Ti-MOF was synthesized using titanium isopropoxide and terephthalic acid by a solvothermal method in N-N Dimethle formamide, according to a published literature. Ti-MOF is constructed by 2,6-benzenedi-carboxylate (BDC) linkers joining titanium isoprpoxide crystal groups to produce an extended 3-Dl cubic porous network, which has the formula unit $Ti_8O_8(OH)_4$ $[O_2C\text{-}C_6H_4\text{-}CO_2]_6$. In the synthesis method of porous MOF based materials using DMF solvents, the solvent exchange should be carried out as this step will facilitate the extraction of the material frameworks. It was therefore finalised to immerse the Ti-MOF sample in excess methanol at ambient temperature without agitating for 2 days. During this solvent exchange step, weakly interacting Methanol molecules, that would be facilely removed under vacuum at high temperature in the upcoming activation step had taken place of DMF molecules. This activation step was also important to obtain a fully porous structure. It was founded that Ti-MOF was achieved as yellow cubic shaped crystals. As a primary characterization PXRD has done which result is shown below.

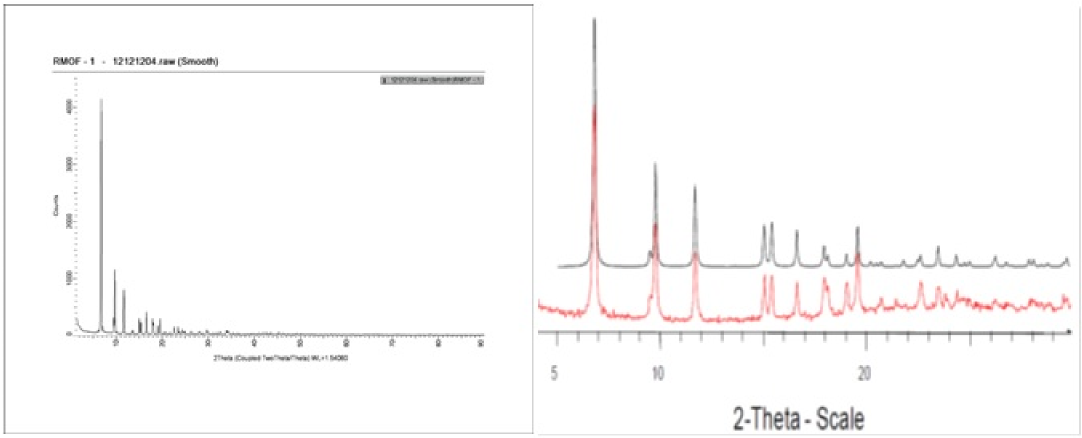

Figure 4.1: PXRD for Ti-MOFs

As a primary characterization PXRD has done. Result is shown above. Comparative studies of experimental, reported and simulated were done and the result shows similarity between the PXRDS of product synthesized and reported in literature. TGA analysis is shown in figure 4.2. It shows that there was a drastic change in weight(7.802%,0.3742 mg) before the temperature crosses 50°C. Acetone used for washing was removed in this temperature. In between 50°C-200°C solvent used for synthesis DMF, methanol, water were removed (5.855%,0.2808 mg). It was observed that above 300°C degradation of Ti-MOF was taken place. So it can be stated that it is thermally stable up to 300°C. DSC analysis is shown in figure 4.2. as the figure describes there was a sudden variation in heat flow at temperature 88.22°C. so above this temperature it does not give expected activity in reactions.

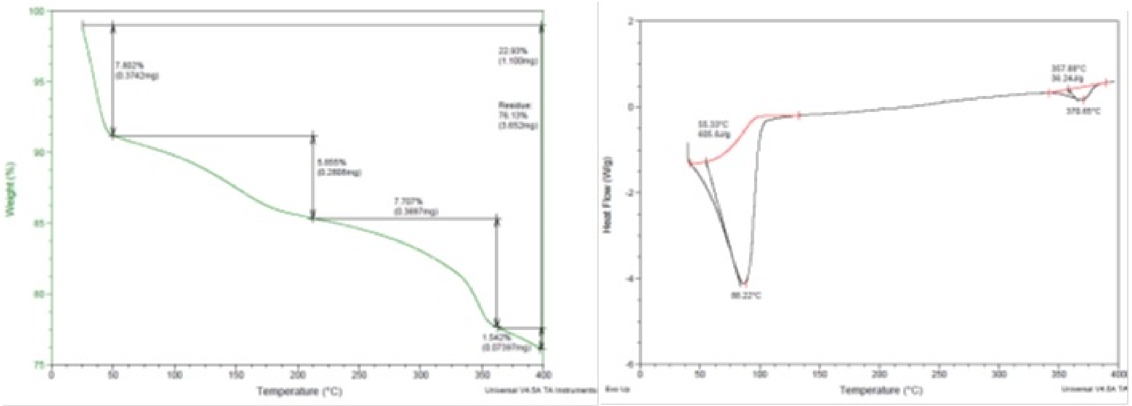

Figure 4.2: TGA and DSC of Ti-MOF

4.2.1 Fe-MOF

Fe-MOF was synthesized according to the published procedure.[46] considering required scale up. Ferric chloride($FeCl_35H_2O$) 32 gm, terephthalic acid 20 gm, DMF 600 ml was taken in round bottom flask(1000 ml) and thoroughly mixed. Reaction mixture was heated using reflux method (heating mantle of 100 ml) at 100°C for 24 hours. The resulting solid formed brownish orange was washed and filtered with DMF. Filtered product was kept in methanol(85 ml) for magnetic stirring, then washed and dried in air final product obtained is 17 gms.

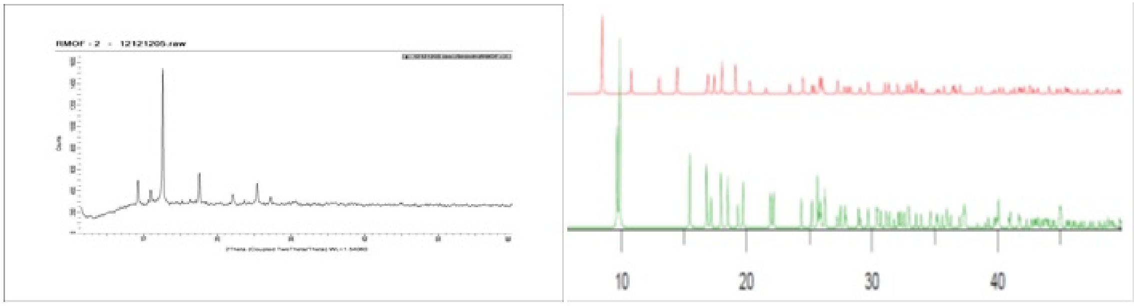

Figure 4.3: PXRD of Fe-MOFF

TGA analysis is shown in Figure 4.4. it shows that there was weight loss of 2.329%,(0.1072 mg) around 150°c and it can be the moisture present in Fe-MOF. At a temperature 280°c there is weight loss of 1.407%(0.06478 mg) and was the solvent DMF used for synthesis. It was observed that above 280°c degradation of Fe-MOF was taken place. So it can be stable till 280°c. DSC analysis of Fe-MOF is presented in the same figure. As the figure describes there was sudden variation in heat flow at temperature 365.81°c. it may be due to structure change or phase change. It can be concluded that Fe-MOF is thermally and structurally stable below 280°c.

