AMERICAN UNIVERSITY OF BEIRUT

DEVELOPMENT OF NEW CATALYSTS BASED ON METAL-ORGANIC FRAMEWORKS FOR EFFICIENT LIQUID BIOFUEL PRODUCTION

ASMAA BILAL JRAD

A thesis

submitted in partial fulfillment of the requirements for the degree of Master of Mechanical Engineering to the Department of Mechanical Engineering of the Faculty of Engineering and Architecture at the American University of Beirut

> Beirut, Lebanon September 2017

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ASMAA BILAL JRAD

Approved by:

Prof. Mohammad Ahmad, PhD, Professor	Advisor	\cap
Department of Chemical Engineering	MalandAlin	K
Prof. Belal Abu Tarboush, PhD, Assistant Professor	Co-Advisor	
Department of Chemical Engineering	Beta	7
Prof. Mohamad Hmadeh, PhD, Assistant Professor	Member of Committee	
Department of Chemistry	AUA	
Prof. Mutasem Shehadeh, PhD, Associate Professor	Member of Committee	
Department of Mechanical Engineering	Maty	

Date of thesis defense: September 4, 2017

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AN ABSTRACT OF THE THESIS OF

<u>Asmaa Bilal Jrad</u>

for

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Title: <u>Development of New Catalysts Based on Metal-Organic Frameworks for</u> <u>Efficient Liquid Biofuel Production</u>

The objective of this research work is to discover a new class of catalysts made of earth abundant, low cost, chemically stable and non-toxic materials that can generate at globally significant rates, efficiencies and scales, emerging biofuels such as butyl butyrate. The thrust of this research project is to understand at a fundamental level the relations between the synthesis, composition, structure and properties of champion materials that confer upon them the capacity to function as efficient esterification catalysts. For this purpose, Zr-based Metal-Organic Frameworks were synthesized and characterized using different techniques such as XRD, BET, SEM and TGA and their acid density was evaluated using back titration. All prepared catalysts were successfully used for the catalysis of the esterification reaction of butyric acid in presence of butanol for the production of butyl butyrate. Catalysts with higher acid density lead to higher conversion rates, and higher catalyst loadings also increased the conversion to butyl butyrate. The UIO-66(COOH)₂ catalyst lead to 91% conversion, very close to the 96% conversion achieved by the conventional homogeneous liquid catalyst H₂SO₄. All catalysts were easily separated from the reaction medium, recycled, and efficiently reused as catalysts for new esterification reactions without significant loss in activity. With this knowledge, catalytic conversion rates and efficiencies of materials can be engineered from a laboratory prototype and optimized to a technologically important archetype able to make biodiesels at a globally significant scale.

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CHAPTER I

INTRODUCTION

The global demand for energy is ever expanding, and the limitations of the conventional fossil fuels in terms of being non-renewable and environmentally harmful, pushes the energy mix towards renewables. The technical advancement and environmental concerns are the drive of the shift towards a more sustainable and renewable energy system that meets the growing demand while reducing carbon emissions.

Liquid biofuels gained a lot of interest in the research field of renewables as they constitute a promising alternative for fossil fuels. However, the challenge remains in boosting the competitiveness of biofuels by maximizing their production and lowering their cost.

Ethanol and butanol are some of the known biofuels, but another chemical compound recently gained interest in the field of biodiesel and bio-additives for conventional fuels and it is Butyl Butyrate. Butyl butyrate is an ester that can be obtained by the esterification reaction of Butyric acid and Butanol, both of which can be obtained from biomass through fermentation processes. One of the reasons behind this interest in Butyl Butyrate is the fact that it's a flammable ester with an octane number similar to that of butanol, one of the most promising biofuels of the future, which allows the addition of butyl butyrate as an additive to petroleum the way butanol is. In addition, butyl butyrate has a Cetane index similar to that of Diesel, and a flash point lower than that of butanol which makes it safer to use. All these properties and many others put Butyl Butyrate under the classification of emerging biofuels.

For esterification reactions, and similar to all chemical reactions, catalysts come at the heart of the production process, as it allows the efficient making and breaking of chemical bonds which is the base for the production of new chemical compounds. Catalysts needed for esterification reactions in general are proton donors and are thus of acidic nature, which allows the efficient production of the desired ester.

Previously, liquid homogeneous catalysts were commonly used in biofuel production such as sulfuric acid and hydrofluoric acid. However, many technical problems were encountered when these catalysts were used because of their corrosive nature. Also, the recovery of the catalyst and its separation from the reaction medium is hard as the catalyst is in one phase with the reaction mixture. Thus homogeneous catalysts are not reusable nor recyclable and more catalyst will be needed when producing biofuels which increases the production cost. The recovery of the catalyst requires the washing of the mixture with water which causes the loss of some of the biofuel and generates a lot of waste water. For all the previously mentioned reasons, homogeneous acid catalysts are considered non-environmentally friendly and economically inefficient, and a lot of effort has been put to replace these and find new green catalysts for the production of biofuels.

Recently, heterogeneous catalysts have been extensively used in industries because of their ability to be recycled without losses in reaction yield. Many types of theses heterogeneous catalysts, such as, zeolites, metal oxides, resins and heterogeneous acid catalyst have been used for organic reactions. However, their use had one or more disadvantages regarding the selectivity, safety, cost, and catalyst disposal.

A new class of porous materials that is being investigated in the catalysis field are the Metal-Organic Frameworks (MOFs). MOFs are novel inorganic-organic

materials that are mainly attractive because of their crystalline nature, very large surface area and the chemical varieties by which they can be constructed. The fact that the channel sizes of MOFs can be controlled and thus their reaction selectivity and diffusion properties can be modified, makes MOFs an interesting alternative to conventional heterogeneous catalysts.



Figure 1: Crystal structure of UIO-66 MOFs incorporating different organic linkers MOFs were originally used for several applications like gas storage,

purification, drug delivery and biomedicine, but they have been gaining a lot of interest as a heterogeneous catalyst in the last two decades because both the organic linker and the inorganic metal clusters contribute to catalytic activity. Their large surface areas and significant pores network allow access to guest molecules which results in an efficient mass transfer and thus efficient catalysis.

MOFs have been recently investigated as heterogeneous catalysts for different organic reactions. The metal nodes and organic linkers were changed in every reaction to obtain the suitable functional groups for the catalysis of every specific reaction. The fact that there are a lot of combinations that could be designed in the field of MOFs as heterogeneous catalysts means that there are still a significant amount of chemical reactions for which special MOFs could be synthesized and tested which makes the research in this area a very promising one.



Figure 2: Crystal structure of ZIF-8

In the special case of esterification reactions, an acidic nature is required in the MOF. In specific, the functional groups of the MOF should be proton donors or in other words Brønsted acids. The acidic properties of the MOF were put under the test since there is a great interest in developing heterogeneous Lewis/Brønsted acid catalyst that can be recycled and reused especially in the industrial sector. In most cases, the MOFs efficiency in reactions that required acidic sites was tested by using the MOFs directly as catalyst in the reactions. However, the cases where MOFs were used for esterification reactions or were developed for the specific target of biofuel production remain rare.

While the industry of biofuel production is in great need to find green, recyclable and efficient catalysts to boost the competitiveness of clean energy, the research to find better catalysts and optimize the production process becomes necessary. The aim of this thesis is to test the performance of different types of Metal-Organic Frameworks (MOFs) and Zeolitic-Imidazolate Frameworks (ZIFs, a sub-family of MOFs) as catalysts for the esterification reaction to produce butyl butyrate. Zirconium-

based MOFs and ZIFs are known for their high thermal and chemical stability which is critical for catalysis applications. To this end, different structures of the Zr-based UIO-66 frameworks (figure 1) with different functional groups and ZIFs (figure 2) will be synthesized, characterized and tested to report their relative catalytic activity, recyclability and selectivity. The effect of the different characteristics of the tested catalysts, such as specific surface area, pore size, active sites, functional groups and metal nodes, on the reported performance of each catalyst will also be explored to obtain a deeper understanding of those materials emerging as new catalysts.

CHAPTER II

LITERATURE REVIEW

A. The Global Energy Shift to Renewables

The global demand for energy is ever expanding, and a wide range of energy sources are used to meet this demand. Among the different energy types, fossil fuels are dominant and make up approximately 75% of the energy mix¹. However, fossil fuels are non-renewable and environmentally harmful, which pushes the world to develop sustainable energy alternatives. Considering the current consumption rates, it is expected that the supply of oil, natural gas and coal could last for approximately 51, 53 and 153 years ². Moreover, fossil fuel combustion and industrial processes have contributed in about 78% of the total green-house gas emissions increase since 1970 ³, which made it the main reason to blame for the disastrous climate change effects.



Figure 3: CO₂ Emissions by Sector ³

Considering the limitations and harms of fossil fuel usages, there is a global need to develop a more sustainable energy system. Recent years have shown an important advancement in this direction, and renewable energy resources are being developed. It is expected that renewables, hydroelectric and nuclear power will account for about half of the global energy supplies growth over the next 20 years, with the renewables being the fastest growing source of energy⁴.



