

Microwave-assisted Dehydration of Fructose into 5-Hydroxymethylfurfural (5-HMF) over Acidic Porous Catalysts

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ABSTRACT

Extensive consumption of carbon resources has led to decreasing reserves of fossil fuels and growing concern about global warming. This dilemma has promoted a shift in the economy to develop new long-term, environmentally friendly, and sustainable sources for fuels and chemicals to replace fossil fuel-based sources. Renewable biomass is an ideal alternative, as it is abundant, and relatively cheap. Among current biofuel resources, 5-hydroxymethylfurfural (5-HMF) is a versatile intermediate between biomass-based carbohydrate chemistry and fossil fuel-based industrial organic chemistry, which can be used to synthesize a broad range of chemicals that are currently derived from fossil fuel-based resources. Carbohydrates became the preferred feedstock for high yield production of 5-HMF, and the most convenient route for the synthesis of 5-HMF is the acid-catalyzed dehydration of hexose. Within this context, a variety of processes were developed for the synthesis of 5-HMF from dehydration of fructose involving various solvents, including water, organic solvents, and biphasic systems. Likewise, a range of catalysts were employed, such as homogeneous acid catalysts and metal chlorides, which showed high catalytic activity. Heterogeneous catalysts have also been receiving attention due to their advantages such as easy recovery and recyclability. In the current research, microwave-assisted synthesis of 5-HMF by dehydration of fructose over various acidic porous catalysts, such as periodic mesoporous organosilica (PMO), carbon materials, and metal organic frameworks (MOFs), was investigated. The results showed that the obtained 5-HMF yields were satisfactory, and more importantly highlighted some of the properties of porous heterogeneous catalysts that may improve the production of 5-HMF.

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ABBREVIATIONS

5-HMF	5-Hydroxymethylfurfural
AC	Activated carbon synthesized via hydrothermal carbonization process
BDC	Benzenedicarboxylate linker
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
BTEB	1,4-Bis(triethoxysilyl)benzene
BTEBP	4,4'-Bis(triethoxysilyl)-1,1'-biphenyl
bip-PMO	Biphenylene-bridged periodic mesoporous organosilica
CMK-3	Ordered carbon material synthesized via hard-template process
DHMF	2,5 Dihydroxymethylfuran
DMF	2,5-Dimethylfuran
DMSO	Dimethylsulfoxide
FDCA	2,5 Furandicarboxylic acid
FTIR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatography
IL	Ionic liquid
KJS	Kruk-Jaroniec-Sayari
MI	Microwave irradiation
MIL-53(Al)	Al-based metal organic framework
MCM	Mobil Composition of Matter

MOF	Metal organic framework
NMR	Nuclear Magnetic Resonance
ODTMA	Octadecyltrimethylammonium chloride (C ₁₈ Cl)
OMC	Ordered mesoporous carbon
PMS	Periodic mesoporous silica
PMO	Periodic mesoporous organosilica
p-PMO	Phenylene-bridged periodic mesoporous organosilica
PSM	post-synthetic modification
-S	Suffix represents sulfonated samples
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TEOS	Tetraethylorthosilicate
TGA	Thermogravimetric Analysis
UiO-66	Zr-based metal organic framework
XRD	X-ray diffraction

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CHAPTER 1 – INTRODUCTION AND MOTIVATION

1.1 Introduction

Fossil fuels are the predominant source of energy in the world, and also serve as a feedstock for many chemicals. The current pressure on fossil fuel reserves raises serious challenges for future energy supplies. Combustion of fossil fuel is also the primary source of greenhouse gases, which pose a serious threat to the environment. Therefore, exploring alternatives to fossil fuels is of great importance. One of the most promising alternatives is biomass, owing to its abundance and renewable nature. Therefore, much attention has been paid to developing sustainable biomass-based processes for chemicals and liquid biofuels. 5-Hydroxymethylfurfural (5-HMF) is one of the most promising biomass platforms. It holds a key position in the production of liquid biofuels and biomass-derived intermediates including a vast number of chemicals. For example, 5-HMF is a precursor for furandicarboxylic acid (FDCA), a compound that can directly replace petroleum-based terephthalic acid in polymer manufacturing of polyethylene terephthalate (PET). The most convenient route for 5-HMF synthesis is acid-catalyzed dehydration of hexoses. Notice that, when using biomass-derived carbohydrates in this synthesis, all of the carbohydrates are hydrothermally converted into fructose. Therefore, the production of 5-HMF by fructose dehydration has been the subject of extensive studies.

An ideal system for the production of 5-HMF from fructose dehydration should selectively convert all the fructose into 5-HMF, which can be achieved by optimizing two main factors: solvents and catalysts. Solvents direct the reaction towards higher selectivity

for 5-HMF over other byproducts by increasing the concentration of important intermediates or preventing undesired side-reactions. Furthermore, solvents play an important role in facilitating the diffusion of substrates during the reaction. Studies on the role of aqueous, organic, and mixed solvents showed that despite the advantages of water as a green solvent, the best results were obtained in a mixed media. As for catalysts, an efficient catalyst must easily convert a substrate into the desired product. A vast number of pioneering researchers have studied various homogeneous catalysts that result in relatively high yields of 5-HMF. However, they pose major challenges regarding their separation and recyclability, as well as system corrosion. The need to overcome these issues led to extensive studies on heterogeneous catalysts in which porous materials received much attention owing to their distinctive structural properties, such as large surface area and tunable pore size. Not only have studies on individual homogeneous and heterogeneous catalysts been conducted, but also efforts have been made to combine both, in which strong acids, *e.g.* sulfonic acid was covalently tethered to solid supports. This area became the goal of biomass catalysis research, but it still requires further work to study the effectiveness of such catalysts in biomass conversion to 5-HMF. Furthermore, comparative studies would be very beneficial to determine the best catalyst support.

In this thesis, the effect of different porous supports on the catalytic activity of sulfonic acid groups for the production of 5-HMF through fructose dehydration will be illustrated. Three main porous materials were chosen as catalyst supports based on silica, carbon, and metal organic frameworks. These materials exhibit interesting structural properties and are promising catalyst supports. The acid-catalyzed reaction was performed

in organic solvents under microwave irradiation. Regarding the experimental work, all the synthesis procedures and catalytic experiments as well as IR, TGA, Nitrogen Porosimetry, and HPLC analysis were conducted by the author. The other material characterizations including NMR, XRD, elemental analysis, SEM and TEM were performed in specialized facilities at the University of Ottawa.

1.2 Methodology

This research is focused on understanding the role of catalyst supports on the catalytic performance of sulfonic acid groups in catalyzing fructose dehydration into 5-HMF in an efficient media. It is thus a contribution to developing an ideal system for the production of 5-HMF by studying the potential and limitations of three major classes of porous materials, namely periodic mesoporous organosilica (PMO), carbon materials, and metal organic frameworks (MOFs). All catalysts were chosen based on their suitable structural properties. This thesis is organized as follows:

Chapter 2 – Literature Review

This chapter is a brief introduction to biomass catalytic transformations, specifically the formation of 5-HMF and the most effective systems of fructose dehydration. It also provides details on porous materials based on silica, carbon, and metal organic frameworks, and describes their unique properties, synthesis methods, and incorporation of sulfonic acid functional groups, which are required for these materials to catalyze fructose dehydration. Overall, this chapter summarizes the basics of designing an efficient dehydration system for the synthesis of 5-HMF from fructose.

Chapter 3 – Experimental and Instrumentation

This chapter provides all the experimental information about the synthesis procedures and the characterization techniques. Further, it describes the procedure of fructose dehydration and the quantitative analysis of 5-HMF, as well as calculations to determine the percentage yield of 5-HMF. The catalysts recyclability steps are also listed.

Chapter 4 – Results and Discussion

In this section, the composition and textural analysis of each acidic porous catalyst are examined in detail, and the catalytic reaction data are provided. The impact of the catalysts' structural properties on the catalytic efficiency is discussed and the most effective catalysts are highlighted. Possible reasons for the less-effective catalytic behavior are also proposed. The reusability of all catalysts is also presented.

Chapter 5 – Conclusion and future work

The objective of this chapter is to summarize the main findings and to shed light on possible future developments of acidic porous catalysts in order to enhance the reaction productivity.

CHAPTER 2 – LITERATURE REVIEW

2.1 Biomass Catalysis

2.1.1 Fossil fuel limitations

Energy resources are of crucial importance to the world's future because of the increasing demand for energy to sustain and enhance our quality of life, industrial energy needs, and the growing global population. There are three main sources of energy: namely fossil fuels, renewable, and nuclear sources.[1][2]. In 1999, the *International Energy Agency (IEA)* reported that fossil fuels, including oil, natural gas, and coal, are the dominant source of energy in the global market since 1971, and it is expected to remain the primary energy resource for years to come. Figure 2.1 shows that in 2020 about 88% of total global energy production will come from fossil fuels, with other sources like hydro and nuclear making up the bulk of the remainder, along with a negligible amount from other renewable sources.[3] Furthermore, in 2007, the *World Energy Investment Outlook (WEIO)* also claimed that fossil fuels would remain the major source of energy with almost the same percentage until 2030.[4] Despite this prediction, fossil fuels have serious issues related to longevity and environmental impact. Many studies have attempted to estimate the fossil fuel reserves depletion time. Topal and Shafiee[5], for example, reported that fossil fuels as a whole will be exhausted by 2112, while petroleum products will be completely exhausted by 2042. Moreover, the rate of consumption is increasing rapidly due to continuing population growth, which leads to higher amounts of CO₂ emissions. The rate of CO₂ emissions was predicted to increase gradually from 14,732 million tons in 1971 to 37,848

million tons in 2020 by the IEA.[1][6] Moreover, consumption of fossil fuels is a major cause of global warming due to greenhouse gases (GHGs), including CO_x and NO_x [7], which is the primary motive in the search for substitute energy sources.

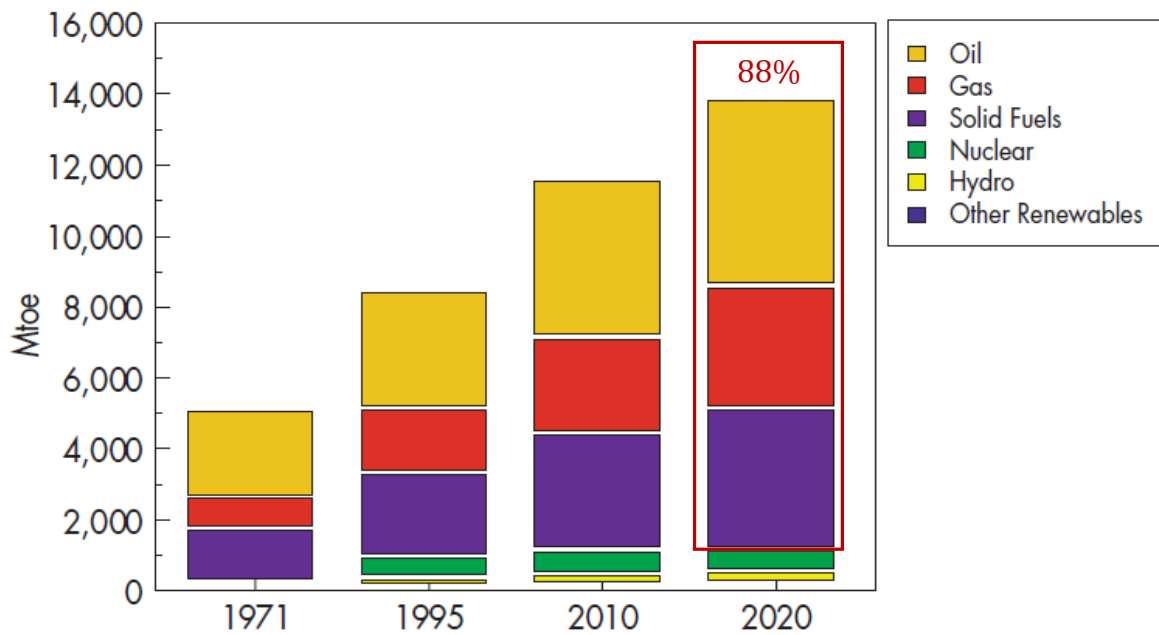


Figure 2.1 World primary energy demand reported by the IEA.[3]¹

Although fossil fuels are a limited resource with unwelcome side effects, world energy demand is certain to remain high and will likely increase. Therefore, researchers are devoting substantial attention to finding a clean, efficient, and economical energy alternatives. Enormous efforts have been expended to develop renewable energy sources (RESs), a term that refers to all forms of energy generated from renewable sources, such as biomass, hydroelectric, solar, wind, geothermal power, and nuclear, with no pollutants or net GHG emissions.[1][2] In 2006, *the European Renewable Energy Council (EREC)* stated that by 2040, RESs will compose nearly half of the global energy supply, with 48% coming

¹ **Mtoe** (megatone) is a unit of energy defined as a million tonne of oil equivalent.