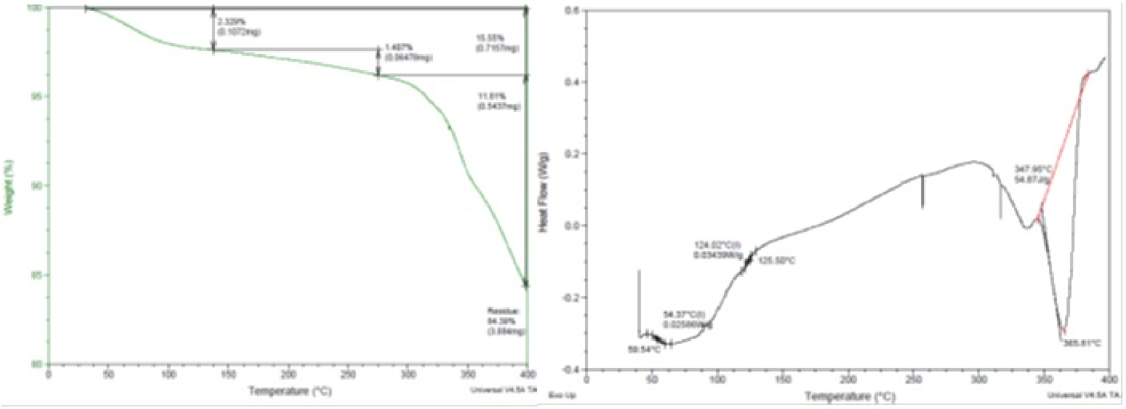

Figure 4.4: TGA and DSC of Fe-MOF

4.2.2 Al-MOF

The purity of the product was determined by powder X-ray diffraction (PXRD) measurements. The powder X-ray diffraction for Al-MOF is shown in figure 4.5.

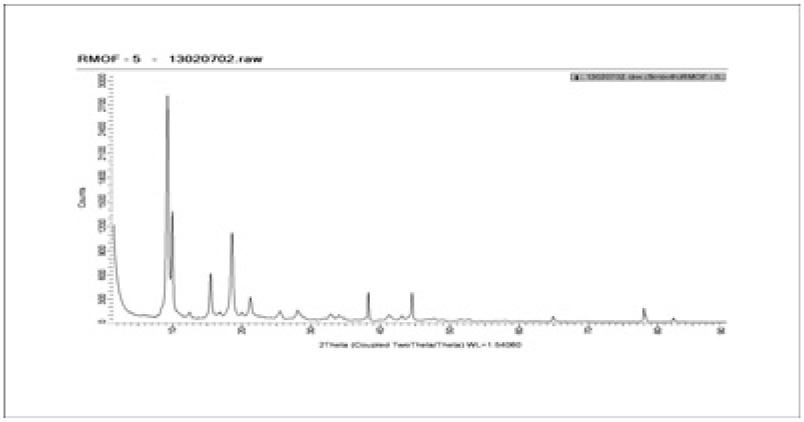

Figure 4.5: PXRD OF Al-MOF

TGA analysis is shown in figure 4.6, it shows that there was weight loss of 0.6948%,(0.04581 mg) around 80°c and it can be the moisture present in that. At a temperature 225°C there is weight loss of 4.673DSC analysis was done and it is shown in the same figure. As the figure describes, there was a sudden variation in heat flow at a temperature 236.22°C. it may be due to the structure change or phase change. It was observed that Al-MOF is thermally and structurally stable below 236.22°C.

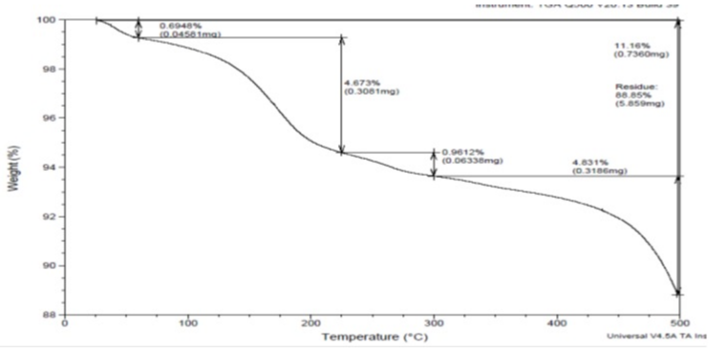

Figure 4.6: TGA of AL-MOF

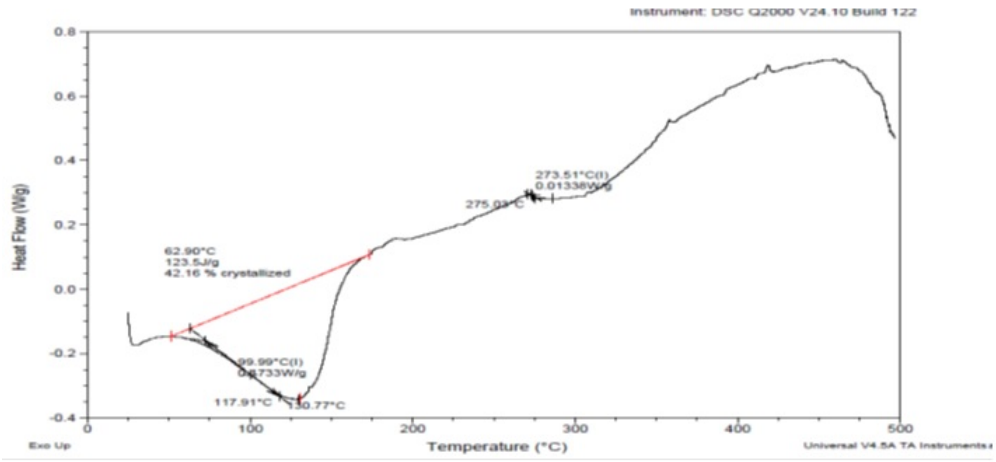

Figure 4.7: DSC of Al-MOF

4.2.3 Zn-MOF

The purity of the products was determined by powder X-ray diffraction(PXRD) measurements. The powder X-ray diffraction for Zn-MOF is shown in figure 4.7, the agreements between simulated and experimental proved that product is pure and does not contain any impurities.