Figure 4: Different Energy Resources Share in the Global Energy Mix. *Renewables consist of biofuels, biomass, solar, wind and geothermal Energy ⁴

Liquid biofuels, a bioenergy type, gained a lot of interest in the research field of renewables as they constitute a promising alternative for liquid fossil fuels. However, the challenge remains in boosting the competitiveness of biofuels by maximising their production and thus lowering their cost.

By definition, bioenergy is a type of energy that is based on organic matter or what is known as biomass, this includes all materials that are biologically originated and that are not fossilised⁵. Bioenergy could be used in its original form, i.e. wood, as a fuel, or it could be refined to form solid, liquid or gaseous fuels that could be used in modern systems such as power plants for electricity production, different transportation types' engines and in industrial processes ⁵.

The reason behind the interest in biofuels is based on the fact that biomass needs to take in carbon from the atmosphere to grow and emits it to air when used for energy production. It is thus considered as a carbon neutral energy resource. Moreover, biomass could be grown over and over again which makes biofuels a sustainable energy source.



Figure 5: Liquid Fuel Demand by Sector⁴

Transportation nowadays accounts for the largest demand for liquid fuels in the world, and it is expected to become just under 60% in 2035⁴. Since biomass is used to produce liquid biofuels, it is considered the main alternative to oil, as biofuels operate the same way liquid fossil fuels do in internal combustion engines.

B. Liquid biofuels

1. Bioethanol:

The first type of biofuel tested in engines was bioethanol. Ethanol was produced by fermentation of simple sugars derived from biomass (e.g. glucose, fructose, and other monosaccharides) and it was used as a fuel with turpentine by the American inventor Samuel Morey in an internal combustion engine that he developed to run a boat at 7 to 8 miles per hour. Later in 1860, an ethanol fuel blend was used to run an internal combustion engine developed by the German engineer Nicolaus August Otto ⁶. This happened even before gasoline was commercially available in 1913. In theory, bioethanol could be produced by fermentation of any plant based materials as they all are essentially composed of cellulose, hemicellulose and lignin that are interwoven with one another to form the plant cell walls. However, further research is now being conducted to find new effective ways to extract simple sugars from lignocellulosic materials as this remains fairly challenging.

Bioethanol is now being commercially produced by fermentation of starch/sugar based plants such as corn, sugar cane, wheat and many more. In 1990, 4 billion gallons of bioethanol were globally produced. This amount increased significantly to reach around 23.3 billion gallons in 2010. In 2016, the production increased to 26.6 billion gallons with 57.8%, 27.4% and 5.1% being the share of U.S., Brazil and the European union of the global production respectively with U.S. aiming to increase the production to replace 10% of the gasoline consumption by bioethanol⁷. Currently, gasoline that is blended with 10% bioethanol is available on the US fuel market ⁸.

2. Biodiesel:

Biodiesel is a yellowish liquid produced by transesterification of vegetable oil, animal fats or waste grease in the presence of an alcohol and an alkaline catalyst. It is thus the mono-alkyl esters of fatty acids and it is being commercially produced to replace petroleum diesel. The higher heating value of biodiesel is 38-45 MJ/kg which is almost 90% that of petroleum biodiesel ⁹.

Before the invention of biodiesel, vegetable oil was tested to run diesel engines, but its high viscosity prevented the efficient use of this oil as a petroleum diesel alternative. It was not until 1937 when the Belgian scientist George Chavanne patented the "Procedure for the transformation of vegetable oils for their uses as fuels" where transesterification was used to produce the first generation of biodiesel ⁹. Later on, many industrial plants were developed for the production of biodiesel. After 2001, the year that witnessed the historical petroleum prices increase, the energy security concerns made biodiesel a well-known fuel in the global fuel market. The global production of biodiesel reached 6289 million gallons in 2013 up from 213 million gallons in 2003 with European Union countries (mainly Germany, France, Spain, Italy and Poland), Argentina and U.S. being the main biodiesel producers ¹⁰. The most popular usage for biodiesel in the U.S. is in the B20 Fuel which contains 20% biodiesel, 80% petroleum diesel. The usage of biodiesel is expected to expand with the growing global demand for biofuels in general.



Figure 6: U.S. Monthly Biodiesel Production ¹⁰

3. Butanol:

Biobutanol is considered as one of the most interesting emerging biofuels because of its properties and advantages over other biofuels and petroleum fuels. Biobutanol is formed via the fermentation of biomass-based sugars into butyrate and hydrogen, which are further fermented using bacteria to form biobutanol. The Biobutanol is also known as biogasoline because engines can run on it without further modification ¹¹. This was demonstrated by David Ramey who drove his Buick 1992 across America in summer 2005, while using 100% Butanol for his unmodified engine ¹². However, the maximum percentage of bioethanol that could be added in the gasoline mixture is 85% ¹¹. Moreover, biobutanol has almost 85% of the energy content of the petroleum gasoline, unlike bioethanol that is believed to have a bit less than 70% of the energy in the conventional gasoline ¹¹. Another benefit for butanol usage is that it is less corrosive than bioethanol which means that changing the materials used in the car or in fuel stations is not required for butanol usage. Biobutanol also has a lower vapor pressure than that of ethanol which makes it safer to use ¹². Most importantly, butanol

does not absorb water if it enters the system, unlike ethanol that blends with water and forms a solution that separates from the petroleum gasoline, which makes butanol a better additive to conventional gasoline.

On the other hand, butanol has got some limitations as a petroleum additive. First of all, its octane number is similar to that of gasoline and therefore cannot be used as an octane number booster unlike ethanol that has a higher octane number than conventional gasoline. Another drawback for the usage of butanol as a biofuel is that its production is more costly than ethanol because it requires a lot of energy to separate and concentrate the butanol after the fermentation process ¹².

4. Butyl Butyrate:

Butyl Butyrate is an ester with a pear-pineapple like aroma. This colourless liquid has been used as a flavouring agent in the food industry, particularly in baked goods, soft candy and chewing gum ¹³. It could also be found naturally in apple juice, orange juice and orange peel oil ¹³.

Being a flammable ester, butyl butyrate has been investigated as a potential biofuel, and researches prevailed very interesting properties that make butyl butyrate an interesting candidate to be the next emerging biofuel ^{14, 15}. First of all, the octane number of butyl butyrate is similar to that of Butanol, which means it could be added to gasoline the way butanol is ¹⁵. Second, its Cetane index is similar to that of diesel which enabled its mixing with diesel to enrich it ^{15-16, 16a}. Other properties that make butyl butyrate interesting as a biofuel is the fact that its flash point is lower than that of butanol which means it is safer in operation and also that it is more hydrophobic than butanol and thus easier to extract from the reaction mixture. Most importantly, Butyl

Butyrate can be produced by the esterification reaction of butanol and butyric acid, and both of which could be obtained from fermentation processes of biomass-based feedstock, which makes it a sustainable fuel. All these properties and many others put Butyl Butyrate under the classification of emerging biofuels.

As in all chemical reactions, catalysts come at the heart of the production process, as it allows the efficient making and breaking of chemical bonds which is the base for the production of new chemical compounds ³. Catalysts needed for esterification reactions in general are proton donors and are thus of acidic nature, which allows the efficient production of the desired ester. The mechanism (shown in Figure 7) begins with protonation of the carbonyl group of the carboxylic acid, which is then attacked by the alcohol. Proton transfer and the subsequent release of water result in an oxonium ion intermediate. A final deprotonation step provides the ester product.



Figure 7: Esterification Reaction Mechanism

C. Catalysts used for the esterification reactions:

1. Homogeneous catalysts:

Catalysts that were commonly used in biofuel production are homogenous catalysts such as sulfuric acid and hydrofluoric acid ¹⁷. However, the use of these

catalysts cause many technical problems because of their corrosive nature. Also the fact that the homogenous catalysts form one phase with the reaction components which makes the recovery of the catalyst and its reusability a very difficult process, and thus more catalyst will be needed when producing biofuels which increases the production cost. The recovery of the catalyst requires the washing of the mixture with water which causes the loss of some of the biofuel and generates a lot of waste water ¹⁷. For all the previously mentioned reasons, homogeneous acid catalysts are considered nonenvironmentally friendly and economically inefficient. Therefore, a lot of effort has been devoted to find new green heterogeneous catalysts for the production of biofuels.

2. Heterogeneous catalysts:

Recently, heterogeneous catalysts have been extensively used in industries because of their ability to be easily separated from the reaction mixture without the need for sophisticated separation units and without any losses of the product yield. Moreover, some heterogeneous catalysts have the ability to be recycled without significant loss in their activity and could be used for many cycles which makes them not only environmentally friendly but also cost effective. However, the main challenge remains in finding heterogeneous solid catalysts with chemical activities comparable to their homogeneous counter parts.

Many types of these heterogeneous catalysts, such as, zeolites, metal oxides, resins and heterogeneous acid catalyst have been used for organic reactions. However, their use had one or more disadvantages regarding the selectivity, safety, cost, and catalyst disposal. Among the well-known heterogeneous catalysts, zeolites are the most commercially used. Those heterogeneous catalysts that have been used since the 1960s,

have served as excellent catalysts in many industrial applications such as petrochemical processes, car exhaust treatment and in most gas-phase reactions ¹⁸.