from biomass (Figure 2.2).[8] Similarly, *the United Nations Conference on Environment and Development* (UNCED) declared that biomass would be able to supply half of global primary energy consumption by 2050.[1] These high expectations for biomass to be a substantial RES are due to many reasons, such as their abundance, regeneration ability, processes of conversion to energy, and environmental impacts.[8]

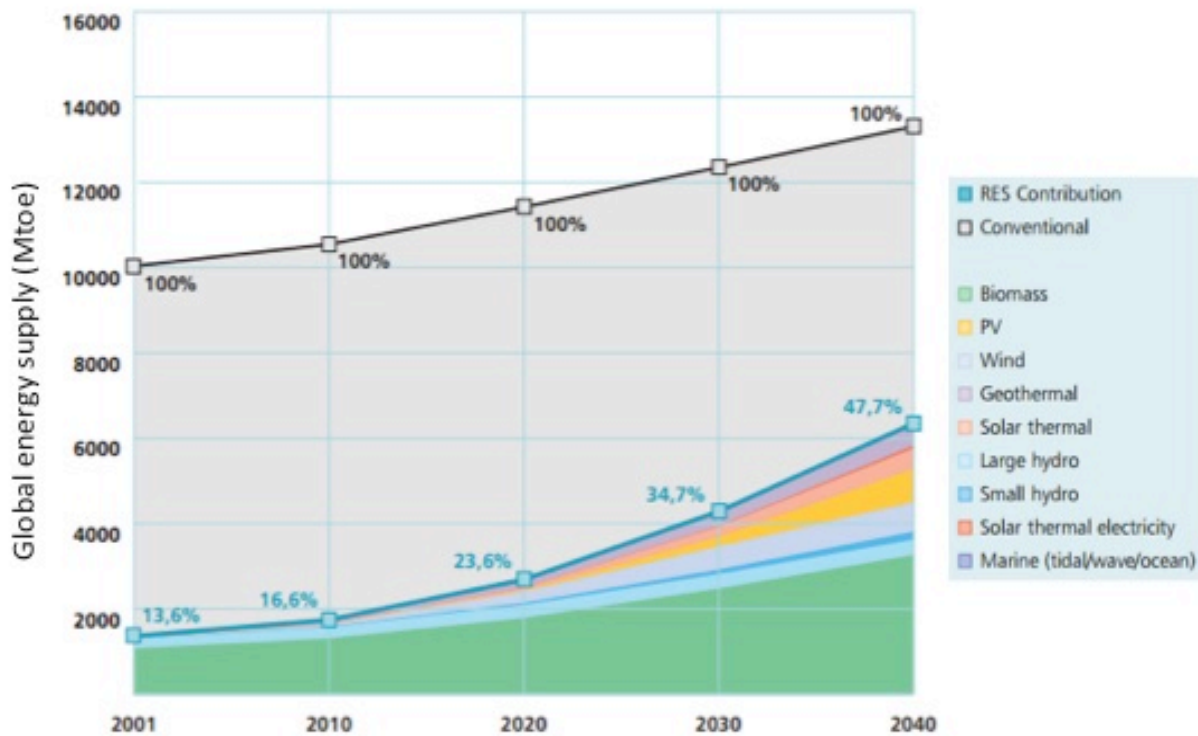


Figure 2.2. Global renewable energy scenario up to 2040.[8]

2.1.2 Biomass as an energy source

Biomass refers to organic matter composed mainly of carbon, hydrogen, and oxygen.[7] Generally speaking, biomass includes all vegetation and organic-based waste. As an alternative to fossil fuels, biomass has a high utilization possibility owing to it being the second-largest energy source in the world after fossil fuels including coal, petroleum and

natural gas.[9] The energy in biomass is stored solar energy in the chemical bonds of the carbohydrate molecules that make up the main substrate of plants. Specifically, Figure 2.3 shows that CO_2 , H_2O , and sunlight are consumed during the process of photosynthesis, so a portion of solar energy is trapped in the carbohydrate building blocks of the plants produced. When the plants decompose and the chemical bonds of the carbohydrates break as a consequence, they release heat and CO_2 , which can be utilized again in another photosynthesis cycle. [1][9][10]

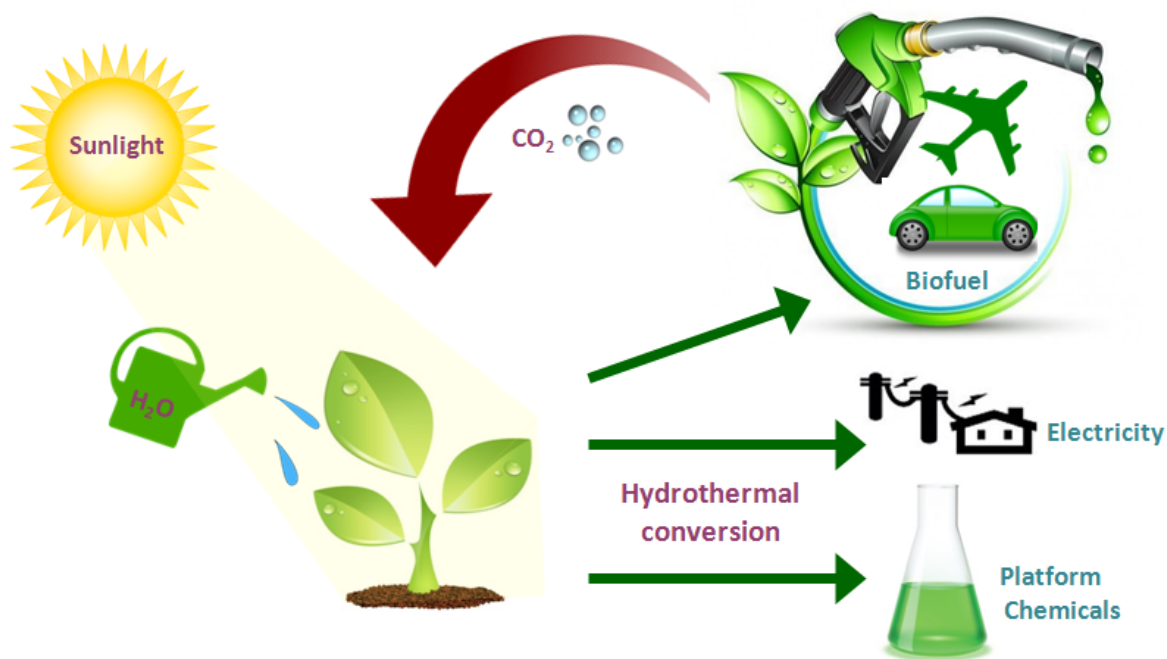


Figure 2.3. Photosynthesis of plants and the products of the hydrothermal conversion of biomass.

Biomass, mainly in the form of wood, was long the foundational energy source for human beings. Combustion of biomass was their main source of heat in the past, and the process is still used actively in many parts of the world.[9] In terms of industry, biomass is utilized to meet important energy needs, including generating electricity, fueling vehicles,

and providing feedstock for chemical synthesis, as indicated in Figure 2.3. In recent years, it has been estimated that biomass contributes 10–14% percent of the world's energy supply.[10] Furthermore, the *WEIO* report of 2014 showed that there is a growing interest in investing in renewable energy sources, with an increase in annual investment from US\$60 billion in 2000 to US\$300 billion in 2011.[11] The importance of biomass as a sustainable energy source is due to the following reasons:

- **Abundance**—the annual world production of biomass was evaluated at 146 billion metric tons a year, with about 75% in the form of carbohydrates. Only 3–4% of this material is used in the food or non-food sectors.[11][12]
- **Low cost**—the cost of producing energy from fossil fuel has reached the point where it is becoming more expensive than the cost of biomass fuels.[1] In addition, biomass is a native resource over a large portion of the earth's landmass, so it is less susceptible to market fluctuations than fossil fuels.
- **Renewable**—biomass is the only renewable source of carbon that can be converted into value-added chemicals and fuels. Additionally, growing plants takes only months, offering a short production cycle compared to fossil fuels.[10]
- **Ecofriendly**—while the combustion of biomass to produce energy is quite similar to fossil fuels, it releases substantially lower amounts of pollutants. It is also considered a less harmful process of waste disposal, since it burns waste to produce energy. In principle, burning biomass does not increase the amount of CO₂ in the air because it is understood to be completely utilized in the photosynthesis process.[1] Furthermore, the amount of pollutants released from biomass conversion into energy is very small

compared to other energy sources. For example, the amount of sulfur dioxide produced from biomass is 90% less than coal.[9]

Biomass advantageously differs from other renewable sources of energy because it can produce energy through many conversion processes such as hydrolysis, pyrolysis or liquefaction, and gasification to produce a wide variety of chemicals and biofuels as presented in Figure 2.4.[1][9][13] The type of the applied conversion process significantly affects the form of energy obtained. For instance, gasification produces gaseous products which are mostly used in generation of heat and electricity in an engine, while products resulting from pyrolysis process can be applied in fuel manufacturing.[1][7][13] Besides that, biomass has several supply sources including wastes (*e.g.*, agricultural and industrial waste), forest products (*e.g.*, wood and trees), energy crops (*e.g.*, starch, sugar, and oilseed), and aquatic plants (Figure 2.4).[8] The value of the energy obtained from a selected biomass material depends essentially on the source of biomass used due to the different carbon/hydrogen content which is determined via the calorific value. Calorific value (CV) of a biomass material is a term indicating the energy content or heat value, that is released when the material is combusted in air. CV is measured based on the percentage of carbon and hydrogen, as the main contributors of the released heat value.[10] The source of biomass and the selected conversion process are of a great importance in the production of value-added chemical and fuels.[10][12]

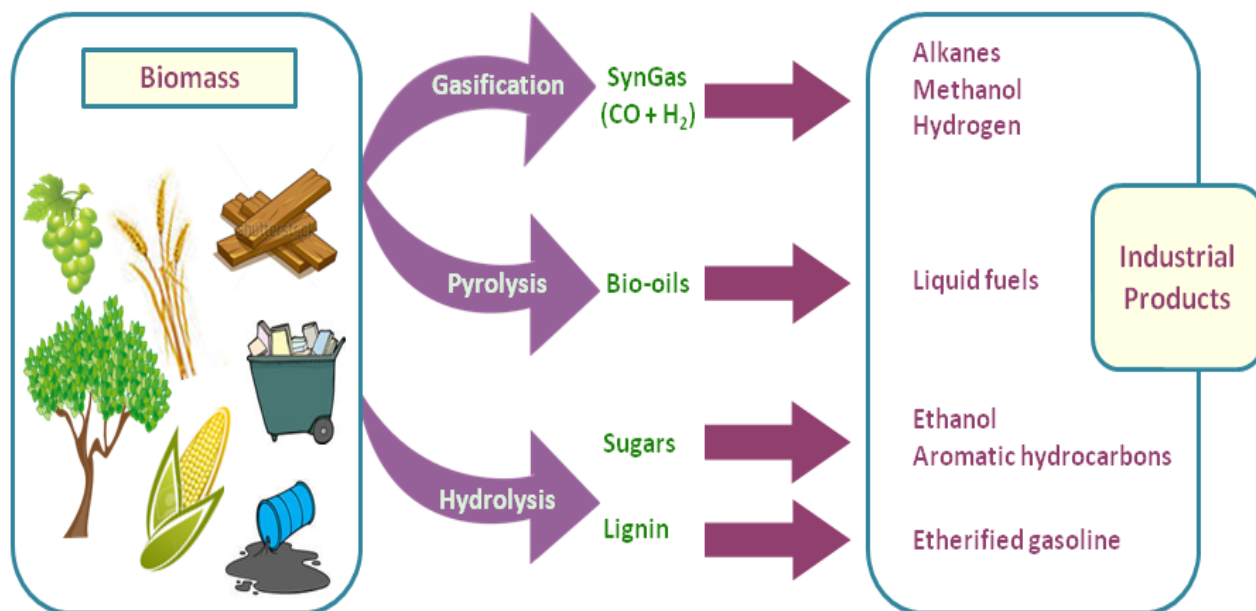


Figure 2.4. Schematic illustration of various sources of biomass and strategies for production of fuels and chemicals from biomass.