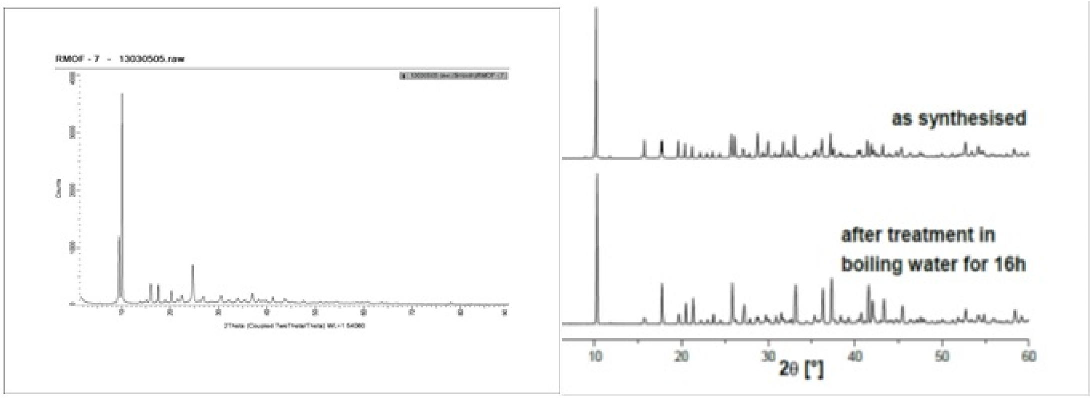

Figure 4.8: PXRD of Zn-MOF

TGA analysis is shown in figure 4.8, as the figure shows there was a weight loss of 63.65%(4.994 mg) for at temperature 350°c, there is a weight loss of 14.70%(1.154 mg) and it could be either the solvent or unreacted initial component used for synthesis. It was observed that above 400°c degradations of Zn-MOF was taken place from the TGA analysis it was observed that can be thermally stable till 400°C.

DSC analysis of Zn-MOF was done and it is shown in the same figure. As the figure describes that there was sudden variation in heat flow and temperature 137.18°C, it may be due to structure change or phase change. So it can be concluded that it is thermally and structurally stable below 137.18°C

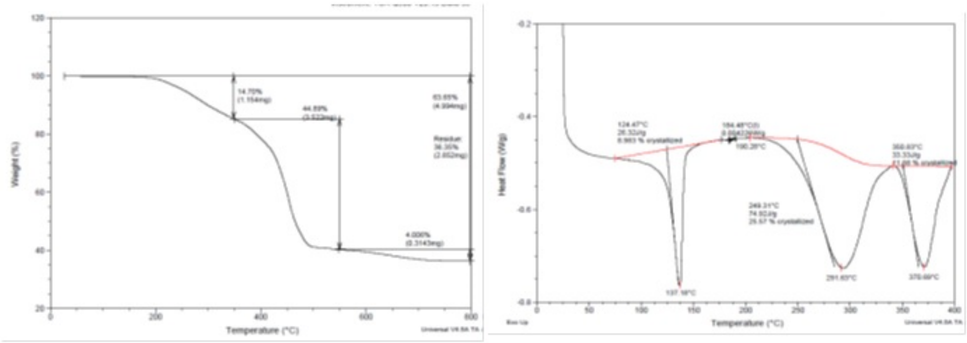

Figure 4.9: TGA and DSC analysis of Zn-MOF

4.2.4 Cu-MOF

The purity of the product was determined by powder X-ray diffraction (PXRD) measurements. It is shown in figure 4.9. the agreements between simulated and experimental patterns proved that Cu-MOF is pure and does not contain any impurities

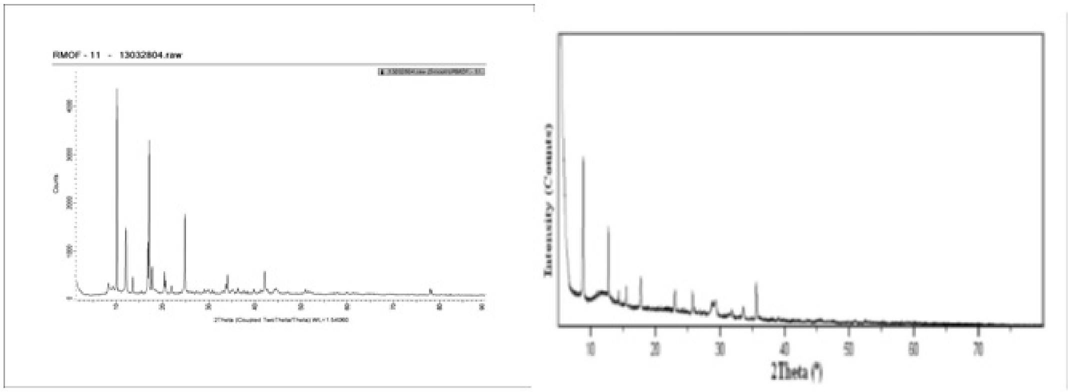

Figure 4.10: PXRD OF Cu-MOF

TGA analysis is shown in figure 4.10. as the figure shows there was a weight loss of 23.18%(1.412 mg) and 44.90%(2.735 mg) around 200°C and 400°C respectively. The earlier one could be the weight loss due to any of reactant or solvent used in synthesis and later could be the loss due to degradation of material. TGA analysis shows that Cu-MOF cannot sustain temperature above 400°C. DSC analysis was sone and it is shown in the same figure. It shows there was sudden variation in heat flow at temperature 128.37°C, may be due to structuralor phase change. So it can be concluded that Cu-MOF is thermally and structurally stable below 128.37°C.

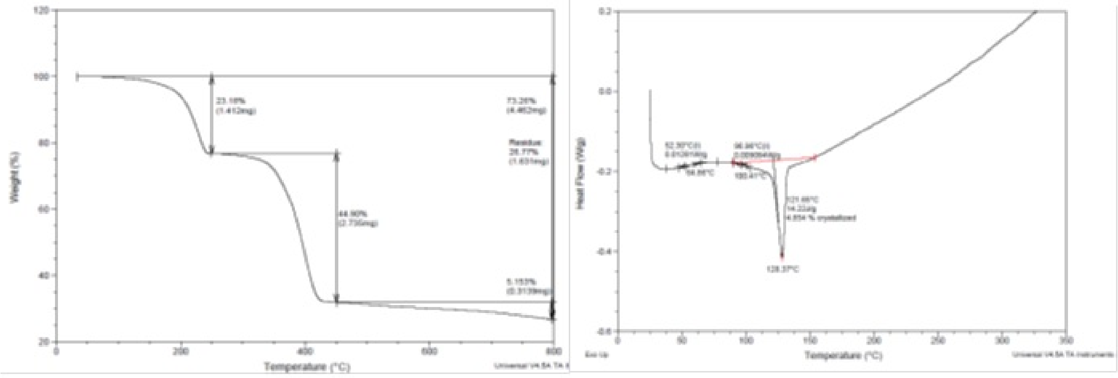

Figure 4.11: TGA and DSC of Cu-MOF

4.3 BET Results

Surface area (SSAs) was determined by nitrogen adsorption at liquid nitrogen temperature (77.55K) on a Micromeritics ASAP 2020 instrument. Before each adsorption, the MOF powder was degassed for 3-4 hr at 300C under vacuum of typically 10^{-3} Pa in order to remove adsorbed species.