Zeolites are aluminosilicates porous structures that are known by their excellent thermal and chemical stability ¹⁹ and their superior selectivity that is derived from the fact that the reaction occurs in very confined spaces, the pores, and only reactants or products that can fit inside the pores can react or be formed ²⁰. However, the micropores of zeolites could cause diffusion limitations when it comes to liquidphase reactions with complex organic substrates especially that the control of the pore size of the zeolites or the prediction of their crystalline structure prior to their synthesis remains challenging ²¹, and it would be beneficial to find a solid catalyst with properties similar to those of zeolites with more flexibility regarding the design of their structures and pore sizes for the efficient catalysis of liquid-phase reactions.

D. Metal-Organic Frameworks:

A new class of porous materials that is being investigated in the catalysis field and that is of significant similarity to zeolites are the Metal-Organic Frameworks (MOFs). MOFs are novel inorganic-organic materials that are mainly attractive because of their crystalline nature, very large surface area (up to 14600 m² g⁻¹)²², and the chemical varieties by which they can be constructed. Although MOFs are showing better thermal stability with time (400-500 °C) their stability cannot be compared to that of zeolites, but the fact that their channel sizes can be controlled and thus their reaction selectivity and diffusion properties can be modified ²², makes MOFs an interesting alternative to zeolites especially in liquid-phase reactions where substrates' molecules are bulkier than those in gas-phase reactions ²³.



Figure 8: The Metal Cluster and the Organic Linker as the Main Components of MOFs and some of its applications²⁴

MOFs are constructed from metal-containing units (Secondary Building Units (SBU)) connected by organic linkers to form two-dimensional or three-dimensional coordination networks ²⁵. Linkers commonly used are rigid systems that create crystalline and stable MOFs such as the poly-carboxylic molecules. A variety of metals in their stable oxidation state were successfully used as nodes for the production of MOFs such as alkaline, alkaline earth, transition metal, and rare earth elements ²⁴. MOFs were originally used for several applications like gas storage ²⁶, purification ²⁷, drug delivery, biomedicine ²⁸ and chemical sensing ²⁹.



Figure 9: Famous Building Blocks of MOFs. (A) Metal Clusters/Secondary Building Units (B) Organic Linkers

MOFs have been gaining a lot of interest as heterogeneous catalysts in the last two decades because both the organic linker and the metal nodes can contribute to catalytic activity ^{30,30b,31}, their large surface areas and significant pores network that allows access to guest molecules which results in an efficient mass transfer and thus efficient catalysis as mentioned earlier for the case of zeolites.

MOFs have been recently investigated as heterogeneous catalysts for different organic reactions, the metal nodes and organic linkers were changed in every reaction to obtain the suitable functional groups for the catalysis of every specific reaction. The fact that there are a lot of combinations that could be designed in the field of MOFs as heterogeneous catalysts means that there are still a significant amount of chemical reactions for which special MOFs could be synthesised and tested which makes the research in this area a very promising one ²⁴.

High conversion rates have been extensively reported in the literature for many organic reactions when MOFs were used as catalysts. In Knoevenagel condensations, it has been reported that MOFs made a better catalyst than conventionally used zeolites and even homogeneous metal salts, however, it is still not very well explored for other condensation reactions ³². High activity of MOFs in condensation reactions of aldehydes with alcohols had been attributed to the Bronsted acidity generated by the organic ligands used ³³. Another use of MOFs as catalysts was in hydrogenation reactions. For this type of reactions, MOFs were loaded with different types of metals and contributed in efficient catalysis of the reaction under better reaction conditions. In one study, MOFs were loaded with Ru-B nanoparticles for the hydrogenation of benzene to cyclohexane. The catalyst used allowed the efficient reaction to occur under mild conditions ³⁴. In another study, palladium nanoclusters were loaded on an ironbased metal organic framework for 4-nitrophenol reduction. The synthesised catalyst showed complete conversion at room temperature in a very short time and with low Pd loadings ³⁵. Other studies also investigated the catalytic performance of MOFs in hydrogenation reactions and reported very interesting results regarding the conversion rates and recyclability and reusability of MOFs ³⁶. MOFs have also been tested as catalysts in the ring-opening reactions. One of the researches in ring-opening of epoxides reported a superior catalytic performance of an iron-based MOF which was attributed to the Lewis acid sites in Iron ions and the high surface area of the MOF³⁷. In

another study on asymmetric ring-opening of epoxides, a mixed MOF was synthesised and efficiently used as a catalyst for the reaction ³⁸.

Other organic reactions for which MOFs were tested and proved to be efficient are ketalization, Friedel-Crafts reaction, cyclization reactions, acetalization, oxidation and polymerization. The previously mentioned references are just a brief example of the successful use of MOFs in catalysis and the growing interest in this research field.

1. Acidity in MOFs

In the special case of esterification reactions, catalysts, which are MOFs in this case, should have an acidic nature. In specific, the functional groups of the MOF should be proton donors, and thus have Brønsted acidity.

Brønsted acidity could be incorporated in metal-organic frameworks in three main ways ³⁹. The first method is the encapsulation of Brønsted acid molecules inside the pores of the MOFs. This could be done while synthesizing the MOFs or as a post-synthetic treatment, or they could be encapsulated in the pores while synthesizing the MOF. Some of the guest molecules that have been successfully incorporated inside the MOF pores are H₂SO₄ and H₃PO₄ ^{40,41}. Although the crystalline structure was not maintained using this treatment, it could be restored after washing away the acidic molecules from the pores. This shows that the acid treatment did not destroy the crystalline structure of the MOFs and that the incorporated Brønsted acid molecules are only guests to the MOF structure. Polyoxometallates (POMs), which are known for their strong Brønsted acidity, have also been incorporated as guest molecules in MOFs.

molecular dimensions of POMs which made it hard to include them inside the pores without blocking them ⁴². However, including POMs in MOFs' pores while synthesizing the latter showed that POMs could be well dispersed in the openings of the MOFs and the synthesised catalyst showed a better performance ⁴³.



Figure 10: Incorporation of Brønsted Acidity within MOFs pores. (A) Post-synthetic Approach (B) One-Step Approach ³⁹

The second method to prepare Brønsted acidic MOFs is by ligating Brønsted acid groups onto the SBU. Hydroxyl groups are some of the most known ligands for Brønsted acidity generation by bridging two or more metal ions in SBU. It is worth mentioning that the acidity strength of the hydroxyl groups is decreased if they are all bound to the same metal cluster type. That is why making MOFs with mixed metals within one SBU is now being considered as a method to increase the acidity of the resulting MOF. In this method, Brønsted acidity is generated by the interaction between the metal clusters and the solvent ligand. Many ligands are interesting in this type of acidity in MOFs such as alcohols, oxalic acids and sulfuric acids. In fact, those ligands could be introduced into vacancies in metal SBU sites after the synthesis of the MOF. This approach had been used in the Zr-based MOF, UIO-66, that had been produced with vacant sites in their SBU ⁴⁴. These vacant sites were later on occupied by oxalic acid that was introduced by a DMF/oxalic acid solution. One carboxylate acid group was bound to the SBU and the other carboxylic acid group was directed inside the pores creating a Brønsted acidity in the UIO-66 openings.

The third and most commonly used method for the introduction of Brønsted acidity in the network of MOFs is by choosing an organic linker with dangling Brønsted acid functional groups or by introducing such functional groups in the linker through post-synthetic methods. For example, a free carboxylic acid functional group was introduced in the Zr-based UIO66 MOF by using H2BDC-COOH instead of H2BDC during its synthesis ⁴⁵. This same MOF was synthesised with another organic linker that is amino-functionalised and that created an anilinium Brønsted acidic medium when protonated ⁴⁶. However, it should be noted that the Brønsted acid medium created by the aniline units in UIO-66(NH2) is considered weak compared to the dangling carboxylic acid groups in the carboxylate functionalized UIO-66 since carboxylic acid is a stronger Brønsted acid than aniline type ammonium groups ³⁹. Sulfonic acid was also used for the introduction of Brønsted acidity in UIO-66⁴⁵. However, a loss in crystallinity and pores network was observed with fully sulfonated linkers, and a dilution with the original linker was needed to retain the crystallinity and porosity of the original MOF. As a result, UIO-66 was successfully synthesised with 25% sulfonated linkers and 50% of its original porosity ^{45,47}. The use of four, five and six carboxylic acid containing

organic linkers for the synthesis of MOFs have also been reported ^{48, 49, 50, 50a}. Although a crystalline nature has been confirmed using such linkers, no further studies regarding the Brønsted acidity of these MOFs have been noted.

2. Identifying Acidity in MOFs

Acid strength in Metal-Organic Frameworks was evaluated using different techniques and methods. One of the ways to qualitatively evaluate the relative acidity of MOFs is the use of Hammett indicators. Hammett indicators are based on the H₀ acidity function defined in the following equation:

$$H_0 = pK_a + \log[B] / [HB^+]$$

Where [B] is the concentration of the indicator in its base form and $[HB^+]$ is the concentration of the indicator in its acid form. There is a series of Hammett indicators that can evaluate different acid strength. If a solid immersed in a certain indicator solution can change its colour from the basic to the acidic one, then the H_0 of the solid is equal or less than the H_0 of the acid conjugate of the indicator. Typically, the lower the H_0 value, the more acidic the compound studied is. One of these indicators was first used to confirm the presence of acidic sites in sulfonated UIO-66 MOF ⁴⁷. Later on, 12 of these indicators were used to assess the relative acidic strength of MOF-808 samples sulfonated using different concentration of sulfuric acid solution ⁴¹. However, this method is limited by the fact that it is not quantitative and that it could be confusing if the sample is coloured.