The chemical structure and organic components of biomass play an important role in the production of fuels and chemicals. In general, biomass is composed of mainly organic elements and a modest amount of inorganics. The elemental content of biomass in decreasing order is carbon (60-30%), oxygen (30-40%), and hydrogen (5-6%). Inorganic elements, such as sulfur, chlorine, calcium, potassium, silicon, magnesium, and aluminum, are found in minuscule amounts in biomass, largely in ash.[7] The main component of biomass (Figure 2.5) is referred to as lignocellulose, which is made of four main materials: cellulose (38-50%), hemicellulose (23-32%), lignin (15-25%), and minor amounts of extractives.[14] The percentages of these components vary according to the type of biomass. The cellulose and hemicellulose contents constitute the carbohydrate portion of biomass, providing structural and mechanical strength. Lignin, the non-carbohydrate portion of biomass, maintains the stability of the structure.[7] Cellulose, the most abundant

natural sugar, is a polysaccharide with the general formula of $C_6H_{10}O_5$ and a high molecular weight of approximately 500,000. It consists of (1,4)-D-glucopyranose units linked in the β -1,4 position, as shown in Figure 2.5. Hemicellulose is a heteropolysaccharide composed primarily of monosaccharides in the D-configuration and pyranose forms, such as glucose, mannose, xylose, and arabinose with molecular weight below 30,000.[7][8][10] Lignin is an aromatic polymer containing phenylpropane units, and hydroxyl and methoxy groups connected by ether bonds that form a very resistant structure against thermal degradation. This resistance is due to the high energy content of lignin compared to cellulose and hemicellulose, which provides higher heating values.[7] Extractives are the smallest components, with less than 2% of the total weight of biomass. They are, nevertheless, of paramount importance as they determine features of plants such as color, smell, and taste. Extractives encompass a wide range of compounds, including phenols, fatty acids, proteins, fats, and resins.[7]

In terms of energy production from biomass, biomass-derived carbohydrates, cellulose, and hemicellulose may decompose thermochemically or biologically into fuels and chemicals. One of the common pathways to convert carbohydrates thermochemically into value-added chemicals, such as aromatic hydrocarbons, is pyrolysis, in which biomass-derived carbohydrates degrade into monosaccharides, which then undergo further chemical reactions, eventually yielding sustainable fuels and building block chemicals.[7][15][16] However, this direct conversion of biomass-derived carbohydrates is a challenging process.[7][15][16] Cellulose, the first carbohydrate obtained from the biomass decomposition process, is resistant to decomposition and is insoluble in most

solvents owing to its crystalline structure established by the hydrogen bonds between the multiple hydroxyl groups, making it difficult to degrade by limiting the access to the β -1,4 glycosidic bond or other functional groups (Figure 2.5).[7][17]

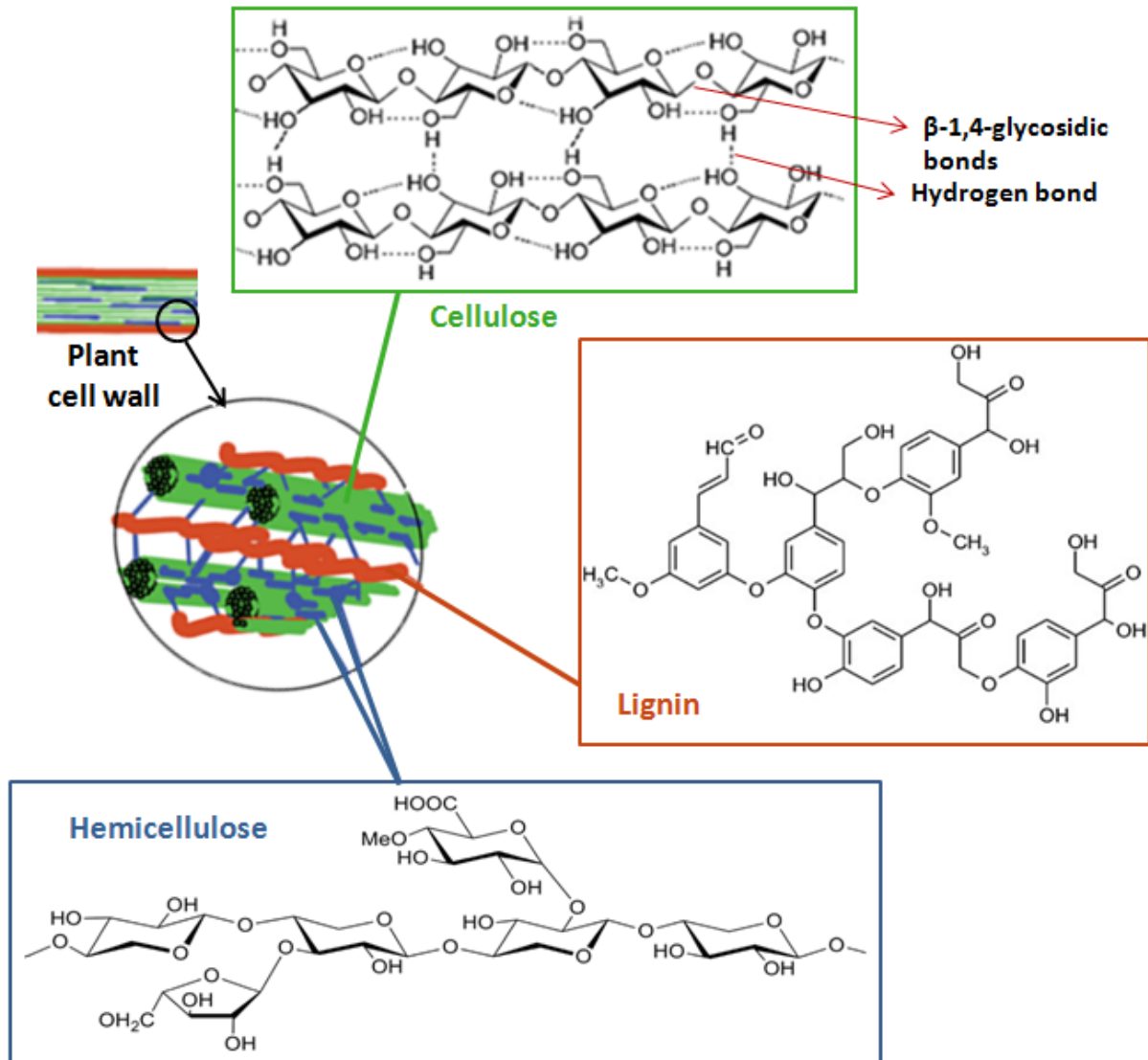


Figure 2.5. The components of biomass and their chemical structures.

2.1.3 Synthesis of 5-HMF from biomass

The present research is focused on the synthesis of scalable quantities of platform chemicals that can be converted into chemical building blocks and liquid biofuels.[18] Among the most promising chemical technologies, abstraction of three molecules of water from carbohydrates, namely hexose in the presence of acidic catalysts to generate 5-hydroxymethylfurfural (5-HMF), has been investigated extensively.[19] 5-HMF is an aromatic polyfunctional molecule that encompasses three functional groups, *i.e.*, a hydroxyl group, an aldehyde, and a furan ring (Figure 2.6), and it can be naturally found in coffee, honey, dried fruits, and fruit juices.[17]

5-HMF is one of the ten most significant biomass-derived platform chemicals, and it gained this important position because it serves as an intermediate compound that is converted into essential feedstock chemicals used in various industries, such as plastics, polymers, pharmaceuticals, and transportation fuels. It can be oxidized into 2,5-furandicarboxylic acid (FDCA), which is used as a platform, that substitutes petroleum-based terephthalic acid, for producing polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).[20] In addition, 5-HMF can be reduced to 2,5-dihydroxymethylfuran (DHMF), which plays the role of alcohol in the synthesis of polyesters, creating an entirely biomass-derived polymer when complexed with FDCA.[17] As for liquid-fuel production, 2,5-dimethylfuran (2,5-DMF) and 2-methylfuran can be derived from 5-HMF as potential transportation fuels.[21] Furthermore, 5-HMF can be used with no further modifications, *e.g.*, in pharmaceuticals research as a potential remedy for sickle cell disease (SCD).[22],

and in industry, such as in fuel cells.[23] Other products of 5-HMF and their possible applications are shown in Figure 2.6.

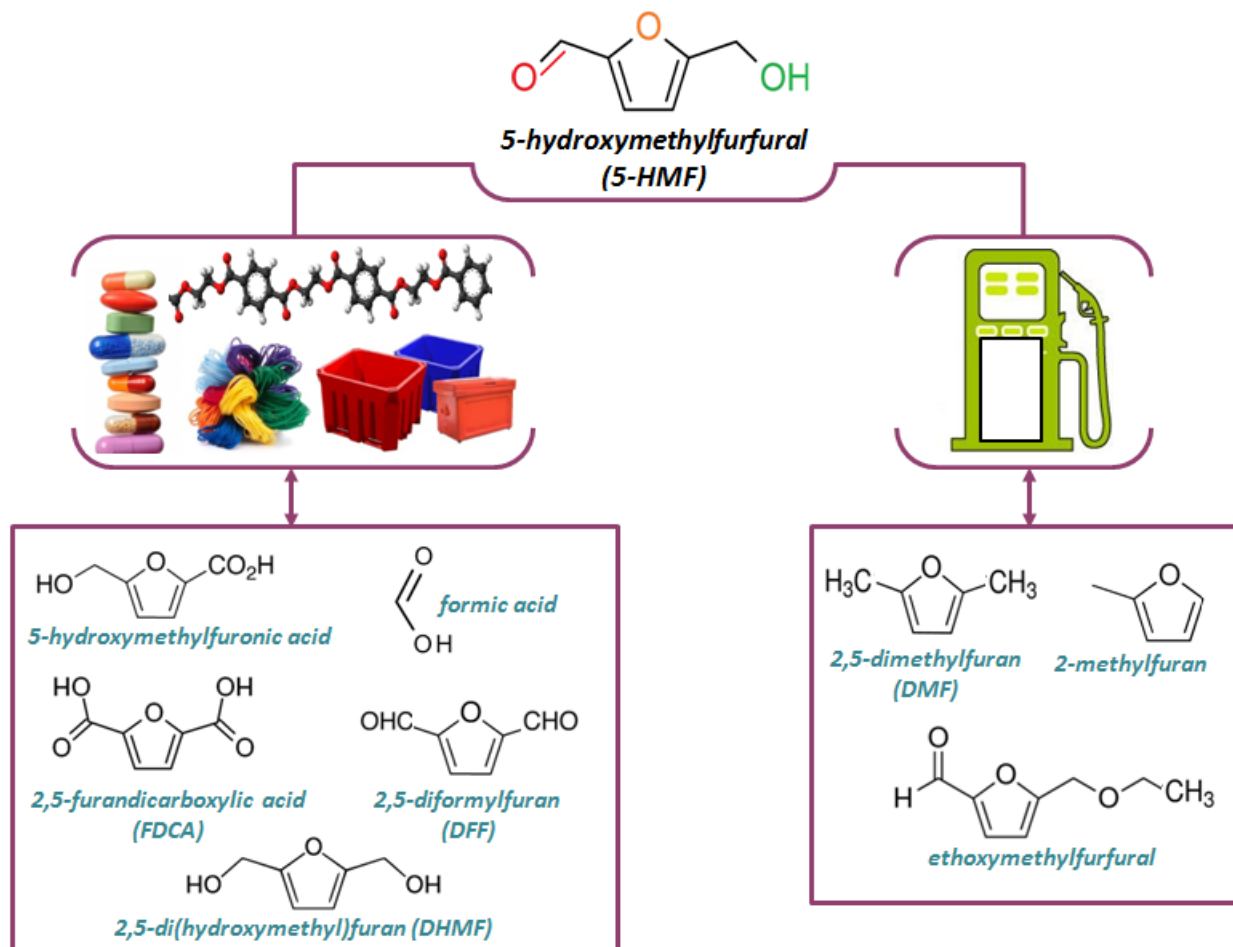


Figure 2.6. The derivatization of 5-HMF to produce valuable chemicals.

A major objective of developing an environmentally sustainable 5-HMF production process is to accomplish a simple access to scalable production of bio-based fuels and chemicals. The major challenges in designing such a process are related to the degradation process of biomass, along with the possible side-reactions of 5-HMF.[24][17] The non-digestible agro-residues are the ideal substrates for the large-scale production of 5-HMF, yet their conversion process is difficult. Also, 5-HMF may undergo side reactions such as

fragmentation, condensation, rehydration, and/or additional dehydration processes, resulting in a number of byproducts (Figure 2.7) that negatively affect the production process by decreasing the yield of 5-HMF.[17] Therefore, a vast number of studies have been conducted to select appropriate catalysts that are capable of enhancing the productivity of the reaction, especially when applied in an effective reaction medium under optimized reaction conditions. However, more work remains to be done to achieve a scalable production system for 5-HMF, in which the amount of byproducts is minimized and the conversion of substrates is maximized. Overall, an ideal production system should result in a high yield of 5-HMF that is selective with complete conversion of biomass-derived carbohydrate in the presence of a strong acidic catalyst. While attempting to achieve this objective, many systems have been proposed that focus on adjusting three main factors: substrates, reaction media, and—most importantly—acidic catalysts.