Table 4.2: BET Surface Area of MOFs

MOF	Surface area(m^2/g)	Pore volume(cm^3/gm)
Ti-MOF	672.9442	0.272245
Fe-MOF	26.8451	0.036279
Al-MOF	484.1181	0.447381
Zn-MOF	5.026	0.01373
Cu-MOF	1.526	0.03730

Normally MOFs are widely known for its high surface area, but in this particular synthesis study surface area obtained was less compared to reported value. Literature says thatsynthesizing of MOFs with high surface area is very difficult with refluxing method as compared to hydrothermal method. Since synthesis study was carried out withsolvothermal reflux method and chances of solvent (DMF), moisture and reactant getting trapped inside the pores of MOFs could be the reason for not achieving reported surface area values.

4.4 Alkylation by Fe-MOF

An alkylation reaction was considered for studying catalytic feasibility of Fe-MOF. it was investigated for its activity as a solid acid catalyst in the FriedelCrafts alkylation of toluene with benzyl chloride to form p-benzyl toluene and o-benzyl toluene as two product mixtures. The initial reaction was carried out using 0.1 gm Fe-MOF at toluene reflux temperature (105-110°C) for six hours. Typically actual weight ratio was taken as 1:1.5

for benzyl chloride to toluene, with initially 0.5 ml(0.55 gm) benzyl chloride taken. So accordingtheoretical proportion of toluene and benzyl chloride were 0.8249gm(8.966 millimole) and 0.55 gm(4.3 millimole) respectively. Samples were collected and GC analysis was done for the resultant product mixture.Detail study for the product species peak identification was done by NMR.There is possibility of formation of HCl as a side product and since it is corrosive in nature, kinetic studies were limited to four hour to avoid errors in results and hence effect of HCl on reaction, reactants and catalyst were not considered.

Table 4.3: Before Reaction

Compounds	Volumes(ml)	Weight(gm)	Millimoles
Toluene	1	0.8730	8.966
Bezylechloride	0.5	0.5500	4.365
n-Decane	1	0.73	5.1

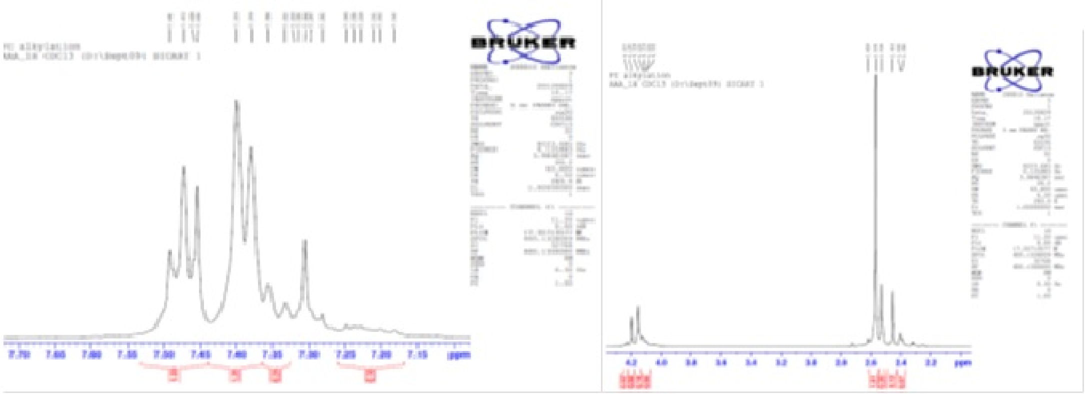

Figure 4.12: NMR analysis of final product mixture

Sample Calculation: from GC analysis, sample calculation from gc analysis,

$$\frac{\text{Weight of limiting reactant}}{\text{weight of standard}} = \frac{\text{area of limiting reactant}}{\text{area of standard}}$$

$$[\text{weight of limiting reactant}] = \frac{\text{area of limiting reactant}}{\text{area of standard}} * [\text{Weight of standard}]$$

$$[\text{moles of limiting reactant}] = \frac{\text{weight of limiting reactant}}{\text{molecular weight of reactant}}$$

$$\%\ \text{Conversion} = \frac{\text{total moles of limiting reactant converted to form product}}{\text{moles initially charged}} * 100$$

So from the reaction above,

$$\%\ \text{conversion} = \frac{0.79-0.25}{0.79} * 100 = 61\%$$

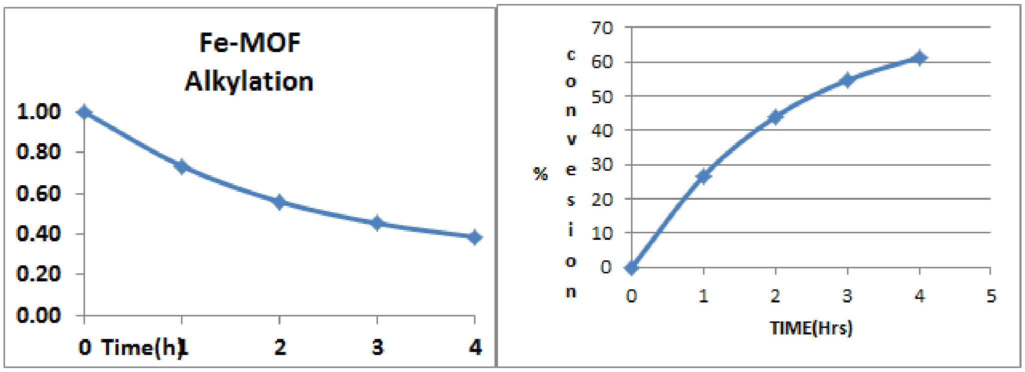

Figure 4.13: fraction of concentration vs time and % conversion vs time

Table 4.4: Adsorption Data

	DMDS area%	n-Hexane area%	DMDS:n-Hexane	Fraction removal of DMDS	% removal of DMDS	Capacity Of Adsoption
Reference	1.797	95.181	0.018			
Zn-MOF	1.338	97.916	0.013	0.004	27.62	6.90
Fe-MOF	1.828	97.216	0.018	0.233	0.40	0.1
Cr-MOF	1.413	97.609	0.014	0.233	23.32	5.83
Al-MOF	1.533	97.906	0.015	0.170	17.06	4.26

Sample Calculation:
$\frac{\text{DMDS concentration}}{\text{n-Hexane concentration}} = \frac{\text{area of DMDS}}{\text{area of n-Hexane}}$

So for Zn-MOF,

DMDS:n-Hexane=(1.338/97.916)=0.013664774

% removal of dmds= $\frac{\text{DMDS:n-Hexane of refernce-DMDS:n-Hexane of adsorbed sample}}{\text{DMDS:n-Hexane of reference}} * 100$

% removal of DMDS= (0.018879818-0.013664774)*100/(0.018879818)=27.6223268%

Now initially there was a solution of 100ml n-Hexane and 0.5 gms DMDS. so in 5ml solution vial, the quantity of dmds can be 0.025gms.