A more accurate and quantitative method for the evaluation of acid strength in a MOF is the use of Acid-base back titration. Typically, a known mass of MOFs in added to a NaOH solution of known molarity and the mixture is left for enough time for the acid-base reaction. Knowing that there would be an excess in base, the MOF crystals are then filtered out of the mixture which is back titrated using an HCl solution of known molarity. The change in concentration of the base solution allows the calculation of the number of moles of NaOH consumed which is equivalent to the number of moles of acid in the MOF. This approach was first applied in 2009 for the evaluation of acidic strength in MOFs ⁵¹.

Another powerful tool to identify Brønsted acidity in MOFs is the use of Infrared Spectroscopy (IR). IR shows vibrational frequencies for different functional groups and could identify the presence of hydroxyl, carboxyl and sulfonyl groups. This allows to confirm the success of the incorporation of new Brønsted acid sites in the MOF structure especially in post-synthetic methods, as it is the case in sulfonation, by comparing the IR spectrum prior to and after the post-synthetic treatment and monitor the changes in the ranges of Brønsted acid functional groups.

CHAPTER III

MATERIALS AND METHODS

A. Materials:

The zirconium chloride (98 %, Acros Organics) and zirconium oxychloride (98 %, Acros Organics), served as the metal salts in the MOF synthesis. The organic linkers used are terephthalic Acid (99 %, Acros Organics), 2-Aminoterephthalic Acid (99 %, Sigma Aldrich) and 1,2,4,5-benzenetetracarboxylic acid (96 %, Sigma Aldrich). All these chemicals were used directly without further purification.

Dimethyl formamide (DMF, Analytical reagent grade, Fisher Scientific) was used as a solvent in the MOF production and for their washing later on. Dichloromethane (DCM, Analytical reagent grade, Fisher Scientific) was used for the second stage of MOFs washing. Acetic Acid (99 %, Acros Organics) and Formic Acid (98-100%, Fisher Scientific) served as modulators in the synthesis of MOFs.

For the GC analysis, Heptane (HPLC grade, Fisher Scientific) was used as a solvent for the reaction mixture. Octanol (99 %, pure, Acros Organics) was the internal standard for GC calibration and analysis. The standards for GC calibration were prepared using 1-Butanol (99 %, extra pure, Acros Organics), n-Butyric Acid (99 %, extra pure, Acros Organics) and Butyl Butyrate (98 %, Acros Organics). The same sources of Butanol and Butyric Acid were used as reactants for the esterification reactions. The total acidity test was done using back titration where Hydrochloric Acid (for analysis, 37 % solution in water, Acros Organics) and Sodium Hydroxide (AC S reagent, ≥97 %, pellets, Sigma Aldrich) were used to prepare titration standards.

B. Zr-based MOFs for Butyl Butyrate production:

For this study, MOFs chosen for the esterification reaction were selected because of their reported chemical and thermal stability. Their names and components are shown in table 1.

The UIO-66 (Universitetet i Oslo/ University of Oslo), UIO-66(COOH)₂ and UIO-66(NH₂) are all Zr-based MOFs ^{52, 53}. They were prepared using the solvothermal technique with DMF being the solvent. Another catalyst was synthesised for this purpose, ZIF-8, which is a type of Zeolitic-Imidazolate frameworks, a subfamily of MOFs. ZIF-8 has also been reported to be very thermally and chemically stable ⁵⁴. The synthesised materials are used to serve as catalysts in the esterification reaction of butyric acid in the presence of alcohol to produce butyl butyrate.

The metal salt and organic linker used for the synthesis of each type of catalyst are listed in table 1 below.

Catalyst Name	Metal salt	Ligand	Ligand Structure
UIO-66	ZrCl ₄	Terephthalic acid	
UIO-66 (COOH) ₂	ZrOCl ₂ .8H ₂ O	1,2,4,5-benzene- tetracarboxylic acid	

Table 1: Metal Salts and Organic Ligand used for the synthesis of tested MOFs
UIO-66-NH ₂	ZrCl4	2-Amino-terephthalic acid	
ZIF-8	Zn(NO ₃) ₂ .6H ₂ O	2-methylimidazole	CH3

1. MOF preparation:

a. <u>Synthesis of UIO-66:</u>

This MOF was synthesised using two scales. First, the MOF was synthesised in a 20 mL vial where terephthalic acid (34 mg, 0.204 mmol) was dissolved in 19 mL of DMF and the mixture was sonicated for 10 minutes. Then ZrCl₄ (53 mg, 0.227 mmol) was added to the solution and the mixture was sonicated for further 10 minutes. 1 mL of Acetic Acid was then added to the solution and the reaction mixture was placed in a preheated oven at 120°C for 52 hours. The precipitated white powder was washed using DMF (3 times for three days) and then DCM (3 times for three days). The product was then collected by centrifugation and dried under dynamic vacuum overnight at 85°C.

The second time this MOF was scaled up using a 500 mL autoclavable reagent bottle. For this scaled-up synthesis of UIO-66, 510 mg of terephthalic acid were dissolved in 285 mL of DMF. After sonication, 795 mg of ZrCl₄ were added to the solution and the mixture was sonicated again. After sonication, 15 mL of Acetic acid were added to the solution before it is placed in the oven. All other washing and activation conditions remained the same in both cases.

b. Synthesis of UIO-66(COOH)2:

In a 20 mL scintillation vial, 1, 2, 4, 5-benzenetetracarboxylic acid (47 mg, 0.184 mmol) was dissolved in 4 mL DMF by sonicating the mixture for 10 minutes. After sonication, ZrOCl₂.8H₂O (59.5 mg, 0.184 mmol) was added to the solution. The mixture was sonicated for another 10 minutes and then 4 mL of formic acid were added to the solution. The reaction mixture was sonicated for a few minutes and was then placed in a preheated oven at 130°C for 5 hours. The obtained white powder was purified by washing with DMF and then with DCM several times, then it was collected by centrifugation and dried in a vacuum oven at 85°C.

The synthesis of this MOF was also successful using a larger scale. In a 50 mL vial, 141.6 mg of the organic linker 1,2,4,5-benzenetetracarboxylic acid was mixed with 9 mL of DMF. The mixture was sonicated for 10 minutes before 178.32 mg of the metal salt ZrOCl₂.8H₂O is added. After further sonication for another 10 minutes, 9mL of formic acid were added to the mixture. The vial was then put in a preheated oven at 130°C for 5 hours. Washing and activation happened in the same manner for the two scales.

c. <u>Synthesis of UIO-66(NH₂):</u>

2-Aminoterphtalic acid (41.12 mg, 0.227 mmol) was dissolved in 19 mL of DMF in a 20 mL scintillation vial. The mixture was sonicated for 10 minutes and then ZrCl₄ (53 mg, 0.227 mmol) was added to the solution. After sonication for another 10 minutes, 1 mL of Acetic acid was added to the solution that was sonicated for a few minutes. The scintillation vial was then placed in a preheated oven at 120°C for 52

hours. After obtaining a yellowish precipitate, washing and drying were done in a similar manner as for other MOFs.

Another scale was tested for the production of bigger quantities of this MOF in one batch. In 500 mL autoclavable reagent bottle, 412 mg of 2-aminoterphtalic acid was dissolved in 190 mL of DMF and the mixture was sonicated for 10 minutes. 530 mg of ZrCl4 were then added to the solution that was sonicated for another 10 minutes before the addition of 10 mL of acetic acid. The mixture was sonicated for a few minutes and was afterwards put in oven at 120°C for 52 hours.

d. Synthesis of ZIF-8:

In a 150 mL becher, 2-methylimidazole (22.7 g, 0.276 mol) was dissolved in 80 g of water by stirring. In a 25 mL Becher, Zn(NO₃)₂.6H₂O (1.17 mg, 0.004 mmol) was dissolved in 8g of DI water by stirring the mixture for a few minutes. The two solutions were then mixed together and stirred for a few minutes at room temperature and a milky mixture is obtained almost immediately after the two solutions are mixed. A white precipitate is collected using centrifugation after washing it several times with DI water. The collected product is dried in a vacuum oven at 85°C.

C. Characterization techniques:

Once the preparation step is done, it is desirable to prevail the structural characteristics, the stability and the homogeneity of the material. Several characterization techniques were used for these purposes and they are listed below.

1. Powder X-Ray Diffraction (PXRD):

Structural characteristics of the synthesised MOFs were determined using XRD diffraction. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 advance X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) at 40 kV, 40 mA (1600 W) using Cu Kα radiation (k=1.5418 Å).

XRD is a non-destructive analytical tool used to identify the crystalline structure in a sample, which is usually done by comparing the diffractogram of the tested sample with a database (simulated patterns) or with the diffractograms reported in literature.



Figure 11: XRD Configuration (Source: Bruker Company)

A periodic and predictable arrangement of the atoms in a sample is an indication of a crystalline structure. The crystal could be broken down into a unit cell and then the stacking of these unit cells in an orderly manner make the crystalline structure. A sample could hold crystalline structures as well as amorphous ones. An amorphous structure is reflected in a diffractogram consisting of a broad shallow rise known as a background hump, while sharp peaks are a reflection of a crystalline structure within a sample. The broader the peak, the less crystalline a structure is. The concentration of a given phase is proportional to the peak area of its corresponding peak.