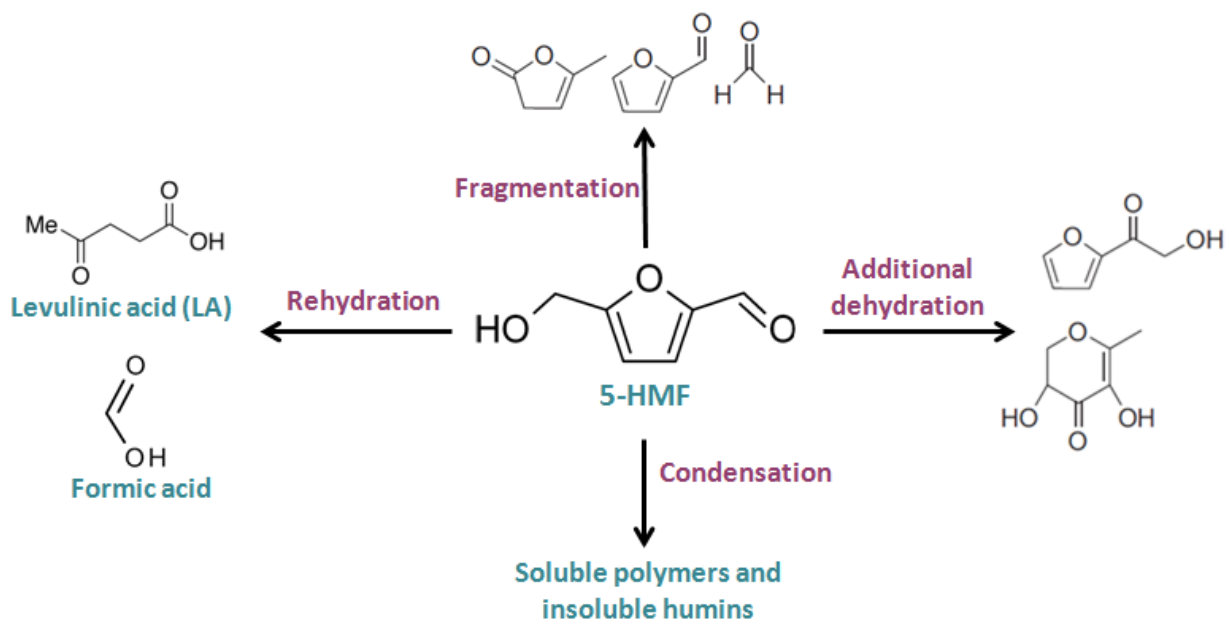


Figure 2.7. Representation of possible byproducts of 5-HMF during the fructose dehydration.

2.1.3.1 Feedstocks for 5-HMF production

A range of different substrates, such as raw biomass, polysaccharides, and monosaccharides (Figure 2.8), were investigated for 5-HMF production. The choice of biomass-based substrates with their different compositions and structures is a key point that drives the development of biomass catalytic conversion processes.

Raw biomass is the first reasonable choice as substrate for 5-HMF synthesis. For example, biomass with a high content of sugars, such as grapes, can be easily converted into 5-HMF without pretreatment.[25] However, to avoid competition with food supply, edible crop-derived biomass is not recommended for use in such commercial production.[26] Studies have also been conducted on other raw biomass sources, such as agricultural and forestry residues, and organic wastes, which are composed of varying amounts of cellulose and hemicellulose.[10] Among these, lignocellulosic biomass containing high proportions of cellulose and hemicellulose is the most suitable substrate as it thermally dissociates into hexose whose direct dehydration produces 5-HMF.[16] However, a separation step has to be carried out initially owing to the different chemical and physical properties of cellulose and hemicellulose, yet few researchers investigated the dehydration of lignocellulose without prior separation.[27][28] On the other hand, disaccharides and polysaccharides, such as sucrose, starch, and cellulose, are interesting substrates because they are the cheapest and the most abundant carbohydrates.[17] The main challenge in using these substrates for 5-HMF production is that they require a pretreatment step, *i.e.* degradation to monosaccharides, which complicates the reaction due to the formation of more byproducts and the challenging degradation process.[16]

Efforts have been aimed at hydrolyzing cellulose into its building block units (D-glucose), which is a crucial step in conversion of biomass in a large-scale production (Figure 2.8). The results, however, were disappointing because of the poor solubility of cellulose and its inactive structure. In addition, the employed methods were costly, produced low 5-HMF yields, along with a large amount of waste.[17]

The use of monosaccharides, such as glucose and fructose, as a feedstock for 5-HMF production is, however, more favorable. Fructose is preferred because it does not undergo isomerization as is the case with glucose (Figure 2.8). In addition, fructose forms intermediates, namely difructose dianhydrides (DFAs)[29][30], in which the most reactive groups for cross-polymerization are blocked, as depicted in Figure 2.8, thus reducing the amount of byproducts. In contrast, glucose forms oligosaccharides, which possess reactive groups, posing a major risk of cross-polymerization.[16][31][32] As can be seen in Figure 2.8, fructose is the actual starting material towards 5-HMF production since all other carbohydrates are converted to fructose before reacting further towards 5-HMF, which is a key step towards efficiently producing 5-HMF from biomass-derived carbohydrates.

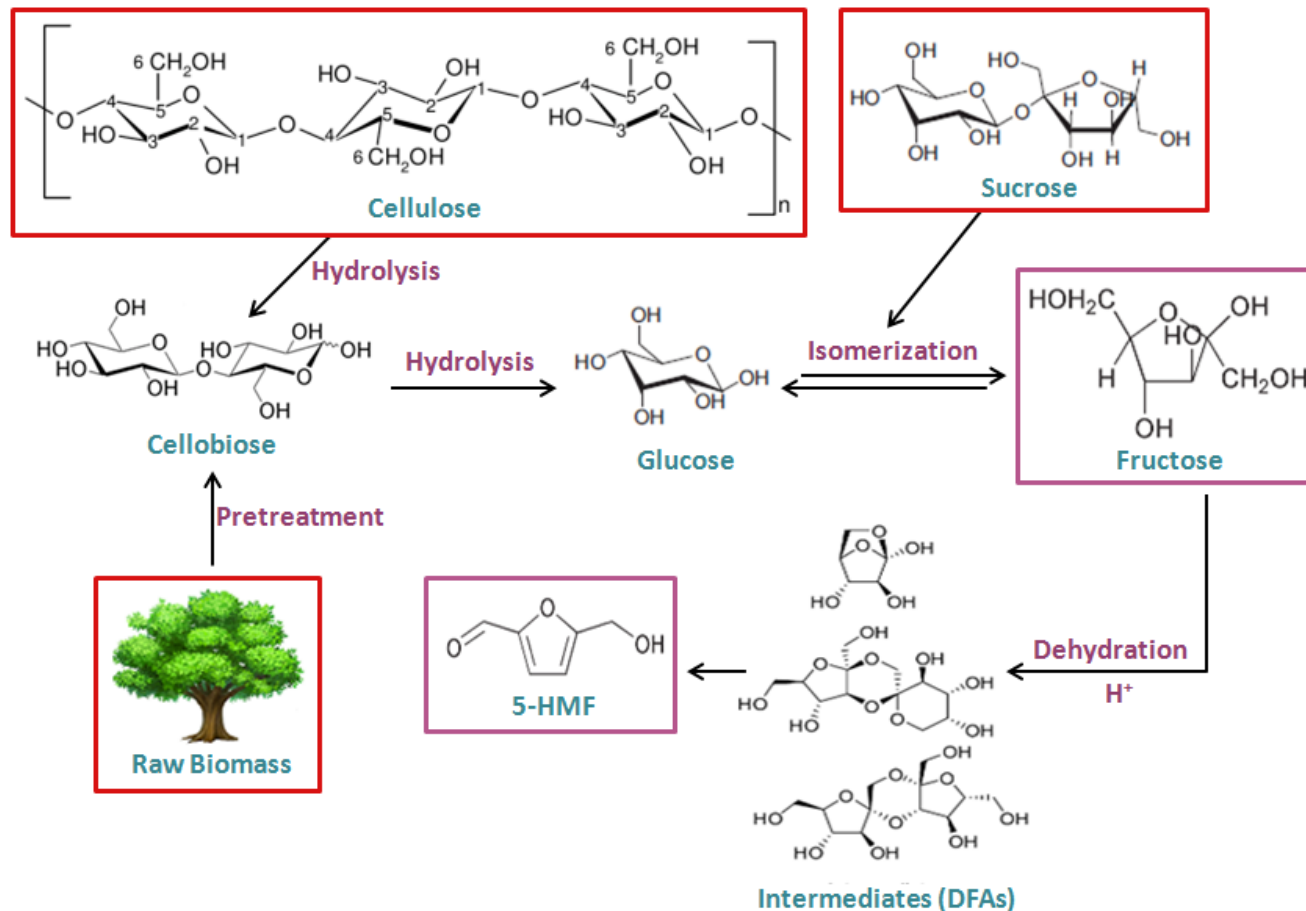


Figure 2.8. Pathways for the conversion of different substrates into 5-HMF.

2.1.3.2 Solvent systems

One of the main factors affecting the efficiency of carbohydrate conversion into 5-HMF is the solvent in which the carbohydrates are dissolved and the dehydration reaction takes place. In this regard, the choice of solvent is pivotal and governs the conversion of substrates and selectivity of the reaction.[17] Generally, a range of solvents, such as aqueous, organic, or mixtures of both, have been applied in 5-HMF synthesis.[24]

Undoubtedly, water is the most convenient solvent as it fits the "Green Chemistry" principles. In addition, water favors the conversion of hexose[24][33], although it also

facilitates the formation of many rehydration and condensation byproducts, such as levulinic acid (LA), formic acid, and soluble and insoluble polymers making the reaction nonselective.[34][35] These undesirable byproducts must be minimized in order to make the 5-HMF production more efficient. An important strategy to overcome the low yield of 5-HMF in water is to use supercritical water to decrease the reaction time, thus suppressing the side-reactions of 5-HMF.[36][37] Another major concern of using water as a reaction medium is the high possibility of catalyst deactivation or leaching.[38][39] In summary, in dehydration of carbohydrates into 5-HMF, water is a very attractive medium as in many organic reactions, yet it causes serious issues mainly related to the formation of byproducts.

Various organic solvents have been tested in the synthesis of 5-HMF from carbohydrates, such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), and tetrahydrofuran (THF). Among these, DMSO was found to be the most efficient solvent, as it facilitates the reaction steps towards a high yield of 5-HMF. This activity was assigned to the ability of DMSO to restrain the hydrolysis of 5-HMF into levulinic and formic acid (Figure 2.7) by bonding with water molecules generated from the reaction, thereby reduces the amount of water in the reaction mixture and thus prevents the rehydration of fructose.[40] For example, Shimizu et al.[41] achieved a high selectivity to 5-HMF (76%) in DMSO with the reaction taking place at 120 °C for 2 h, and the detected amount of levulinic and formic acid was 2%, and 1%, respectively. Another property of DMSO is that its ability to stabilize some important intermediates, such as fructosyl oxocarbenium ion and difructose dianhydrides (DFAs), which were proved to

drive the reaction towards forming 5-HMF instead of byproducts.[42][43][44] However, the main drawback with using DMSO as a solvent is related to recyclability. 5-HMF is miscible in DMSO, which makes the extraction step essential prior to recycling. Extraction of 5-HMF (291 °C) from DMSO (196 °C) consumes a large amount of energy because of the high boiling point of DMSO. This has led to approaches in which DMSO is mixed with low-boiling organic solvents to reduce the boiling point of the solvent system. Smith et al.[45] proposed a solvent system consisting of DMSO and acetone (boiling point 56 °C) in a various ratios. The obtained yield of 5-HMF was 73% in a ratio of 7:3 at 150 °C for 5 min under microwave irradiation, while only around 34% of 5-HMF yield was obtained in pure DMSO. Therefore, an organic solvent mixture with high yield of 5-HMF, negligible amount of byproducts, and reduced energy consumption is achieved when the solvent mixture consists of DMSO and a low-boiling point organic solvent.

A new approach was introduced in which a water-immiscible organic solvent (*e.g.*, methylisobutylketone (MIBK), tetrahydrofuran (THF), or benzonitrile) is added to the aqueous system. Such an approach aimed to achieve a continuous extraction of 5-HMF from the reaction mixture, resulting in reduced side-reactions of 5-HMF and better separation.[35] Unfortunately, partition of 5-HMF in biphasic systems from the aqueous phase into the organic phase was poor *e.g.* 5-HMF yield of 33% using an acidic ion-exchange catalyst in H₂O/MIBK[46], leading to the consumption of large amounts of the organic extractant phase.[47] However, according to Dumesic et al.[46][48], adding modifiers in both phases successfully increased the extraction percentage, *e.g.*, a high 5-HMF yield of 56% was obtained when the reaction was conducted in a two-phase reaction

system (Figure 2.9) consisting of an aqueous phase with DMSO and poly(1-vinyl-2-pyrrolidinone) (PVP), and an organic phase (the extraction phase) of MIBK modified with 2-butanol. Dumesic and his group attributed the enhancement of 5-HMF yield in the modified phases to the role of the added modifiers, DMSO/PVP, and 2-butanol, in decreasing the amount of byproducts, and improving the partition of 5-HMF, respectively.