So in Zn-MOF 27.62% of 0.025 gms will be adsorbed, and that is 0.006906gms will be adsorbed
Adsorption capacity = $\frac{\text{gms DMDS adsorbed in each vial}}{\text{wt of MOFs in each vial}} * 100 = (0.006906) * \frac{100}{0.1} =$ 6.90%

Chapter 5

Conclusion

From the discussion in the previous chapters it can be stated that MOFs- a new class of hybrid material, which is combination of metal (inorganic) and ligands (organic) having wide range of applicability various process and chemical industries. Because it is having some salient features like high surface area, good porosity, highly crystalline in nature, uniform pore size distribution akin to zeolites(molecular sieving properties), low to moderate heat of adsorption, low bulk packing density etc. it is different in nature than other porous organic and inorganic materials. its method of synthesis like solvothermal, crystallization is quite simple in manner which can lead to tailor made size and shapes of pores. And hence, it can be used in wide range of applications like gas storage, adsorptive separation, catalysis etc.

Since the last one year of the project, various types of MOFs have been made by using involving metals like Fe, Al, Ti, Zn, Cu, Cr, Co etc with organic ligands mainly PTA(pera terephthalic acid), also known as BDC(benzene dicarboxylate) and TMA(trimisic acid), also known as(benzene tricarboxylate). They were characterized using a variety of techniques like PXRD, TGA, DSC and BET surface area. characterization analysis shows that synthesized MOFs have good crystallinity and thermal, structural stability up to a moderate temperature range which can be optimum for applications. BET surface area of synthesized MOFs is not up to reported values, since the synthesis were carried out by solvothermal reflux method, which is difficult for achieving high surface area.

Catalytic application study of each MOFs synthesized were carried out to identify the catalytic activity. Since the project was an exploratory in nature objective was to identify the catalytic application rather than detailed study.

Among all the MOFs synthesized, Fe-MOFs show catalytic applicability. As GC analysis shows deviation from what actual quantities of reactant initially taken than theoretical, conversion of the reaction can be found out. also in this reaction, it was found to be up to the mark. Since themulti-product mixture contain two isomers ortho and peragropus and other components as well, the stoichiometric factor (response factor) of the desired product to standard is not known. And hence yield cannot be found out.

From literature survey, it was known that gas storage and selective gas separation on MOFs are well studied at lab scale.So in this exploratory kind of project work liquid(DMDS) adsorptive separations on synthesized MOFs were explored.also in adsorption study of DMDS material, Zn, Al and Cr based MOFs showed their adsorption capacity 6.9, 5.8,and 4.2% respectively. other MOFs are not suitable for adsorption process of this sulfur containing compound.

It is contradiction that Fe-MOF is catalytically active for friedelcrafts alkylation reaction whereas on the other side the same is not suitable for the adsorption application.

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Appendix A

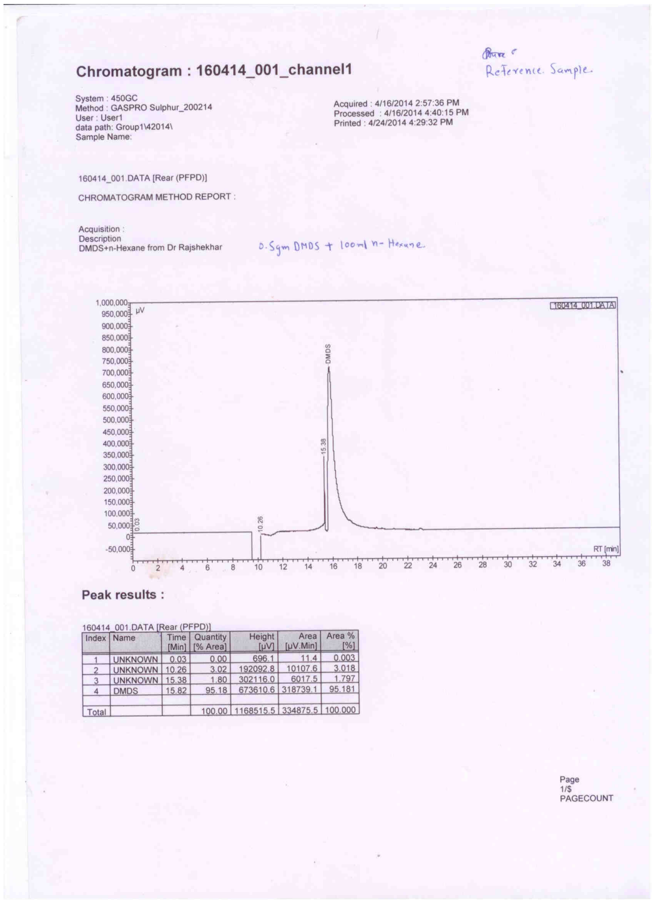
Chemicals used

Sr No	Chemical	Molecular Formula	Molar Mass	Density (kg/m^3)	Boiling Point(^0C)	Melting Point(^0C)
1	Methanol	CH_3OH	32	791.80	64.7	-97.6
2	Dimethyle Formamide	C_3H_7NO	73.09	944.00	152	-60.5
3	Terepthalic Acid(BDC)	$C_8H_6O_4$	166.13	1520.00	-	300
4	Trimisic Acid(BTC)	$C_9H_6O_6$	210	-	-	300
5	Titanium Isopropoxide	$C_{12}H_{28}O_4Ti$	284	937.00	232	
6	Ferric Chloride	$FeCl_35H_2O$	252.2	2900.00	315	306
7	Sodium Hydroxide	NaOH	40	2130.00	138.8	318
8	Copper Sulfate	$CuSO_45H_2O$	249.62	3600.00	-	110
9	Aluminium Nitrate	$Al(NO_3)_3$	213	1720.00	135	72.8
10	Zinc Nitrate	$Zn(NO_3)_26H_2O$	297.36	2060.00	-	110

11	Benzyle Chloride	C_7H_7Cl	126.58	1100.00	179	-39
12	Toluene	C_7H_8	92.14	866.90	110.6	-95
13	n-Decane	$C_{10}H_{22}$	142	730.00	174.1	-30.5
14	Benzene	C_6H_6	78.11	876.50	80.1	5.5
15	Copper Nitrate	$Cu(NO_3)_2$	187.58	3050.00	256	170
16	Acetone	CH_3COCH_3	58.08	791.00	56	-95
17	Cromium Nitrate	$CrNO_3$	238.011	185.00	-	60.06
18	Hydrogen Peroxide	H_2O_2	34	1135.00	150.2	-0.43

Appendix B

GC Results of DMDS Adsorption



Chromatogram : 160414_001_channel1

Reference Sample.

System : 450GC
Method : GASPRO Sulphur_200214
User : User1
data path: Group1\42014\
Sample Name:

Acquired : 4/16/2014 2:57:36 PM
Processed : 4/16/2014 4:40:15 PM
Printed : 4/24/2014 4:29:32 PM

160414_001.DATA [Rear (PFPD)]

CHROMATOGRAM METHOD REPORT :

Acquisition :
Description
DMDS+n-Hexane from Dr Rajshekhar

0.5gm DMDS + 100ml n-Hexane.