As the samples were already in powder form, they were directly put on a flat sample holder in the path of the incident X-ray beam which is diffracted at different angles and is collected by a detector. The intensity of the peaks are measured between two chosen angles of the incident beam and at controlled and identical increments. The diffractogram is then the plot of the intensities of the peaks with respect to the angle 2Theta shown in figure 11.

XRD is used directly after the synthesis of the MOFs to confirm their purity and crystallinity and that their XRD patterns match the reported ones in the literature. After the use of MOFs as catalysts, they were separated from the liquid part of the reaction by centrifugation. They were then washed and activated in vacuum oven. The resultant recycled powder was also characterized using XRD after every recovery cycle. This helped to confirm whether or not the catalysts' crystalline nature was maintained under the reaction conditions. The stability of the recovered catalysts could be assured by them having a matching XRD pattern of the fresh MOFs, which revealed their ability to be recycled and reused to catalyse new reactions before they are depleted.

2. Thermogravimetric Analysis (TGA):

TGA is used to determine the thermal stability of the MOF. This technique records the change of mass of a substance with respect to temperature while being heated using a controlled heating rate, gas atmosphere and flow rate (figure 12). Thermogravimetric Analysis (TGA) was performed with a Netzsch TG 209 F1 Libra

apparatus. The analyses were recorded in N_2 flow from 30 to 800°C at a heating rate of 3 K. min⁻¹.



Figure 12: TGA Configuration (Source: Netzsch company)

Approximately, 5 mg of the samples to be tested were accurately weighed and were placed in crucibles within a crucible holder. The auto-sampler then puts the crucibles in the furnace one by one for analysis.

The use of TGA was very useful as some of the MOFs require heat treatments prior to their use as catalysts (activation process) or prior to their testing using other characterization techniques (BET). TGA helps identifying the parameters of these treatments. It also helps knowing the thermal reaction conditions that the catalysts could handle.

3. Scanning Electron Microscopy (SEM):

Scanning electron microscopy (SEM) was performed using a MIRA3 Tescan electron microscope after the samples were coated with a thin layer (20 nm) of Gold. SEM images prevail the morphology, grain size, grain shape, and defects in the MOFs.



Figure 13: SEM Configuration

Once the sample is put in its holder and the chamber containing it is put under vacuum, a beam of electrons is directed towards the sample and secondary electrons are produced by the latter. These secondary electrons are picked up by a backscatter detector that produces a voltage which is then transformed into an image that is identical to the shape of the sample surface (figure 13).

4. N₂ sorption for Brunauer-Emmett-Teller (BET) calculation:

The surface area of the samples synthesised were determined by an autosorb iQ-Microscope-XR (Quantachrome Instruments, Boynton Beach, FL, USA) gas

analyser using Nitrogen gas. The Brunauer-Emmett-Teller (BET) and Langmuir methods were used to determine the surface area with respect to P/P0. The measurement of the surface area was done after degassing and thus activation of the samples at 130°C overnight. Temperature and time of degassing were changed when the results obtained were not satisfying.



Figure 14: BET Configuration (Source: Quantachrome Instruments)

After sample degassing, the sample cell is moved to the physisorption station for analysis. The drive shaft then lifts the coolant container to immerse the sample cell in liquid Nitrogen which helps maintaining a controlled temperature throughout the analysis time (figure 14).

BET is an important characterization tool that serves in determining the specific surface area of the MOFs, a crucial parameter in mass transfer in a heterogeneous reaction and thus it is a major factor in predicting the performance of the MOF as a heterogeneous catalyst. BET also determines the void volume in the sample (space occupied by pores) that allows the access of substrate to the catalytic sites of the MOF, which is related to the specific surface area and is also an important criteria in catalysts.

5. Heterogeneity test:

This test is performed to investigate on whether or not any active sites of the catalyst are leaching inside the reaction medium. A true heterogeneous catalyst will retain all of its active sites while being in a reaction medium.

In order to confirm the heterogeneity of the catalyst, the reaction is allowed to occur with the normal catalyst loading until the sample at t = 6 hours is taken from the reaction. Afterwards, the reaction mixture is moved to a falcon tube and the catalyst is completely separated from the reaction solution by centrifugation. The liquid part of the reaction is then returned to the round bottom flask which is heated again to 110°C for the reaction to continue until 24 hours from the beginning of the reaction. Samples are then normally collected at 8 and 24 hours.

If the catalyst is acting like a heterogeneous one, then the conversion curve after t=6 h will not show any significant increase in the yield of butyl butyrate. This part of the conversion curve will thus be similar to that of the reaction that have occurred without catalyst, unlike other conversion curves that correspond to reactions where the catalysts were kept in the reaction solution at all times. However, if conversion turns out to be relatively similar in the two cases (with and without catalyst removal at t = 6 h), then this could be explained by a leaching of the active sites of the catalyst inside the reaction medium which means the catalyst is not 100% heterogeneous.

6. Total Acidity Test:

Since esterification reactions depend on active acid sites, the total acidity in the catalysts should give a clear indication of the relative catalyst performance in the studied reaction. In other words, an increased acidity in the catalyst should result in a better conversion to butyl butyrate. Thus, this test is of great importance in the analysis of the different conversion rates of the catalysts tested.

The total acidity test was performed using standard back titration. A Hydrochloric Acid solution of 0.05M concentration (C_{a0}) was prepared to be the acid titrant. Then, a 0.04M NaOH solution (C_{b0}) was prepared and was titrated against the acid solution to confirm their concentrations.

After the preparation of the base and acid standards, 30 mL of the sodium hydroxide solution was mixed with 150 mg of each type of catalyst for 60 minutes during which the acidic sites in the MOFs were allowed to react with the strong base solution.



Figure 15: Acidity Test Set-up

However, it was predicted that the number of moles of base will be more than that of acid in the solution, which means that there will be remaining basic sites in the NaOH/Catalyst solution. However, the latter will have a lower base concentration (C_{b1}) after the reaction with the catalyst. The catalyst crystals were filtered from the NaOH/Catalyst solution and 10 mL of it was titrated against the 0.05M HCl solution using a burette filled with the acid (figure 15). A stirring plate and a stirring bar placed inside the NaOH/Catalyst solution were used for the mixing of the titrated solution and a pH meter (Mettler Toledo, S220 SevenCompact pH/Ion) was used to determine the equivalence point.

As the initial concentrations of the base and acid were already known, the difference between the calculated concentration of the NaOH/Catalyst solution from titration (C_{b1}) and the concentration of the initial NaOH solution (C_{b0}), enables the calculation of the number of moles of NaOH consumed by the catalyst (n_{bc}). The number of moles of base consumed is equivalent to the number of moles of acid in the catalyst (n_{ac}) which is then converted to the equivalent mmol of H₂SO₄ per gram of catalyst. This means that the catalyst performs as if it had a certain number of millimoles of sulfuric acid per gram of catalyst. The test was repeated three times for every catalyst type.

The calculations were done as follows:

$$C_{b1} = \frac{V_{a0}}{V_{b1}} * C_{a0}$$

Where:

- C_{b1} : is the calculated concentration of the NaOH/Catalyst solution being titrated
- C_{a0} : is the initial concentration (0.05 M) of the HCl solution (the titrant)

- *V*_{a0}: is the volume of acid needed to neutralise the NaOH/Catalyst solution (equivalence point)
- V_{b1} : is the volume of base (10 mL) being titrated

$$n_{bc} = C_{b0} * V_{b0} - C_{b1} * V_{b0}$$

Where:

- V_{b0} is the volume of base (30 mL) mixed with the catalyst
- C_{b0} is the initial concentration (0.04 M) of the NaOH solution

$$n_{bc}/1g \ of \ catalyst = \frac{n_{bc}}{m_c}$$

Where:

- n_{bc}/1g of catalyst :is the number of moles of base consumed per 1g of catalyst
- m_c : is the mass of catalyst (0.150 g) mixed with the base in grams.

$$\frac{mmol \ of \ H_2SO_4}{1g \ of \ catalyst} = \left(\frac{n_{bc}}{1g \ of \ catalyst}\right) * \frac{1}{2 * 0.001}$$

Where:

• $\frac{mmol \ of \ H_2 SO_4}{1g \ of \ catalyst}$ is the equivalent number of moles of $H_2 SO_4$ in mmol per 1g of

catalyst.

D. Esterification of butyric acid

Different loadings of each catalyst were used to study, not only the effect of the different types of catalyst, but also the effect of the catalyst quantity on the reaction yield. The catalyst loading was changed between 1, 2 and 5% in the first set of

experiments. The prepared catalysts were put in a vacuum oven at 85°C overnight for dehydration and further activation before the reaction. Based on the literature, 2:1 n-butanol to butyric acid ratio was used, as this alcohol:carboxylic acid ratio was proved to be the optimum for esterification reactions. The reaction was carried out in a 50 mL round-bottom flask connected to a water condenser. 10 mL of butanol, 5 mL of butyric acid and the appropriate amount of catalyst were added to the round bottom flask that was heated to 110°C. The round bottom flask was heated using an oil bath placed on a magnetic stirrer and the solution was mixed with a magnetic bar to increase heat and mass transfer in the reaction medium.