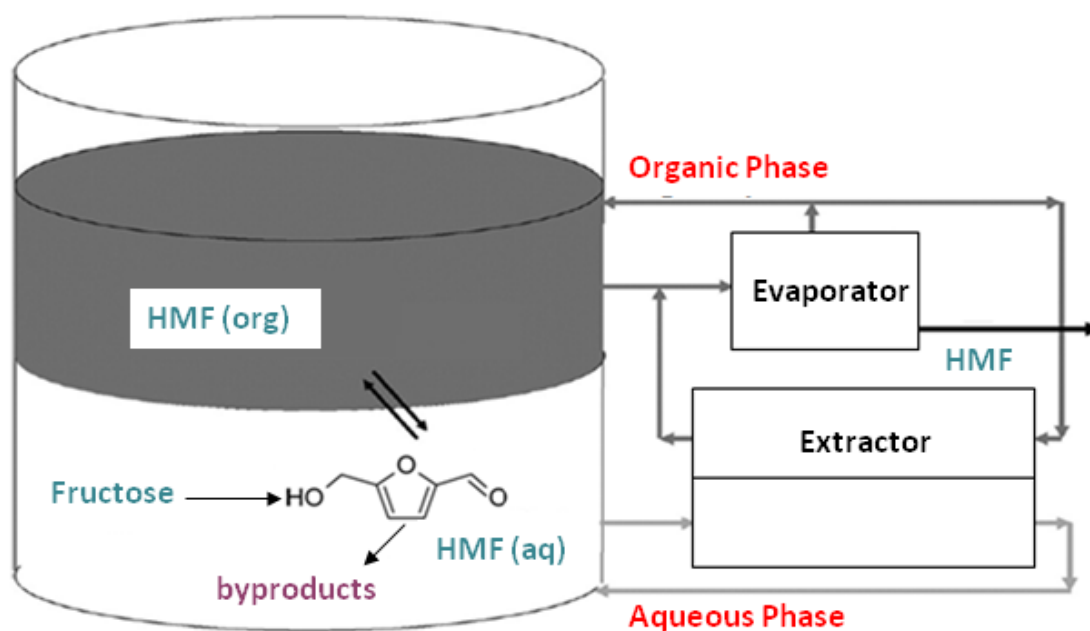


Figure 2.9. Schematic illustration of a two-phase reaction system for the production of 5-HMF through countercurrent extraction and evaporation steps. The aqueous phase consists of fructose, DMSO, PVP, and catalyst, and the organic phase consists of MIBK and 2-butanol.[46]

Recently, ionic liquids (ILs) have been introduced as solvents for the synthesis of 5-HMF. ILs are salts that are composed of ions, and mostly liquid at a temperature below ca. 100 °C.[49] There is great interest in ILs as green solvents because of their high stability, low vapor pressure, easy recyclability, and tunable chemical and physical properties.[49] Moreover, ILs were found to be capable of dissolving considerable amount of carbohydrates. Hence, ionic liquids can significantly enhance the straightforward

conversion of raw biomass into 5-HMF. For instance, a 61% yield of 5-HMF was produced upon heating wheat straw with [BMIM]Cl² at 160 °C for 15 min under microwave irradiation.[50] Nevertheless, ionic liquids suffer from some serious drawbacks. The high viscosity of ionic liquids is one of the main issues related to their solvation features because it decreases the mass transfer between the catalyst and the substrate.[51] Other problems related to ionic liquids are equipment corrosion, high cost, and unfavorable ecological footprints.[24]

As detailed above, numerous approaches have been attempted to enhance the production of 5-HMF by controlling the substrates and solvents. In addition, tremendous attention has been paid to developing innovative catalysts, since the catalyst is the key factor in enhancing the productivity of the reaction. For this reason, the catalysts will be discussed separately in more detail in the following section.

2.1.4 Catalysis

Catalysts are chemical materials that provide an alternative route for a reaction with lower activation energy, without being consumed during the process.[52] Catalysts can be involved repeatedly in sequential cycles, and so only a small amount of catalyst is needed. Generally speaking, homogeneous catalysis is a term describing a catalytic reaction where reactants, catalysts, and products are in the same phase, whereas heterogeneous catalysis involves different phases.[53] The catalyst efficiency can be expressed in terms of turnover number (TON) or turnover frequency (TOF) calculations.[53] In a homogeneous catalytic

² 1-Butyl-3-methylimidazolium chloride

system, “ the TON is the number of cycles that a one molecule of a catalyst can run through before it deactivates “[53], while the TOF is the number of reactant molecules that can be converted over one molecule of catalyst in one second. In a heterogeneous catalytic system, however, both TON and TOF are defined with respect to active sites.

The energy diagram of a catalytic process is illustrated in Figure 2.10. In a typical reaction, products form as a result of successful reactant collisions, which requires a very high kinetic energy, resulting in enough energy to overcome the activation energy barrier. In the presence of a catalyst, the required kinetic energy of reactants becomes lower as the activation energy barrier is remarkably decreased. However, the total energy between the reactants and the products does not change. Finally, the product is separated, detached from the catalyst in an endothermic step, and the catalyst may recover to be used in a new cycle.[52][53] In total, catalysts provide a faster route to a desired product.

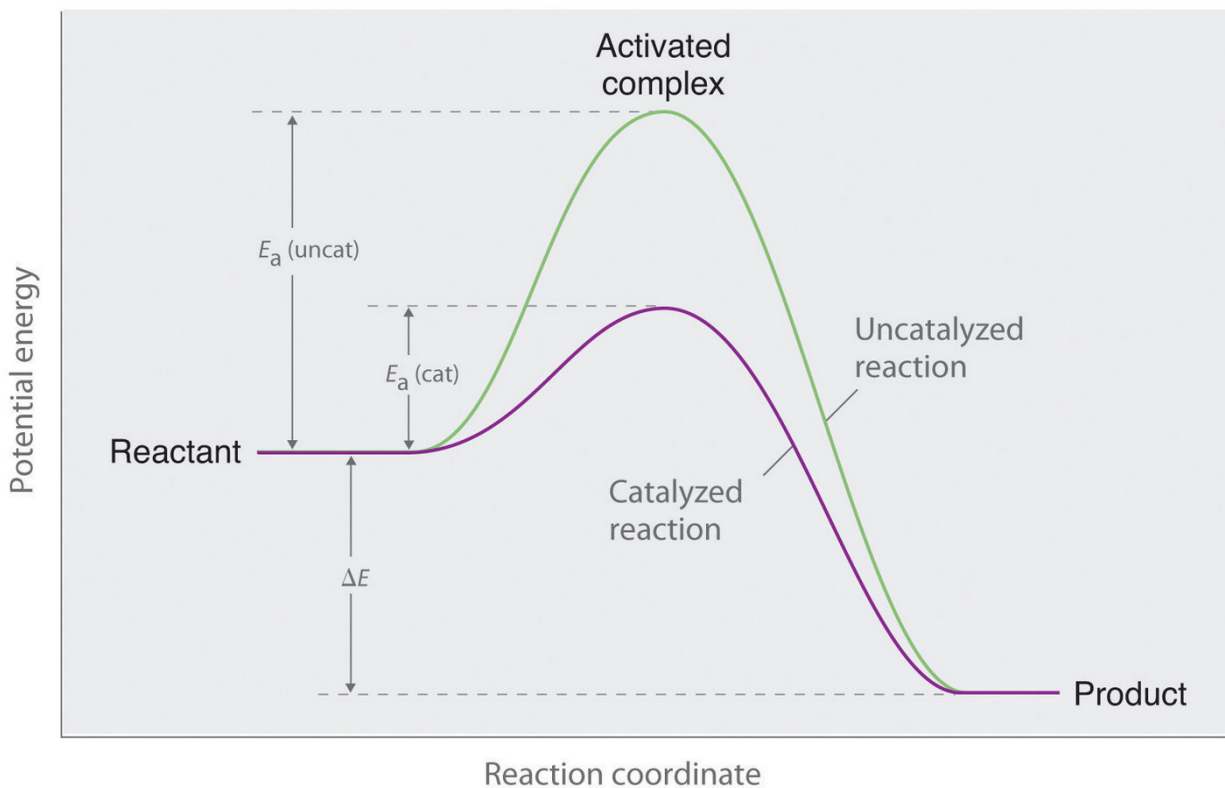


Figure 2.10. Potential energy diagram for catalyzed and non-catalyzed reactions.[52]

2.1.5 Acid-catalyzed fructose dehydration

The dehydration of fructose into 5-HMF occurs via sequential steps leading to abstraction of three molecules of water in the presence of acidic catalysts. This reaction is schematically simplified in Figure 2.11. There are two proposed mechanisms for fructose conversion into 5-HMF, which are either cyclic[54] or acyclic[55] (Figure 2.11, route 1 and 2, respectively). The cyclic mechanism involves the formation of a fructofuranosyl cationic intermediate, whereas in the acyclic route, an enediol intermediate is formed. Although the acyclic route seems to be the favored route for most scientists, Anatal et al.[44] proved experimentally that cyclic intermediates are formed during the dehydration process, and enediol intermediates were not observed in reaction mixtures where a high yield of 5-HMF

is achieved. In the cyclic mechanism, the reaction initiated by protonation of the OH groups of the fructose ring in position alpha to oxygen [33], followed by spontaneous dehydration which leads to the formation of an enol intermediate that rearranges and causes the removal of the second water molecule. Subsequently, deprotonation occurs resulting in the regeneration of the catalyst and the formation of 5-HMF. This reaction can be catalyzed by either a Brønsted or a Lewis acid. However, earlier studies proved that only strong Brønsted acids, such as H_2SO_4 and H_3PO_4 , can effectively catalyze the dehydration reaction.[44] This high catalytic efficiency is perhaps due to the ease of the protonation step caused by the strong Brønsted acids[56].

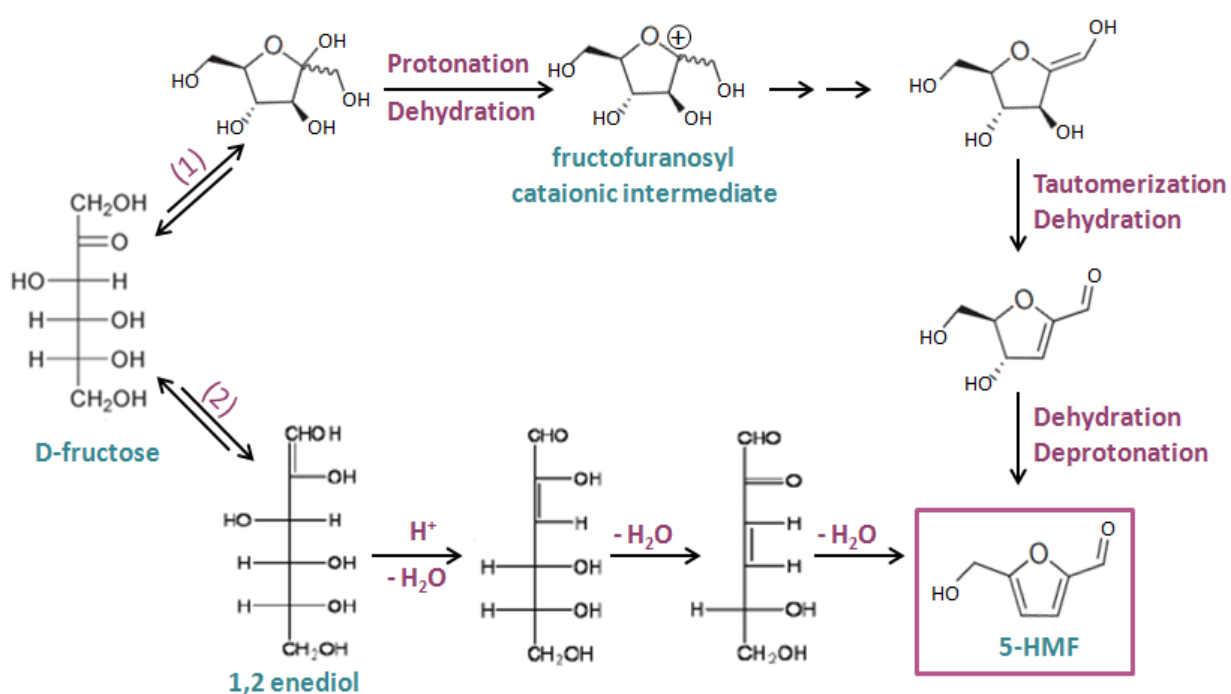


Figure 2.11. Acid-catalyzed fructose dehydration to 5-HMF by (1) cyclic and (2) acyclic routes.

In the dehydration of fructose, many studies have used homogeneous or heterogeneous catalytic systems, which are brought into focus in the next sections. The

fructose dehydration is, in principle, possible without a catalyst[57], although catalyst-free systems have not been satisfactory.[58] Scientists have put more effort into trying to enhance these systems by controlling the reaction conditions to compensate for the role of catalysts. Examples of non-catalytic systems along with the conditions that drive the dehydration reaction are listed in Table 2.1. For example, Riisager et al.[57] used the acidic byproducts of 5-HMF rehydration, Levulinic and formic acid, to autocatalyze the fructose dehydration. Another approach was to use a solvent that can act as a catalyst, such as ionic liquids.[14] However, considering a system that contains ionic liquids as a catalyst-free system is questionable since ionic liquids show high catalytic activity during fructose dehydration.[59] Moreover, the yield of 5-HMF obtained from systems in which ILs are considered as either catalyst or solvent are similar.[24] This indicates that ionic liquids most probably strongly catalyze the fructose dehydration whether they are meant to be used catalysts or solvent.[60]

Table 2.1. Dehydration of fructose in catalyst-free systems.