Peak results :

160414_001.DATA [Rear (PFPD)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	0.03	0.00	696.1	11.4	0.003
2	UNKNOWN	10.26	3.02	192092.8	10107.6	3.018
3	UNKNOWN	15.38	1.80	302116.0	6017.5	1.797
4	DMDS	15.82	95.18	673610.6	318739.1	95.181
Total			100.00	1168515.5	334875.5	100.000

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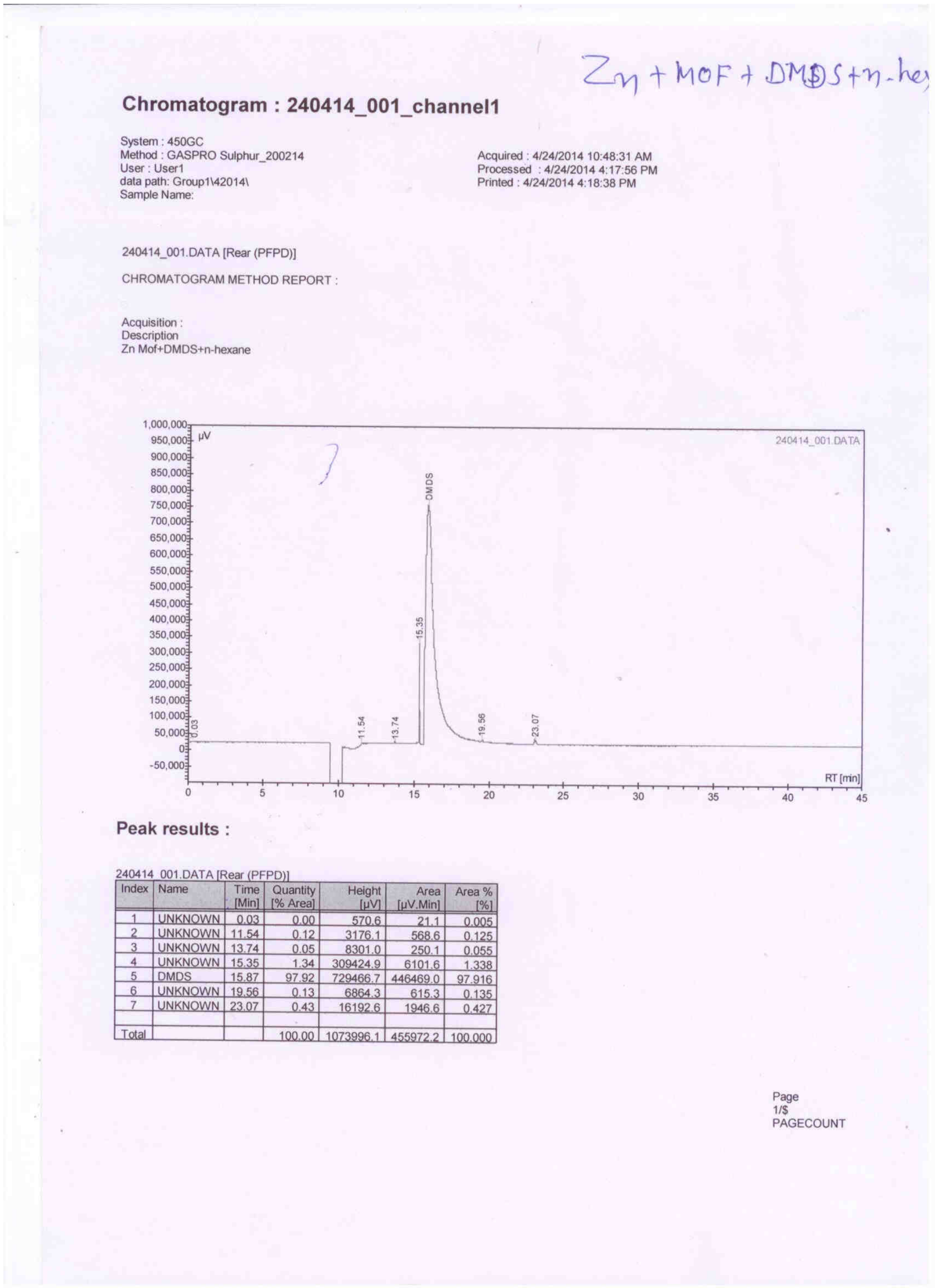
Figure B.1: Reference Sample



Zn + MOF + DMDS+n-he

Chromatogram : 240414_001_channel1

System : 450GC
Method : GASPRO Sulphur_200214
User : User1
data path: Group1\42014\
Sample Name:

Acquired : 4/24/2014 10:48:31 AM
Processed : 4/24/2014 4:17:56 PM
Printed : 4/24/2014 4:18:38 PM

240414_001.DATA [Rear (PFPD)]

CHROMATOGRAM METHOD REPORT :

Acquisition :
Description
Zn Mof+DMDS+n-hexane

Peak results :

240414_001.DATA [Rear (PFPD)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	0.03	0.00	570.6	21.1	0.005
2	UNKNOWN	11.54	0.12	3176.1	568.6	0.125
3	UNKNOWN	13.74	0.05	8301.0	250.1	0.055
4	UNKNOWN	15.35	1.34	309424.9	6101.6	1.338
5	DMDS	15.87	97.92	729466.7	446469.0	97.916
6	UNKNOWN	19.56	0.13	6864.3	615.3	0.135
7	UNKNOWN	23.07	0.43	16192.6	1946.6	0.427
Total			100.00	1073996.1	455972.2	100.000