In order to track the conversion of the reactants to butyl butyrate, samples (around 60μ L) were collected from the reaction medium at 0, 1, 2, 3, 4, 5, 6 and 24 hours, using an electronic pipette, and were added to a 4 mL vial containing 2 mL of a n-heptane/octanol solution where the concentration of the octanol was known. The diluted solution was then placed in a 5 mL syringe fitted with a filter (0.2 μ m PTFE filter) to remove catalyst particles. The filtered samples were placed in 1.5 mL GC vials for analysis. After every reaction the catalyst was easily separated from the reaction product by centrifugation. The catalysts was reused in other esterification reactions after washing it several times first with DMF and then with DCM, and after drying and activation in a vacuum oven at 85°C overnight. Every experiment was repeated at least three times to ensure results are reproducible.

E. GC for samples analyses

Samples taken regularly from the reaction solution were analysed using gas chromatography (Thermo Scientific, Trace GC Ultra, Gas Chromatograph), which was connected to a flame ionization detector (FID). The components of the samples were separated on a Teknokroma capillary wax column (30 m X 0.32 mm X 0.25 μ m). The temperature of the column was changed according to a predefined program. The temperature of the inlet and the detector were set to 300°C. The injection volume was 1 μ L, the carrying gas used was hydrogen and the split ratio was set to 100:1.

1. GC calibration

For the GC calibration, octanol was used as an internal standard to ensure that calibration standards were properly prepared and that the system is running well during every sample analysis. Heptane was chosen as a solvent for octanol and butyl butyrate for the GC calibration and throughout the testing phase.

In order to obtain the different dilutions for the calibration, two solutions were first prepared. The first solution contained butyl butyrate, n-butanol and butyric acid at 10 mg/mL concentration each, and the second contained octanol at 10 mg/mL concentration. The solutions were prepared as follows: 1g of butyl butyrate, 1 g of nbutanol and 1g of butyric acid were added to a 100 mL volumetric flask and the rest of the flask was filled with heptane to the mark to obtain the first solution. In another 100 mL volumetric flask 1g of octanol was added and then Heptane filled the remainder of the flask to the mark to obtain the 10 mg/mL concentration of octanol for the second solution.

After this step, different dilutions were prepared from the first butyl butyrate, n-butanol, butyric acid/heptane solution in five 10 mL volumetric flasks. The solution was diluted with heptane to obtain dilutions with 2, 4, 6, 8 and 10 mg/mL concentration of the different reaction components. At this stage, 0.75 mL of each dilution was added

to an Eppendorf tube with 0.25 mL of the octanol/heptane solution to make the GC calibration samples. Before the calibration samples were injected for GC analysis, samples containing diluted butyl butyrate, butyric acid, n-butanol and octanol separately were analysed to identify the retention time of each component. Each calibration standard was injected to the GC three times and the average peak area of each component was calculated.

Table 2 shows the injected concentration and the corresponding peak area for different reaction components, and figure 16 represents the calibration curve obtained after running the standards for calibration.

Table 2: Injec	ted Concentration	s and Correspon over 3 t	nding GC Peak Are runs)	eas for Differen	nt Components (Av	erage

Butanol		Butyl		Butyric Acid		Octanol	
		Butyrate					
Injected	Peak	Injected	Peak	Injected	Peak	Injected	Peak
Concentration	Area	Concentration	Area	Concentration	Area	Concentration	Area
(mg/mL)		(mg/mL)		(mg/mL)		(mg/mL)	
1.5	16422622	1.5	21606884	1.5	15727180	2.5	42713259
3	39647218	3	42730023	3	30655425	2.5	40386345
4.5	52026776	4.5	64110899	4.5	45857874	2.5	40405398
6	82664892	6	85123091	6	61003504	2.5	41563957
7.5	101585224	7.5	102472287	7.5	73472189	2.5	40424403



Figure 16: Calibration Curves in Terms of X and Y ratios

$$X_{ratio} = \frac{C_{is}}{C_s}$$
$$Y_{ratio} = \frac{PA_{is}}{PA_s}$$

Where:

- C_{is} is the concentration of the injected solution
- C_s is the concentration of the standard
- *PA*_{*is*} is the GC peak area corresponding to a specific component of the injected solution
- PA_s is the peak area of the standard.

Knowing the peak area of each component by means of the GC, and knowing the concentration of the internal standard from the prepared solution, the GC calibration curve enables the calculation of the concentration of each component in the injected 1μ L. This last concentration corresponds to that of the prepared GC samples, which is taken from the reaction medium and it is of known dilution factor, thus the concentration of each component in the reaction medium could be calculated. The system was perfectly sealed and the volume was measured at the end of every reaction to make sure of this and in order to calculate the number of moles of each component at every time a sample was taken from the reaction medium. The conversion to butyl butyrate was calculated as the ratio between the final number of moles of butyl butyrate and the initial number of moles of butyric acid.

F. Catalyst recycling

After every reaction, and after taking the final samples, the reaction mixture is put in falcon tubes and the catalysts were easily separated by centrifugation for about 10 minutes at 5500 rpm. The supernatant which corresponds to the liquid part in the reaction was poured out of the falcon tube and was stored in special containers, while the solid part, corresponding to the catalyst, was washed three times with DMF and three times with DCM. The catalyst is then put in vacuum oven at 85°C overnight for drying and activation. The catalyst would then be weighed to record losses and becomes ready for further usages.

To make sure the catalyst is still stable after every reaction, XRD patterns were recorded for the recycled catalysts and compared with fresh ones to confirm they are still of the same crystalline nature. Samples are taken from the reaction mixture every two hours for the first 8 hours of the reaction and the last sample is taken after 24 hours of reaction. The aim of this is to compare the performance of the catalyst when it is fresh with it after being recycled.

CHAPTER IV

RESULTS AND DISCUSSION

A. Characterization:

A combination of spectroscopic and microscopic techniques, thermogravimetric analysis and X-ray diffraction was employed to fully characterize all the MOF structures before and after the catalytic reaction.

1. Scanning Electron Microscopy

SEM images of different synthesised MOFs are shown in figures 17, 18 and 19. The images show that the UIO-66 samples are pure and display identical octahedral crystal shape regardless the functional groups, however, the size of these crystals changes for different functional groups. The UIO-66(COOH)₂ has got the largest crystals while UIO-66 and UIO-66(NH₂) SEM images show a smaller crystal size for these MOFs. Similarly, SEM images of synthesized ZIF-8 are shown in figure 20 and they reveal the nano-sized spherical particles.



Figure 17: SEM images of UIO66(NH₂)



Figure 18: SEM images of UIO66





Figure 19: SEM images of UIO66(COOH)₂



Figure 20: SEM images of ZIF-8

2. Powder X-ray Diffraction

Figure 21 shows the PXRD patterns for the synthesised UIO-66-X MOFs and the simulated one. The PXRD patterns clearly reveal the sharp narrow peaks of the synthesised MOFs that are in complete accordance with the data provided from literature. This reflects the high crystallinity and purity of all prepared catalysts. Similarly, figure 19 shows that PXRD pattern of the synthesised and simulated ZIF-8. The PXRD of the as synthesized ZIF-8 matches the simulated pattern with no extra-peaks which demonstrates the high purity and crystallinity of our ZIF-8 sample.



Figure 21: PXRD pattern of UIO-66-X MOFs. (a) UIO-66 Simulated (b) UIO-66 Synthesized (c) UIO-66(NH₂) (d) UIO-66(COOH)



Figure 22: PXRD pattern of ZIF-8. (a) ZIF-8 Simulated (b) ZIF-8 Synthesized.

3. BET:

The textural properties of the synthesised MOFs were determined by surface area analysis and the N_2 isotherms are shown in figure 23. All the results obtained are in good agreement with values reported in the literature ^{52, 53}. The calculated surface areas of UIO-66, UIO-66(COOH)₂ and UIO-66(NH₂) are 992, 270 and 848 respectively. The obtained small values in the surface area are expected for the functionalized UIO-66 structures especially for the UIO-66-(COOH)₂ since these groups are blocking the pores aperture and therefore leading to a decrease of the accessible surface area.





Figure 23: Nitrogen Physiosorption Isotherm (A) UIO-66(NH₂) (B) UIO-66 (C) UIO-66(COOH)₂

4. Thermogravimetric Analysis

The thermal stability of the synthesised catalysts was evaluated by TGA. The curves in figure 24 represent the variation of the tested sample weight with respect to temperature. All curves shows two main weight losses for the tested MOFs. The first one occurs at a temperature between 50 and 100°C and is of about 10% of the total sample weight. This weight loss is attributed to the evaporation of the physiosorbed water/solvent. For the functionalised UIO-66 MOFs the TGA curves show gradual and slight weight loss (around 15% in total) between 100 and 400°C. This could be attributed to the departure of these functional groups. A significant weight loss of around 40% of the catalyst weight is observed between 400 °C and 500°C for UIO-66, UIO-66(COOH)₂ and UIO-66(NH₂) and at around 600°C for ZIF-8 respectively. This plateau is an indication of the disintegration of these MOFs at those temperatures.