Catalyst alternatives	5-HMF yield (%)	Reference
High temperature and pressure	22	[58]
Autocatalysis by formed Levulinic and formic acid	35	[57]
Solvent acts as a catalyst (ionic liquid [Bmim]Cl)	63	[14]

Regarding acid-catalyzed fructose dehydration, in his recent review, Raghavan et al.[24] estimated that about 100 organic and inorganic acidic materials have been used as homogeneous and heterogeneous catalysts in 5-HMF manufacturing. Although conventional methods use homogeneous acidic catalysts like H₂SO₄, the best candidate

materials are heterogeneous acidic catalysts. Regardless of the high productivity of homogeneous catalysts, laboratory-scale research on heterogeneous catalysts has been carried out to replace homogeneous catalysts at the industrial-scale in accordance with the principle of green chemistry and the benefit of solid acid materials.[47] All former catalytic types and their performance in fructose dehydration will be discussed, highlighting the most effective ones. The effective catalyst must fulfill both high conversion and selectivity.

2.1.5.1 Homogeneous catalysts

In fructose dehydration, homogeneous catalysis occurs in the liquid phase, often in the presence of a solvent, where both fructose and the catalyst are dissolved. Homogeneous acidic catalysts, such as H_2SO_4 , H_3PO_4 , and HCl , have been extensively studied (Table 2.2) due to their availability, low cost, and most importantly the high yield of 5-HMF. The catalytic activity of organic acids and ionic liquids has also been studied. In Table 2.2, a range of results of homogeneously catalyzed reactions are presented, illustrating the high conversion of fructose, and the effect of solvent on the yield of 5-HMF. The high conversion of fructose in homogeneous systems may be explained by the high mass transfer between the catalysts and fructose, which are in the same phase. Most significantly, the yield of 5-HMF was improved in organic and biphasic solvents in comparison with aqueous media. For instance, Dumesic et al.[46] produced a higher yield of 5-HMF in a HCl -catalyzed reaction in a biphasic system compared to the aqueous system (47% vs. 18%). To highlight this solvent effect, the results in Table 2.2 are listed in order of increasing 5-HMF yield for each catalyst used in several solvents. This demonstrates the efficiency of organic solvents over aqueous solvents, especially DMSO, as its high efficient solvation properties can be

clearly observed by the high yield of 5-HMF. As mentioned above, ionic liquids have the ability to effectively catalyze the 5-HMF synthesis, and a great number of experiments have tested different ionic liquids in this reaction.[59][61][62] As presented in Table 2.2, very high yields of 5-HMF, ranging from 51% to 67%, were achieved in IL catalytic systems. However, the recyclability of ionic liquids as catalysts is gradually reduced after each cycle due to the increasing water content in the ionic liquid as a result of the water generated by the reaction.[63] In addition, ionic liquids are prohibitively expensive to be used at an industrial scale. Although homogeneous catalysts are excellent in terms of catalytic productivity, particularly in the conversion of substrate, they suffer from serious issues related to separation and purification of 5-HMF and recycling.

Table 2.2. Laboratory-scale 5-HMF production from fructose dehydration in the presence of various homogeneous catalysts.

Catalyst	Solvent	Temperature (°C)	Reaction time (min)	Conversion (%)	Yield (wt%)	Reference
H ₃ PO ₄	Subcritical water	240	2	100	39	[37]
		180	10	80	20	[64]
		240	2	100	20	[37]
		250	0.5	92	34	[44]
H ₂ SO ₄	Subcritical acetone-water	180	2	90	48	[23]
	Water-DMSO/MIBK-2-butanol	180	3	85	42	[46]
HCl	Water	150	120	92	19	[23]
	Subcritical water	240	2	63	12	[37]
	Water-DMSO-MIBK-2-butanol	170	4	95	64	[48]
Formic acid	Subcritical water	250	0.5	56	16	[44]
Acetic acid	Water	150	120	84	34	[23]
Lactic acid		150	120	96	45	[23]
Boron trifluoride etherate	DMF	100	90	-	38	[56]
	DMSO	100	45	-	69	[56]
[HMIM]Cl ³	-	90	45	100	64	[59]
[C ₆ (mpy) ₂][NiCl ₄] ₂ ⁴	DMSO	110	60	95	67	[62]
[EMIM][HSO ₄] ⁵	Toluene	100	30	100	55	[61]

³ 1-Hexyl-3-methylimidazolium chloride

⁴ 1,10-Hexane-1,6 diylbis (3-methylpyridinium) tetrachloronickelate (II)

⁵ 1-Ethyl-3-methylimidazolium hydrogen sulfate

2.1.5.2 Heterogeneous catalysts

The early commercially successful applications such as the Haber-Bosch process (1910) for the synthesis of ammonia, a key ingredient for many fertilizers, from H₂ and N₂ gases at high pressure using an osmium catalyst gave a new impetus to the design of novel and improved catalysts for a great variety of reactions. Since then, heterogeneous catalysis has profoundly impacted our lives, especially with the advancement of green chemistry. Currently, heterogeneous catalysis dominates the petrochemical and oil industries, among others.[66] As a result, a great deal of work has focused on biomass conversion over heterogeneous catalysts, which have received much attention due to their many advantageous features, including:

- The catalyst is easily separated from the reaction medium, and can often be recycled several times without significant loss of catalytic activity.
- The catalysts generally have high thermal and chemical stability during the reaction and the separation steps, allowing them to perform reactions at high temperature, and thus can reduce the reaction time and the possible product decomposition.
- The structure morphology provides better accessibility and dispersion of the active sites.
- The purity of the product is often high.
- The selectivity of the reaction is generally high.

Besides the former advantages, the most important one provided by heterogeneous catalysis is that the catalytic active sites on the surface of catalysts can be modified in a variety of ways, which helps in designing more efficient catalysts for a certain reaction. In

fructose dehydration, a strong acidic catalyst is required in order for the reaction to proceed. As formerly discussed, H_2SO_4 was very active with about a 42% yield of 5-HMF produced in biphasic system at 180 °C for 3 min. However, when SO_3H was attached to the surface of solid materials, *e.g.*, acidic ion-exchange resin, the obtained yield was dramatically increased to 61%. [46] Therefore, the acidity of heterogeneous catalysts can be modified giving rise to catalysts with acid strength beyond those of concentrated mineral acids.[67] These modifications are mainly related to the morphology of the catalyst surface, in particular, the surface area and porosity, which allow the strength and the number of the acidic sites to be adjusted.[67][68] Typically, a catalyst with high surface area, appropriate pore size, and good distribution of the acid sites on the surface is expected to be highly effective in fructose dehydration, especially in the presence of suitable solvents. The types of heterogeneous catalysts used in fructose dehydration can be categorized as follows: zeolites, heteropolyacids, metal oxides, ion-exchange resins, and acid-supported catalysts.[58]

Various zeolites (aluminosilicates), such as H-mordenite and ZSM-5, have been studied as catalysts for fructose dehydration (Table 2.3). The advantages of these materials as catalysts are their shape selectivity, controllable pore size, and adjustable acidity by altering the Si/Al ratio.[69] As an example, one of the pioneering works showed that H-mordenite, with a Si/Al ratio of 11 and low mesoporous volume, can effectively convert fructose to 5-HMF in water with a 48% yield.[47] In recent work, Bols et al.[70] obtained a 65% yield of 5-HMF when H-ZSM-5 catalyzed the reaction in DMSO. Another recent study investigated the effect of organic solvents on fructose dehydration over various

zeolites.[71] The results showed that the selectivity to 5-HMF in MIBK increased in the following order: BEA < ZSM-5 < H-MOR. This effect was assigned to the different strengths of the acid sites. Another class of heterogeneous catalysts is the strongly acidic heteropolyacids (HPAs), which are anionic metal oxygen clusters of early transition metals.[44] Heteropolyacids exhibited good activities in the production of 5-HMF as presented in Table 2.3. For instance, $H_3PW_{12}O_{40}$ produced a 5-HMF yield of 68%, and fructose conversion of 97%.[72] However, their low surface area (1–10 m²/g) limits their industrial application.[73] Moreover, their easy solvation makes their recyclability difficult.[24] Metal oxides and mixed metal oxides are another class of catalysts that are widely employed in fructose dehydration. For example, Qi et al.[74] achieved a high fructose conversion of 93.6% with 5-HMF yield of 46% in an acetone/DMSO mixture using highly acidic sulfated zirconia.

Table 2.3. Laboratory-scale 5-HMF production from fructose dehydration in the presence of various heterogeneous catalysts.

Catalyst	Solvent	Temperature (°C)	Reaction time (min)	Conversion (%)	Yield (wt%)	Reference
H-ZSM-5	DMSO	110	–	–	46	[70]
H-Mordenite (Si:Al=11)	Water	165	60	76	48	[47]
SiO ₂ /H-MOR	Water-MIBK	165	300	75	33	[71]
Ag ₃ PW ₁₂ O ₄₀ ⁶		120	60	83	54	[75]
H ₃ PW ₁₂ O ₄₀ ⁷		120	60	86	31	[75]
	DMSO	120	120	97	68	[72]
[MIMPS] ₃ PW ₁₂ O ₄₀ ⁸	Sec-butanol	120	120	99	69	[72]
TiO ₂ nanoparticle	THF	150	180	>99	38	[76]
SO ₄ ²⁻ /ZrO ₂	Acetone / DMSO	180	5	91	46	[74]

Metal halides have been extensively investigated in catalyzing fructose dehydration. For instance, Saha et al.[77] successfully demonstrated a high yield of 5-HMF from fructose catalyzed by AlCl₃ in different solvents, and the maximum yield (49%) was achieved in DMSO under microwave irradiation for 5 min. Nonetheless, metal halides catalysts were initially limited to systems where the solvent is an ionic liquid (Table 2.4.). In addition, metal halides are more favorable in glucose dehydration than in fructose. Generally, the pathway of the conversion of glucose into 5-HMF involves isomerization of glucose to fructose followed by dehydration of fructose to 5-HMF. Since the isomerization step is a Lewis-acid catalyzed reaction, metal halides are preferable. More specifically, metal cations can stabilize the anionic intermediates of glucose by forming coordination complexes facilitating the isomerization route into fructose, and thus the production of 5-HMF.[78][79] Further, metal phosphates have strong acidic properties, and therefore, can

⁶ silver salt of dodecatungstophosphoric acid

⁷ dodecatungstophosphoric acid

⁸ a heteropolyacid salt of an IL-forming cation functionalized with a propanesulfonate group, 1-(3-sulfonicacid)propyl-3-methyl imidazolium phosphotungstate

be utilized in fructose dehydration. Strontium and zirconium phosphates were found to be the most active catalysts among other metal phosphates in fructose dehydration with a 5-HMF yield of 55% and 35%, respectively.[80][81]

Table 2.4. Laboratory-scale production of 5-HMF from fructose dehydration in the presence of metal halides and ion-exchange resins.

Catalyst	Solvent	Temperature (°C)	Reaction time (min)	Conversion (%)	Yield (wt%)	Reference
AlCl ₃	Water/MIBK	130 (MI ⁹)	5	-	41	[77]
	DMSO	140 (MI)	5	-	49	[77]
ZrCl ₄	[BMIM]Cl	- (MI)	2	89	65	[82]
NiCl ₂ .6H ₂ O	[TetraEG (mim) ₂] [OMs] ₂ ¹⁰	100	40	100	57	[83]
FeCl ₃		100	40	100	51	[83]
CuCl ₂ .6H ₂ O		100	40	100	45	[83]
Amberlyst-70	THF-water	130	10	91	54	[84]
Nafion R50 ion exchange resin	DMSO	80	300	95	55	[85]
Amberlyst-15	[BMIM]Cl	80	10	99	58	[86]
Amberlyst-15	BMIM ¹¹ +BF ₄ /DMSO	80	32 h	-	61	[79]
DOWEX 50WX8-100 strong acidic ion-exchange resin	Acetone/ DMSO	150	20	99	58	[45]

Ion-exchange resins, specifically sulfonated copolymers, were among the first catalysts to be used as heterogeneous catalysts for the production of 5-HMF[24], and some of the most significant results obtained over various ion-exchange resins are presented in Table 2.4. Fructose dehydration requires a strong acidic catalyst, such as Amberlyst-15.[69]

⁹ Microwave irradiation

¹⁰ Tetra ethylene glycol-bis (3-methylimidazolium) dimesylate

¹¹ 1-Butyl-3-methylimidazolium

Qi et al.[86] developed a catalytic system for fructose dehydration involving Amberlyst-15 as a catalyst and ionic liquid as the solvent. They achieved a 58% yield of 5-HMF and high fructose conversion of 99% in 10 min at 80 °C. In addition, the form of ion-exchange resins affected its catalytic performance; for instance, crushed Amberlyst-15 gave a yield of 5-HMF close to 70% with a complete conversion of fructose, in contrast to the original Amberlyst-15 pellets with a diameter in the range of 0.71–0.50 mm, which gave a 53% yield.[41] In spite of the significant catalytic performance, ion-exchange resins are thermally stable only up to 130 °C, above which they deactivate owing to desulfonation of the acid sites.[69] However, ion-exchange resins have been experimentally shown to be stable until 150 °C in fructose dehydration.[87]

Acidic solid catalysts prepared by supporting mineral acids, such as sulfonic acid, on materials with large tunable surface areas are very promising as strong acidic catalysts.[56] Recent effort was focused on this matter to improve the production 5-HMF. Silica and carbon materials have often been used as supports for sulfonic acid in the production of 5-HMF. In a recent report, a set of modified SBA-15 silica-supported sulfonic acid groups were found to be capable of catalyzing the dehydration of fructose in a biphasic system affording 5-HMF with a 52–59% yield (Table 2.5).[88] Later, Bispo et al.[38] designed several sulfonated periodic mesoporous organosilica (PMO) catalysts for fructose dehydration, and obtained a maximum yield of 5-HMF of 58%. They assigned the catalytic activity of the series of sulfonated PMO catalysts to the sulfonic acid site density, the location of the sulfonic acid sites, and the surface hydrophobicity. As for carbon supports, Guo et al.[89] prepared an amorphous lignin-derived carbon material, functionalized with

sulfonic acid, and used it to catalyze fructose dehydration. The result was quite impressive as a 59% yield of 5-HMF and 100% fructose conversion was achieved using such a cheap and abundant material. Sulfonated porous carbon has also been synthesized and used as a catalyst in fructose dehydration, and a yield of 43% 5-HMF was achieved.[90] Interesting results of the aforementioned approaches are listed in Table 2.5.