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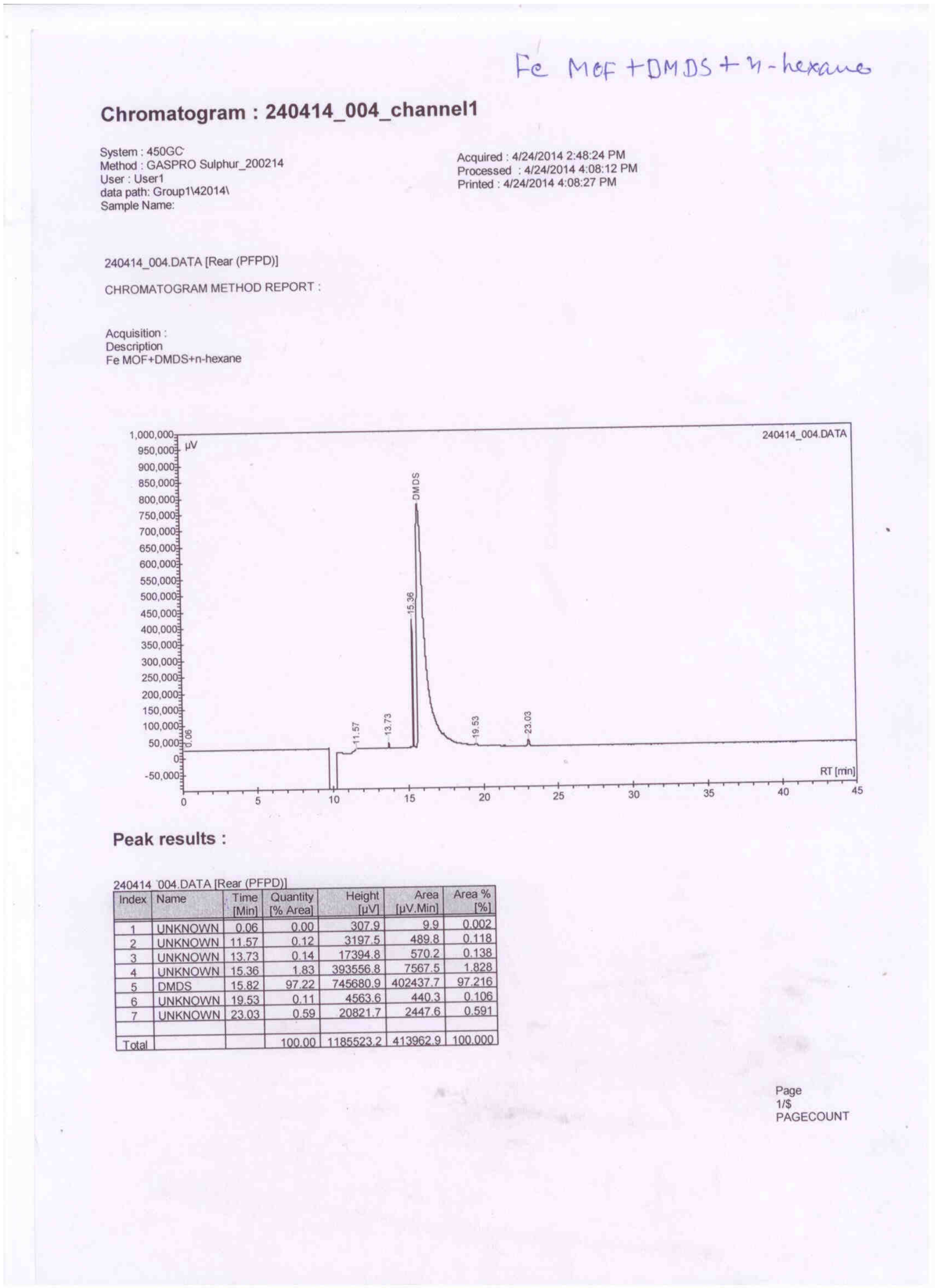
Figure B.2: Zn-MOF Adsorption



Fe MOF + DMDS + n-hexane

Chromatogram : 240414_004_channel1

System : 450GC
Method : GASPRO Sulphur_200214
User : User1
data path: Group1\42014\
Sample Name:

Acquired : 4/24/2014 2:48:24 PM
Processed : 4/24/2014 4:08:12 PM
Printed : 4/24/2014 4:08:27 PM

240414_004.DATA [Rear (PFPD)]

CHROMATOGRAM METHOD REPORT :

Acquisition :
Description
Fe MOF+DMDS+n-hexane

Peak results :

240414_004.DATA [Rear (PFPD)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	0.06	0.00	307.9	9.9	0.002
2	UNKNOWN	11.57	0.12	3197.5	489.8	0.118
3	UNKNOWN	13.73	0.14	17394.8	570.2	0.138
4	UNKNOWN	15.36	1.83	393556.8	7567.5	1.828
5	DMDS	15.82	97.22	745680.9	402437.7	97.216
6	UNKNOWN	19.53	0.11	4563.6	440.3	0.106
7	UNKNOWN	23.03	0.59	20821.7	2447.6	0.591
Total			100.00	1185523.2	413962.9	100.000

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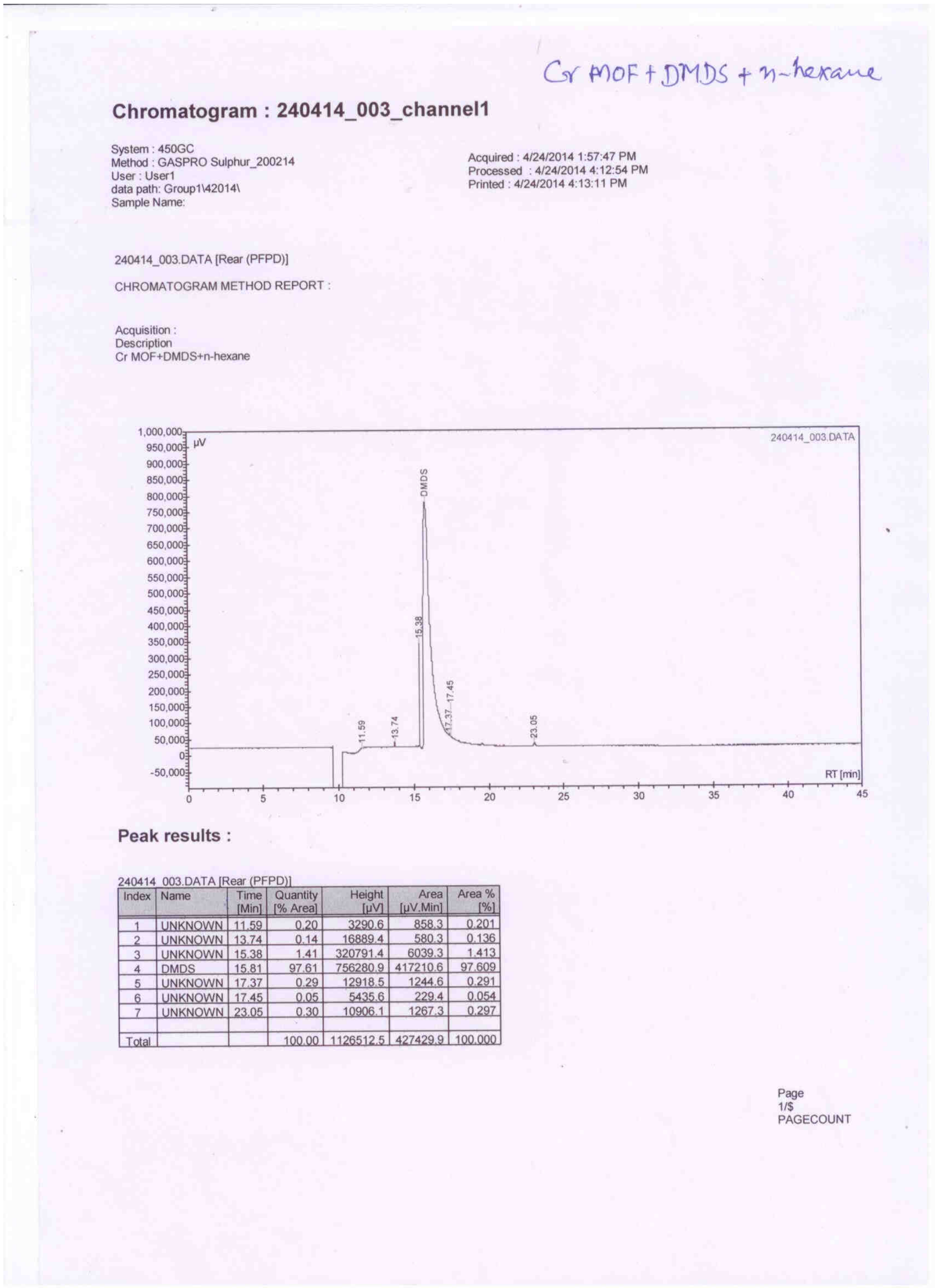
Figure B.3: Fe-MOF Adsorption