Figure 24: TGA Curves for Different Catalysts

B. Esterification reaction study:

The synthesized and fully characterized MOFs were used as catalysts for the esterification reaction of butyric acid in presence of butanol to produce butyl butyrate, an emerging biofuel. Every reaction was allowed to run for 24 hours. Samples were taken once every two hours for the first 8 hours of reaction and the last sample was taken after 24 hours of the reaction. This allowed to monitor the conversion to butyl butyrate and to understand the effect of the catalyst loading, catalyst type and catalyst recycling on their activity in the esterification reaction.

The esterification reactions were allowed to occur at a constant alcohol to carboxylic acid ratio of 2:1. The effect of the catalyst type, catalyst loading, reaction time and catalyst recycling on the conversion to Butyl Butyrate were studied.

The study started by testing 4 catalysts which are the UIO-66, UIO-66(COOH)₂, UIO-66(NH₂) and the ZIF-8. All catalysts were chosen based on their reported stability, acidity and activity. However, although ZIF-8 has been reported as a very sable MOF in the literature ⁵⁴, its use as a catalyst in the esterification reaction of butyric acid caused its complete dissolution in the reaction mixture. Later on, ZIF-8 was synthesised in a different manner to make sure its synthesis route did not affect its properties and it was used again as a catalyst in the esterification reaction. After approximately 30 minutes, it totally dissolved in the reaction mixture that turned completely colourless. ZIF-8 was thus removed from the study as it did not show the required chemical stability. The other UIO-66 MOFs series with their different functional groups showed no signs of chemical instability whatsoever and retained their physical properties and crystallinity throughout the study.

1. Effect of catalyst loading and reaction time

The catalyst loading of the three different MOFs was changed between 1, 2 and 5% of the Butyric Acid weight and the reaction was given 24 hours to occur. The catalysts were put in vacuum oven overnight at 85°C for further activation and were weighed for testing directly before their usage as catalysts in the esterification reaction. The time t = 0 hr was the time at which the reaction temperature reached 110°C which explains the non-zero conversion at t=0 in some cases. These experimental conditions were chosen based on related reports in the literature ⁵⁵.

At the beginning of the reaction, the conversion increased quickly and reached almost 70%, 60% and 45% for 5% loading of UIO-66(COOH)₂, UIO-66 and UIO-66(NH₂) respectively after 8 hours of reaction. As the reaction progressed in time, the reaction rate slowed down but the butyl butyrate concentration still increased until almost stabilization of the conversion rate after 24 hours.

The effect of the change in catalyst loading followed the same trend for all three MOFs. An increase in the catalyst loading caused an increase in the conversion rate to Butyl Butyrate for all UIO-66X MOFs. This could be explained by the fact that increasing the catalyst quantity will cause an increase in the quantity of active acid sites in the reaction medium. This would make access to those sites easier for the reacting components and would thus promote a faster reaction between the butyric acid and butanol to form butyl butyrate. For the rest of the study, the catalyst loading was fixed at 5% since the highest conversion rates were obtained using this loading. Figures 25, 26 and 28 show the conversion curves using UIO-66(COOH)₂, UIO-66 and UIO-66(NH₂) respectively and using the 3 different loadings.



*Figure 25: Conversion to Butyl Butyrate as a function of time using 1, 2 and 5% loading of UIO-66(COOH)*₂



Figure 26: Conversion to Butyl Butyrate as a function of time using 1, 2 and 5% loading of UIO-66



Figure 27: Conversion to Butyl Butyrate as a function of time using 1, 2 and 5% loading of UIO-66(NH₂)

2. Acidity test:

Esterification reactions require proton donors, or Brønsted acid sites, in order to occur efficiently and give high yields and conversion rates. For this reason the total acidity test is of great importance to predict and explain the performance of every catalyst synthesised. Total acidity was estimated using back titration method. Every catalyst was allowed to react with a prepared standard NaOH solution of known concentration (0.04

M). Enough time was given for the acidic sites in the MOFs to react with the strong base solution. Then the solid catalyst was separated by centrifugation and 10 mL of the basic supernatant was titrated against an HCl solution of known concentration (0.05M) to monitor the change in the base concentration and thus calculate an estimation of the acid content in the MOFs. The titration curves of the prepared NaOH solution (fresh NaOH) and the reaction supernatant of the NaOH solution with the different MOFs are



depicted in figure 28.

Figure 28: pH Curves of the different NaOH/Catalyst solutions titrated with HCl (0.05 M)

First the titration of the fresh NaOH solution (0.04 M) against the HCl solution (0.05 M) was done to make sure the standards were prepared correctly. The resultant pH curve is also used as a reference to be compared with pH curves of other NaOH/catalyst solutions.

The blue curve corresponds to the reference pH curve and the equivalence point was reached after the addition of approximately 8.1 mL of HCl. This confirmed the concentrations of prepared solutions. Then the NaOH/Catalyst solutions were titrated one by one against the same HCl solution.

The first thing to notice is that less volume of acid was needed to reach the equivalence point in all three NaOH/Catalyst reaction supernatant than it was needed for the fresh NaOH solution. This means that the number of moles of base had decreased after the addition of the MOFs in the NaOH solution which demonstrates that all tested MOFs have acidic active sites.

However, different catalysts with their different functional groups did not have the same acidity. A volume of about 2.1 mL, 1.1mL and 0.2 mL of the 0.05M HCL solution was required to neutralise the HO⁻ left in the NaOH solution after its reaction with the UIO-66(NH₂), UIO-66 and UIO-66(COOH)₂ catalysts respectively. This means that the UIO-66(COOH)₂ is the most acidic, followed by UIO-66 and then UIO-66(NH₂). This result was expected as the UIO-66(COOH)₂ MOF has two free carboxylic acid functional groups which are stronger Brønsted acids than the amino linkers in UIO-66(NH)₂ as indicated previously in the literature ³⁹. Moreover, free acidic hydroxyl groups in the UIO-66 MOF are available on the Zirconium cluster where defects in the structure exist, which might have contributed to its acid density ³⁹.

The table below summarises the results obtained in the acidity test. The concentration of the base in the NaOH/Catalyst solution is inversely proportional to the acid strength and density in the tested MOFs. Knowing the volume of base originally added in the NaOH/catalyst solution (30 mL) and the volume of the same solution used for the titration (10 mL), the number of moles of base remaining after the reaction with

the MOF and thus the number of moles of base consumed by the MOF could be calculated. The number of moles of H_2SO_4 per gram of catalyst is half that of base consumed in the NaOH/Catalyst solution as 2 moles of NaOH are required to neutralize 1 mol of H_2SO_4 .

Reaction	V _{a0}	C _{b1}	n _{bc}	n _{bc} /g	n _(H2SO4) /g
Supernatant	(mL)	(mol/L)	(mmol)	(mmol/g)	(mmol/g)
NaOH/UIO-66	1.1	0.006	1.02	6.8	3.4
NaOH/UIO- 66(COOH)2	0.2	0.0015	1.155	7.7	3.85
NaOH/UIO-66(NH2)	2.1	0.0115	0.855	5.7	2.85

Table 3: Acidity test results for tested MOFs

3. Effect of functional group

Three types of catalyst were tested for the esterification reaction of butyric acid in the presence of alcohol. As explained earlier in the literature review, MOFs are formed mainly of two parts, the metal cluster and the organic linker. All prepared UIO-66X MOFs are Zr-based and thus the difference in the reaction yield cannot be attributed essentially to the metal cluster itself. However, the organic linker used to build the framework of every catalyst was different, and thus the different characteristics and conversion rates could be linked to this change in organic linker.

For a fixed catalyst loading, different catalysts did not give similar conversion rates. The characteristics that could affect the catalyst performance and the conversion rate corresponding to every catalyst are given in table 4.

MOF	UIO-66(COOH) ₂	UIO-66	UIO-66(NH ₂)
Organic Linker	1,2,4,5-benzene- tetracarboxylic acid	Terephthalic acid	2-Amino-terephthalic acid
Organic Linker Structure			
Acidity n(H ₂ SO ₄)/g (mmol/g)	3.85	3.4	2.85
Surface Area (m ² /g)	270	992	848
Conversion to Butyl Butyrate (5% loading) %	91	83	75

Table 4: Comparison of main characteristics of the three different UIO-66X MOFs

It is clear that the change of the organic linker used caused a change in the surface area and acid density of the catalysts. However, the conversion rate was directly proportional to the acid density and highly influenced by it. A greater acid density lead to higher conversion even when the surface area of more efficient catalyst was lower. A conversion rate of 91, 83 and 75% (average over three runs) was achieved when the catalyst used was 5% of UIO-66(COOH)₂, UIO-66 and UIO-66(NH₂) respectively. Although UIO-66(COOH)₂ had the lowest surface area among the two other MOFs, but it also had the highest total acidity and lead to the highest conversion to butyl butyrate

of approximately 91%, very close to the 96% achieved by the liquid homogeneous strong acid H₂SO₄.