Table 2.5. Laboratory-scale production of 5-HMF from fructose dehydration in sulfonated catalyst supports.

Catalyst	Solvent	Temperature (°C)	Reaction time (min)	Conversion (%)	Yield (wt%)	Reference
pSO ₃ H-SBA-15 ¹²	Water/	130	140	79	52	[88]
TESAS-SBA-15 ¹³	MIBK:2-	130	141	84	59	[88]
SSA-SBA-15 ¹⁴	butanol	130	140	81	52	[88]
Propyl sulfonic acid phenyl-PMO	MIBK/2-butanol	160	75	95	58	[38]
Sulfonated Lignin-derived carbon	[BMIM] Cl	110 (MI)	10	100	59	[89]
Sulfonated cellulose-derived carbon		160	15	-	57	[91]
Sulfonated porous carbon	DMSO	110	4 h	-	43	[90]

The efficiency of fructose dehydration can be further improved by microwave heating. Researchers acquired a high yield of 5-HMF under microwave irradiation (MI), and this improvement was assigned to several particular thermal effects.[92] It is believed that microwave irradiation creates effective internal heating by directly coupling microwave energy with solvents, substrates, and catalysts.[92] An example of the improvement in the yield of 5-HMF production by MI is the work of Guo et al.[89] in which the yield of 5-HMF

¹² Propylsulfonic acid-functionalized SBA-15

¹³ 3-(Propylthio)propane-1-sulfonic acid-functionalized SBA-15

¹⁴ 3-(Propylsulfonyl)propane-1-sulfonic acid-functionalized SBA-15

increased from 16% under traditional heating to 39% under microwave irradiation. MI improves the yield and selectivity of 5-HMF, and decreases the reaction time. Moreover, microwave irradiation is also an energy-saving method, which is consistent with the green chemistry concept.[92]

In summary, extensive work has been conducted on heterogeneous catalysts. Further, many of these laboratory-scale results are going through rapid screening investigations, and further laboratory experiments by some companies to identify the best candidate catalyst for large-scale applications.[96] This growing interest in the laboratory- and industrial-scale applications clearly reveals the importance of exploring an adequate heterogeneous catalysts for 5-HMF production. A starting point towards that, perhaps, would be the catalyst supports, since strong acid sites in combination with a tunable surface area are the most desired properties in a catalyst. Furthermore, the results from porous material-supported sulfonic acid catalysts (Table 2.5) are very propitious. Therefore, our work is focused on the synthesis of 5-HMF from fructose dehydration over various acid-supported catalysts, such as periodic mesoporous organosilica (PMO), carbon materials, and metal organic frameworks (MOFs). Hence, a brief introduction to these materials follows in the next section.

2.2 Porous Materials

2.2.1 *General introduction to porous materials*

Porous materials are defined as solid materials containing pores in the form of cavities, channels, or interstices. Porous materials usually display porosity of 0.2 to 0.95. [93]The porosity is a term used to measure the void spaces in the materials as a fraction of pore volume to the total volume. Porous materials are available in different structures, and they often exhibit large surface areas, with a variety of pore sizes, and sometimes flexible frameworks. Such properties could be tunable with specific features for a particular application. Generally speaking, porous materials exhibit different pores that are classified into two main types; open pores and closed pores, as illustrated in Figure 2.12. Open pores are known to be connected to their surroundings, and closed pores are described as enclosed and isolated from their environment. Some pores have at least two openings and are called penetrating pores. Open porosity is of a great importance for porous materials to be applied in most industrial applications, and further a high fraction of open pores is required for separation and catalysis. In addition, the shape, connectivity, and size distribution of the pores of such materials illustrate their importance in specific applications, such as catalysis, adsorption and separation.[93] For instance, narrow pore size distribution is necessary in selective filtration, and large specific surface area is important for catalytic applications. Porous materials can be categorized based on various criteria such as pore shape, pore size, compositions, and synthesis methods. Due to the importance of pore diameters for porous materials to be used as supports in catalysis application, classification regarding pore diameter will be explained. Porous materials are

categorized into three classes depending on their average pore diameter according to the IUPAC classification.[94] The three categories are:

- 1 – Microporous materials with pore diameters less than 2 nm.
- 2 – Mesoporous materials with pore diameters between 2 and 5 nm.
- 3 – Macroporous materials with pore diameters larger than 5 nm.

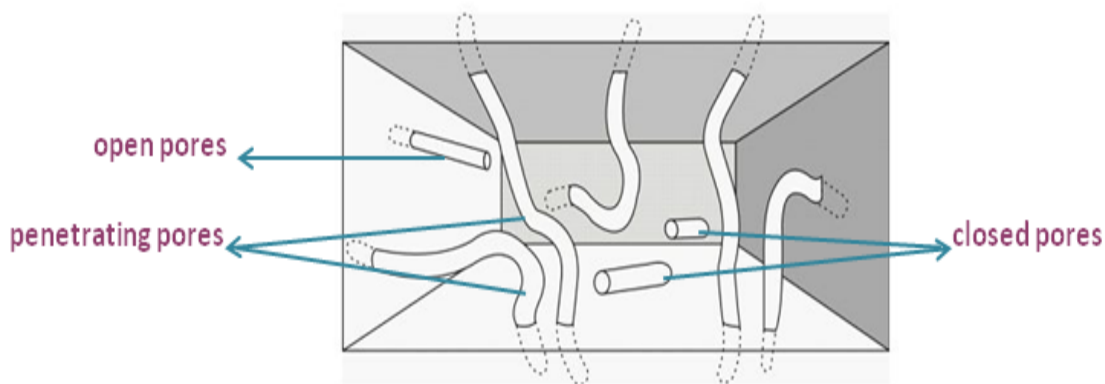


Figure 2.12. Illustration of a cross section of porous materials.

Porous materials may be comprised of inorganic, organic, or hybrid species, resulting in different types of materials, including pillared clays, metal oxides, carbon, sol-gel materials, and porous polymers.[95] Herein, porous carbon, silica, and hybrid material will be briefly introduced. Carbonaceous materials may exist in amorphous or crystalline structure giving rise to significant structural properties such as large surface area, and various pore sizes. In addition, the distinctive properties of sp , sp^2 and sp^3 hybridized carbon atoms in carbon frameworks enables the formation of different structures, such as layers, tubes and spheres.[96] Therefore, carbonaceous materials have been widely used in various applications from daily necessities, e.g. purification of drinking water by activated

carbon to utilization in modern industries, such as supported materials typically as electrodes for electrochemical applications. This is due to the chemical properties such as inert nature, good conductivity, and chemical stability, as well as the well-understood chemistry. Moreover, acidic carbon materials can maintain strong acidity even in aqueous medium, participating in many acid-catalyzed reactions in industrial applications.

Porous silica materials are very popular among other porous materials due to their easy synthesis, remarkable physical properties, and the possibility of modifying their surface with functional groups because of plentiful active silanol groups (Si-OH) found on the silica surface. Zeolites, which are silicaluminates, are a good representative of crystalline microporous materials with over 40 naturally occurring species and about 150 synthetic zeolites.[97] Despite the fact that zeolites are a versatile class of materials, their small pore size restricts their application. For example, catalytic reactions within a zeolite pore system are limited to molecules that can diffuse inside the pores. Therefore, efforts have been made to overcome these restrictions and to design porous silicas with larger pore sizes. In the early 1990s, Mobil researchers discovered the so-called M41S *periodic mesoporous silica* (PMS) using sol-gel condensation of a silica source in the presence of a supramolecular structure-directing agent.[98] They identified three silicate phases with pore diameters ranging from 2 to 10 nm, *i.e.*, a hexagonal phase (MCM-41), a cubic phase (MCM-48), and a lamellar phase (MCM-50), as illustrated in Figure 2.13.[95] The discovery of M41S attracted researchers' attention, that led to many innovative discoveries in this field, including the synthesis of new phases of PMS, such as SBA-type, disordered HMS, MSU-n, MSU-V, and KIT-n, and others.[97][99] The accomplishment of synthesis PMS

created great opportunities for the synthesis of ordered mesoporous carbon materials via *hard template* method that leads to expanding their practical utility.[100]

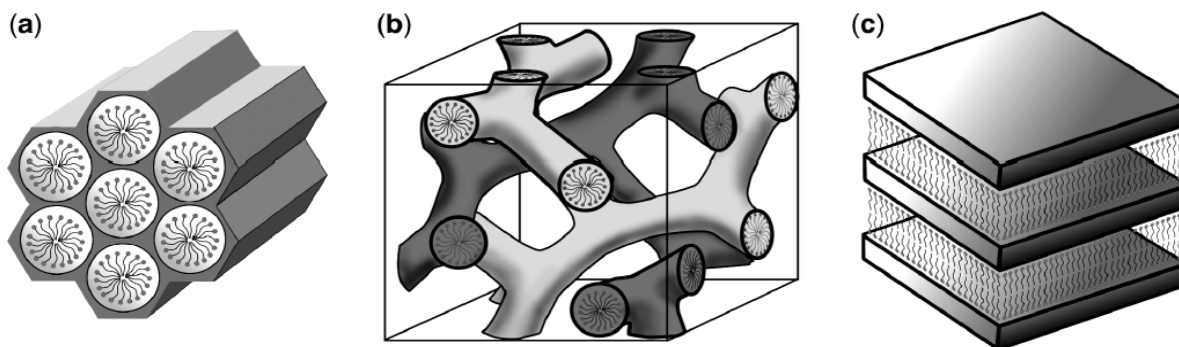


Figure 2.13. Idealized module of the three silicate phases of M41S: (a) hexagonal phase MCM-41, (b) cubic phase MCM-48, (c) and lamellar phase MCM-50.[97]

The synthesis of PMS requires four main ingredients in adequate amounts—a solvent, a silica source, a surfactant, and an acid or a base to adjust the pH. The nature and proportions of these components are a key factor in designing various PMS. In other words, the type of mesosilica phase acquired from the synthesis depends on different factors, including: surfactant type, pH, temperature, and additives. Generally speaking, the surfactant self-assembles into a liquid-crystal template (Figure 2.14), which plays the role of a supramolecular template, around which the source of silica condenses and grows in a "skin-tight" style. After removal of the template by extraction or calcination, the structure of the template is replicated in the corresponding PMS material.[95][97][98][99]

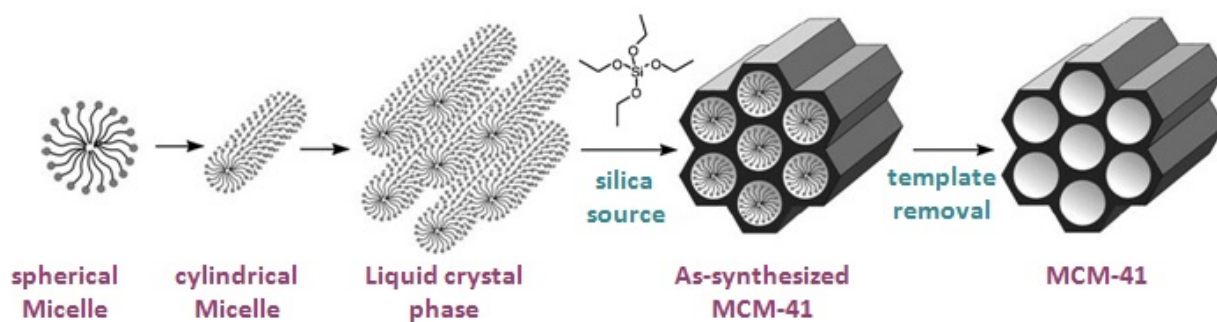


Figure 2.14. Formation of mesoporous materials by liquid-crystal template mechanism.