Cr MOF + DMDS + n-hexane

Chromatogram : 240414_003_channel1

System : 450GC
Method : GASPRO Sulphur_200214
User : User1
data path: Group1\42014\
Sample Name:

Acquired : 4/24/2014 1:57:47 PM
Processed : 4/24/2014 4:12:54 PM
Printed : 4/24/2014 4:13:11 PM

240414_003.DATA [Rear (PFPD)]

CHROMATOGRAM METHOD REPORT :

Acquisition :
Description
Cr MOF+DMDS+n-hexane

Peak results :

240414_003.DATA [Rear (PFPD)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	11.59	0.20	3290.6	858.3	0.201
2	UNKNOWN	13.74	0.14	16889.4	580.3	0.136
3	UNKNOWN	15.38	1.41	320791.4	6039.3	1.413
4	DMDS	15.81	97.61	756280.9	417210.6	97.609
5	UNKNOWN	17.37	0.29	12918.5	1244.6	0.291
6	UNKNOWN	17.45	0.05	5435.6	229.4	0.054
7	UNKNOWN	23.05	0.30	10906.1	1267.3	0.297
Total			100.00	1126512.5	427429.9	100.000

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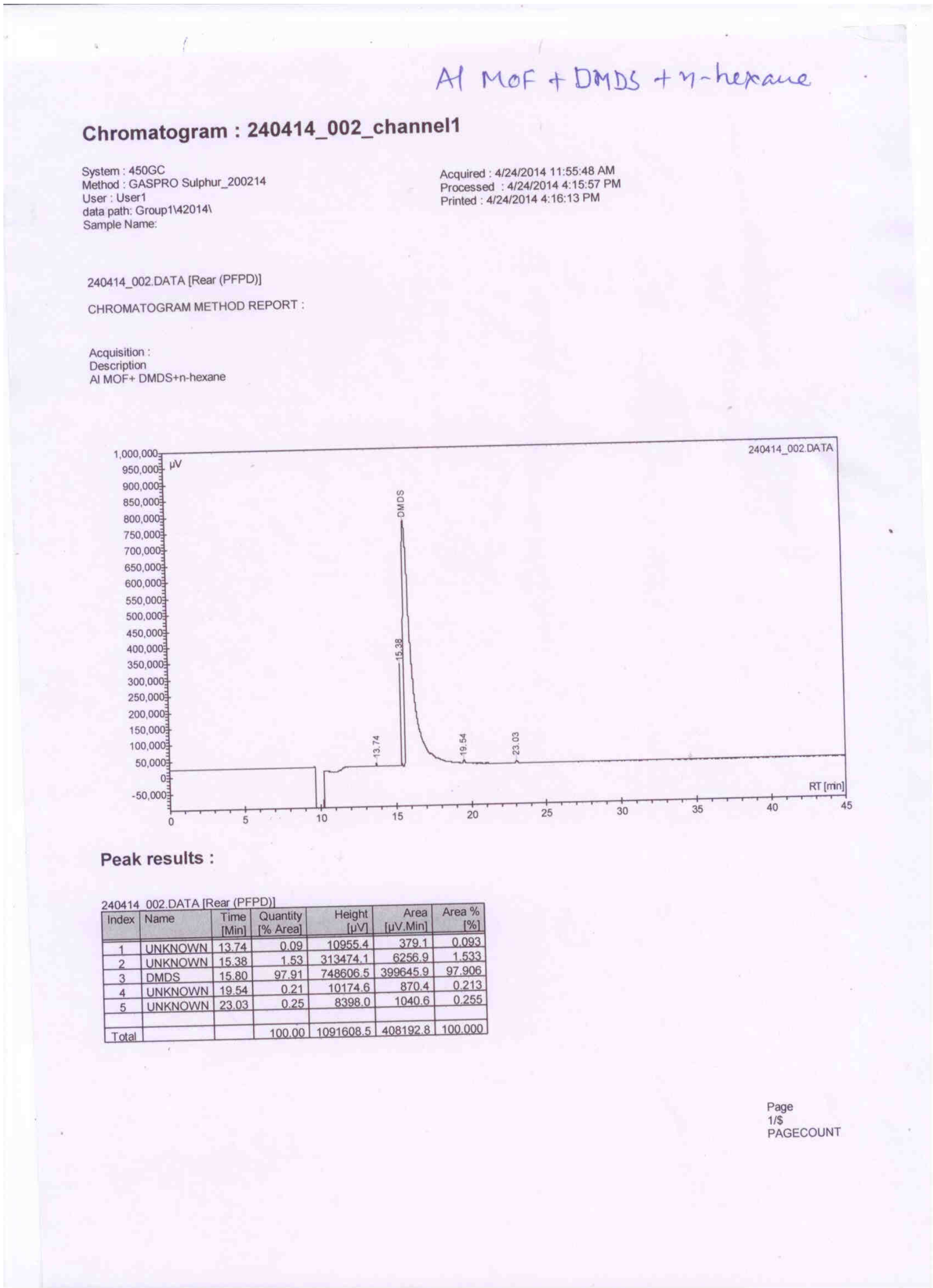
Figure B.4: Cr-MOF Adsorption



Al MOF + DMDS + n-hexane

Chromatogram : 240414_002_channel1

System : 450GC
Method : GASPRO Sulphur_200214
User : User1
data path: Group1\42014\
Sample Name:

Acquired : 4/24/2014 11:55:48 AM
Processed : 4/24/2014 4:15:57 PM
Printed : 4/24/2014 4:16:13 PM

240414_002.DATA [Rear (PFPD)]

CHROMATOGRAM METHOD REPORT :

Acquisition :
Description
Al MOF+ DMDS+n-hexane

Peak results :

240414_002.DATA [Rear (PFPD)]

Index	Name	Time [Min]	Quantity [% Area]	Height [µV]	Area [µV.Min]	Area % [%]
1	UNKNOWN	13.74	0.09	10955.4	379.1	0.093
2	UNKNOWN	15.38	1.53	313474.1	6256.9	1.533
3	DMDS	15.80	97.91	748606.5	399645.9	97.906
4	UNKNOWN	19.54	0.21	10174.6	870.4	0.213
5	UNKNOWN	23.03	0.25	8398.0	1040.6	0.255
Total			100.00	1091608.5	408192.8	100.000

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Figure B.5: Al-MOF Adsorption