This could be attributed to the 2 free carboxylic acid groups dangling from the organic linker of UIO-66(COOH)₂ which are of known Brønsted acidity. The hydroxyl groups created by the defects in UIO-66 MOFs that resulted in an acid density slightly inferior to that of UIO-66(COOH)₂ contributed to almost 83% conversion. Although it had significantly higher surface area, the small difference in acid density and Brønsted acidity strength between hydroxyl and carboxyl functional groups had a visible impact on the reaction rate. This was more significant when comparing the performance of UIO-66(COOH)₂ to that of UIO-66(NH₂). Carboxylic acid active sites have stronger Brønsted acidity than amino activated linkers. Moreover, the total acidity test revealed that UIO-66(NH₂) was less abundant in acidic sites as it had a significantly lower acid density. This was directly reflected by a drop of the conversion rate from 91% to 75% when UIO-66(NH₂) was used instead of UIO-66(COOH)₂. In this case also the surface area of the catalyst showing lower conversion was higher than the catalyst leading to the highest conversion. This could be explained in two ways. On one hand, this could mean that the surface area of UIO-66(COOH)₂ was sufficient to make the acid sites well accessible and thus an increase in this surface area did not have a significant effect on the performance of the other catalysts as all the active sites were already involved in the reaction at lower surface areas. On the other hand, the results could mean that even if a smaller percentage of the total active sites were accessible at the lower surface area of UIO-66(COOH)₂ than it was for UIO-66 and UIO-66(NH₂), the total Brønsted acidic sites involved in the esterification reaction given the higher acid density of UIO-

66(COOH)₂ were still more than the ones involved when using UIO-66 and UIO-66(NH₂) having lower acid densities.

Figure 29 shows a comparison of the conversion curves of different catalysts used and the conversion curve when liquid sulfuric acid is used. The conversion curve

100 95 91 90 83 80 • 75 70 Butyl Butyrate Yield 60 50 • 45 40 **UIO66** 30 • UIO66(COOH)2 20 • UIO66(NH2) Sulfuric Acid 10 • No Catalyst 0 0 2 4 6 8 10 12 14 16 18 20 22 24 26 Time (Hours)

of a reaction that occurred without any catalyst was used as a control.

Figure 29: Conversion to Butyl Butyrate using the various acid catalysts

4. Heterogeneity test

After successfully running the esterification reactions using MOFs, and after confirming they have an acidic nature, it was then interesting to know if this acidity and thus activity is retained in the heterogeneous catalyst structure or if it leaching out in the reaction medium. If active sites are leaching in the reaction mixture, a decreased activity of the catalyst will be observed after every recovery cycle and thus its recycling wouldn't be as beneficial. The heterogeneity test was performed for all MOF catalysts to assess their heterogeneous nature. This was done by monitoring the conversion of the reaction after removing the catalyst from the reaction medium by centrifugation.

After stoping the reaction after six hours (t = 6hr), the catalysts were centrifuged out and the reaction continued afterwards without the catalyst. The results are shown in figure 30 for all three MOFs tested.



Figure 30: Heterogeneity test results using different catalyst

It is clearly shown that no significant conversion was obtained after removing the catalyst for all three cases reflecting a heterogeneous nature of the catalysts. However, this heterogeneous nature is not the same for all three cases. For the UIO-66 and UIO-66(COOH)₂ only 14 and 12% additional conversion to butyl butyrate was observed after the catalyst removal, which is comparable to the 13% value for the reaction that occurs without catalyst. This reflects little or no leaching of acidic sites in the reaction medium. As for the UIO-66(NH₂), the reaction conversion to butyl butyrate over the last 18 hours is higher and is of the order of 21%. Although this percentage is still significantly less than the 37% conversion that is obtained if the catalyst was not removed, but it is still relatively higher than the 13 % of conversion in case the reaction was operating with no catalyst or active sites in the medium. This reflects that there might have been active sites leaching throughout the reaction that contributed to this increased conversion after the solid catalyst was removed. Also, some of the MOF particles are too small to be removed by centrifugation and they could contribute to the catalytic process.

C. Effect of Catalyst Recycling

There are mainly two characteristics to be investigated in a heterogeneous catalyst for it to be recyclable: Stability and Activity. That is why after every catalyst recovery cycle, MOFs' stability is assessed using XRD and its activity as a catalyst is tested in a new esterification reaction.

After every usage of a MOF in the esterification reaction, the heterogeneous reaction mixture was centrifuged. MOFs were then separated, washed and activated again for further usage. Before using the MOF for another cycle, XRD is used to ensure that the crystalline structure of the recovered powder is still intact and that it is still stable. Results are shown in figure 31. UIO-66X MOFs have shown great stability in the reaction medium as it is reflected by their XRD patterns. All peaks that are present for fresh MOFs are also maintained in recycled MOFs for all three recycling cycles, which reveals a robust and reliable structure which is essential in heterogeneous catalysts.



Figure 31: XRD Patterns (A) UIO-66(NH2) (B) UIO-66(COOH)2 (C) UIO-66 (a) Fresh MOF (b) First recovery cycle (c) Second recovery cycle (d) Third recovery cycle

The second factor to consider when catalysts are recycled is their activity after recycling relative to that when they are freshly used. Figure 32 shows the conversion to Butyl Butyrate using UIO-66, UIO-66(COOH)₂ and UIO-66(NH₂) as catalysts in the esterification reaction as fresh catalysts and as recycled catalysts over three recovery cycles. In confirmation with the results of the heterogeneity test, all catalysts showed little activity loss and no major deactivation of the catalysts was noted. Although UIO-66 and UIO-66(COOH)₂ performed better than UIO-66(NH₂) in recovery, all catalysts had good stability and activity after several usages in the esterification reaction. In another study, a catalyst synthesised from the carbonization of Miscanthus x giganteu
was sulfonated and used for the esterification reaction of butyric acid with butanol to produce butyl butyrate ⁵⁵. Although the freshly synthesised catalyst performed well (94.5 % conversion to butyl butyrate), but the recovery of the catalyst caused its significant deactivation (almost 50% less conversion after 4 hours of reaction for the first recovery cycle). Deactivation of the heterogeneous catalyst after its recovery deprives it from a major advantage over homogeneous catalysts which is the ability to be reused. Although using a heterogeneous catalyst will eliminate the need to have a separation unit to purify the product from the catalyst itself, but the need to use a new heterogeneous catalyst loading every time will increase the production cost of butyl butyrate. The maintained activity in MOFs tested proves that they could be used as efficient heterogeneous catalysts in many organic reactions.



Figure 32: Conversion to Butyl Butyrate using UIO-66, UIO-66(COOH)2 and UIO-66(NH2) over three recovery cycles

CHAPTER V

CONCLUSION & FUTURE WORK

In this research work, the activity of a new class of heterogeneous, low cost, chemically and thermally stable catalysts was investigated. Zr-based Metal-Organic Frameworks were successfully synthesized and used for the catalysis of the esterification reaction of butyric acid to produce a gasoline and Diesel emerging bio-alternative/additive, Butyl Butyrate.

The work done in this thesis allowed understanding the relation between the structure and properties of the new emerging materials, MOFs, and their catalytic activity in esterification reactions that would allow the efficient, environmentally friendly and globally scaled production of liquid petroleum-based fuels alternative.

All catalysts were successfully synthesized and their characterization revealed their high purity and crystallinity. The Zeolitic Imidazolate Framework ZIF-8 was surprisingly not stable in the reaction medium despite the extensive research reporting its exceptional stability. Other Zr-based MOFs produced, UIO-66, UIO-66(COOH)₂ and UIO-66(NH₂), showed high stability and were successfully used as catalysts in the esterification reaction.

For all catalysts used, an increase in the catalyst loading lead to a better Butyl Butyrate yield. A 5% loading of UIO-66(COOH)₂ lead to 91% conversion to butyl butyrate, slightly inferior than the conversion reached using the conventional homogeneous liquid catalyst H₂SO₄ (96%). The acid density in the catalysts was tightly related to the structure of the framework and the organic ligand used. Catalysts with higher acid densities showed better catalytic activity. The surface area of MOFs did not seem to have an effect as significant as that of the acid density as the conversion was

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proportional to the abundance of acidic sites even when lower values of surface area were encountered. Most importantly, all catalysts were easily separable from the reaction medium and they were recovered and successfully used for other esterification reactions over three recovery cycles without a significant loss in the catalytic activity. MOFs have thus proved to be very interesting heterogeneous catalysts that, in case well developed, could be the next generation of industrial catalysts for biofuels production.

The research done in this thesis will be part of a bigger future project. After investigating the main factors influencing the conversion and catalytic activity, efforts will focus on developing a catalyst for the one-step hydrogenation esterification reaction to produce butyl butyrate directly from butyric acid. This will require the catalyst to be of bifunctional nature and to be active both in the hydrogenation and esterification reactions. The activity in the esterification reaction was shown to depend highly on the acidity of the MOF that could be modified either by changing the organic linker while synthesizing the MOF or by post-synthetic treatments such as sulfonation. Thus the catalytic activity of the MOF in the esterification reaction will be enhanced by further increasing the acid density and abundance in the framework using previously mentioned methods. The second part would then be the incorporation of a noble metal in the framework that would make it active in the hydrogenation reactions. This will be done through a post-synthetic treatment in which the MOFs will incorporate a new noble metal in their structure. The development of catalysts that allow the efficient and successful synthesis of butyl butyrate by the one-step hydrogenation esterification reaction would make a valuable step in the field of catalysis for biofuels production.

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