Further development of the area of porous materials field was achieved by the successful design of organic-inorganic hybrid porous materials. The interest in developing hybrid materials originates from the potential of combining the particular advantages of organic and inorganic materials in one single material, particularly, the diverse chemical functionalities of the organic part combined with the chemical, mechanical, and thermal robustness of the inorganic component.[97] In 1999, two forms of organic-inorganic hybrid porous materials emerged. One of them was self-assembled periodic mesoporous organosilica (PMO) using silsesquioxane precursors. The other form of novel porous hybrid materials is metal-organic frameworks (MOFs), which are basically composed of inorganic nodes and organic spacers giving rise to a crystalline structure.[97][101] Since this discovery, intense work has been carried out on utilizing these organic-inorganic hybrid materials in a wide range of applications, including gas storage, adsorption, catalysis, light harvesting, and LEDs. Furthermore, introducing organic functional groups, such as OH, SH, COOH, NH₂, or SO₃H into the organic-inorganic host materials, paved the way for more applications where functional porous hybrid materials are desired. A brief introduction for both types of materials as well as carbonaceous materials will be discussed hereafter.

2.2.2 Organofunctionalization of PMS

As mentioned above, periodic mesoporous silicas are important materials. From a chemical point of view, PMS is an ideal starting inorganic material for functionalization owing to the high surface area and ordered porosity, and more importantly, the numerous reactive silanol groups.[98][102]

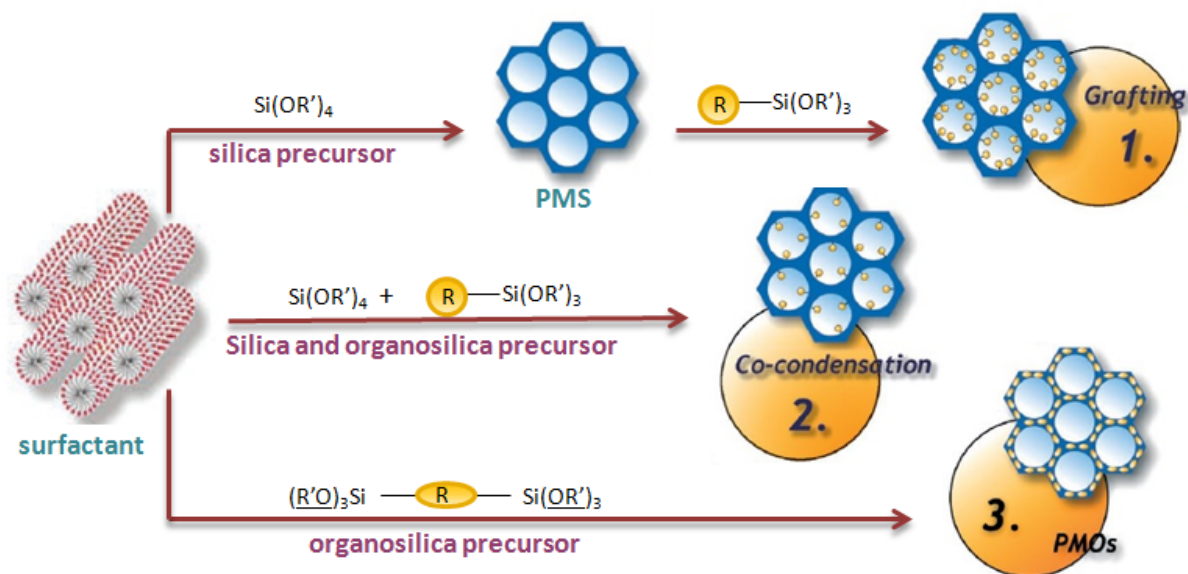


Figure 2.15. Methods for organic modification of periodic mesoporous silicas.[102]

There are three principle pathways to organofunctionalize periodic mesoporous silicas as presented in Figure 2.15.[102] The first method is a post-synthetic functionalization, also known as grafting (1 in Figure 2.15), which refers to the post-synthesis modifications of the pore surface of pure inorganic silica materials, *e.g.*, M41S, with organic or organometallic species. The disadvantages of this method are that the obtained organosilica often shows non-uniform distribution of the organic groups, and the lining of the wall reduces the porosity of the hybrid materials.[98] The second method is

co-condensation, in which the silica and the organosilica precursors are simultaneously condensed in the presence of a supramolecular structure-directing agent as depicted in 2 in Figure 2.15.[97] This synthesis process overcomes the disadvantages of the grafting method, yet the main drawback of this method is that the mesoscopic order is decreased upon increasing concentration of organosilica precursor, leading to reduced content of organic functional groups.[97][98] The third alternative to synthesize mesoporous organosilica is to use bridged silsesquioxanes as a single source precursor in the presence of a supramolecular structure-directing agent, which leads to direct incorporation of the organic components into the pore walls, giving a higher density of organic groups in comparison to the grafting or co-condensation methods. Nevertheless, this makes most of the functional organic groups inaccessible, yet they strengthen the rigidity of the walls and the entire framework[101] The materials obtained from the latter synthesis method are called periodic mesoporous organosilicas (PMOs), also known as bridged organosilica. Similar to PMS, PMOs are commonly characterized by a periodically ordered pore system and narrow pore size distribution.[101]

2.2.3 Periodic mesoporous organosilica (PMO)

The PMOs synthesis uses the self-assembly approach of preparing periodic mesoporous silica, but in the presence of bridged silsesquioxanes as precursors.[97][99] The bridged silsesquioxanes correspond to two trialkoxysilane groups connected by an organic functional bridge, which can be represented as $(R'O)_3Si-R-Si(OR')_3$, where **R** and OR' refer to the organic bridge, and the hydrolyzable groups (OCH₃, OC₂H₅), respectively.[101] The synthesis of PMOs is similar to the synthesis of M41S-type materials.

A schematic representation of the main stages in the synthesis of PMOs is shown in Figure 2.16. Generally, micelles are formed by a surfactant, and then silsesquioxane hydrolyzes and condenses to form the organosilica in either an acidic or basic medium. After an ageing process, the PMO is formed, and the surfactant is extracted.[101]

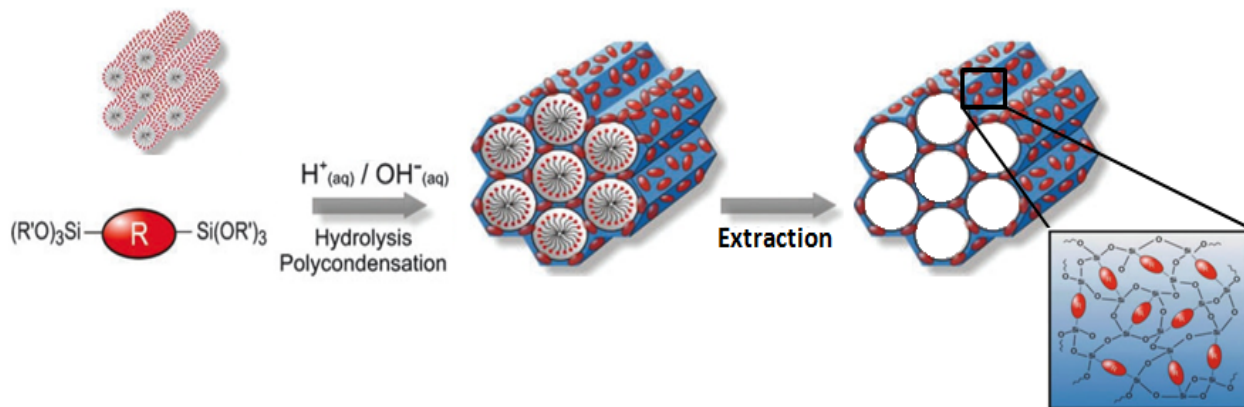


Figure 2.16. Schematic representation of the synthesis of PMOs using silsesquioxane precursors.

A large number of surfactants and block copolymers may be used under acidic, neutral, or basic conditions. Furthermore, a large variety of organic bridges can be introduced into the structure of the PMO. In addition to the functionality that is brought by organic bridges, they can enhance the structural properties of PMOs. Specifically, a rigid organic bridge can sustain a self-assembling procedure at the molecular scale, which may produce a PMO with an additional level of periodicity that presents a crystal-like arrangement of the organic components within the pore walls (Figure 2.17).[97] The first ordered PMO with a crystal-like wall structure was successfully synthesized by Inagaki and his co-workers using BTEB as precursor and ODTMA as structure directing agent under basic conditions.[103] This material exhibited a periodicity of 7.6 Å on the molecular scale as a result of the alternating layers of silica and benzene as presented in Figure 2.17.

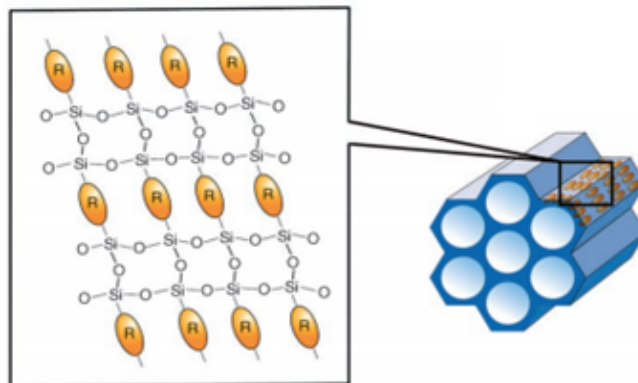


Figure 2.17. Schematic representation of the crystal-like arrangement of organic bridges (R) within the pore walls of PMO.[102]

As functional organic groups are the key components of PMO materials, extensive research has been conducted to expand the variety of organic linkers and thus the range of potential applications. Beside the simple organic bridges, such as ethylene, ethenylene, methylene, and phenylene, advanced functional bridges, such as metal complex ligands and chiral bridges, have also been used to synthesize specific PMOs with certain applications, such as chromatographic separation or chiral catalysis.[98] The first PMO with an ethylene linker was reported in 1999 by three independent groups. Ethylene-bridged PMO was the first synthesized PMO material reported by Inagaki et al.[104] In the same year, Stein et al. published another report on ethylene-bridged PMO.[105] Inagaki and Stein proposed similar procedures to that used for MCM-41, but with slightly different cationic surfactants, namely ODTMA and CTAB, respectively. The ethylene-bridged PMO synthesized by ODTMA exhibited high mesoscopic order, while the one derived from CTAB lacked long-range order. In addition, the synthesis of ethylene-bridged PMO was also reported at the same time by Ozin et al.[106]

Large-pore periodic mesoporous organosilicas are very attractive for applications where large or bulky molecules are involved. One approach to expand the pore size of PMOs is to use a triblock copolymer as a structure-directing agent, which was first used to synthesize large-pore ethylene-bridged PMO. However, the functionality of ethylene groups (-CH₂-CH₂-) is limited, which has motivated many researchers to prepare large-pore phenylene-PMO, due to its high thermal stability, high functionality, and suitability for further modifications.[101] Goto and Inagaki [107] successfully synthesized phenylene-PMO with a pore size up to 7.4 nm using a triblock copolymer as a structural-directing agent upon post-synthesis treatment procedure with water at 100 °C for 12 h. This latter treatment was performed to improve the structural ordering.

PMOs can be further functionalized by pre-synthesis functionalization of the hybrid silsesquioxane precursor, or by post-synthesis modification.[101] Sulfonated PMO can be synthesized by either the pre- or post-synthesis functionalization. As for the first method, thioether functional groups are incorporated into the structure of PMO using an organosilica precursor containing hydrogen sulfide moieties. Then, sulfonic acid groups are generated by a simple post-synthesis oxidation treatment.[101][108] The other method to sulfonate PMO is to perform post-synthesis sulfonation. Inagaki et al. were the first to synthesize sulfonated phenylene-bridged PMO by exposing the original PMO to 25% SO₃H/H₂SO₄, which gave a final acidity of 0.4 mmolg⁻¹. [109] A higher acidity level, ranging between 0.4 and 0.7 mmolg⁻¹, was achieved upon using chlorosulfonic acid.[110]

In terms of applications, several works have been conducted using PMO materials to prepare heterogeneous catalysts, for which the PMO is the basis of the support[38][39] The PMOs are especially promising supports for liquid-phase acid catalysis because they have a high specific surface area and pore volume, together with a regular pore structure and tunable pore size, which enables rapid diffusion of reactants and products through the pores, thus minimizing side-reactions.[111]

2.2.4 Carbon materials

Carbon materials, which are entirely composed of carbon with various physical structures, exist in two main forms: amorphous and crystalline solid carbon. They possess beneficial characteristics, including diverse porous structures, high surface area, large pore volume, and surface inertness.[112] These characteristics make them useful for many applications, such as gas separation, water purification, electrode materials, adsorption, and catalysis. In addition, the easy modification of their structural properties by controlling the activation and treatment methods may lead to enhanced pore structure or may generate functionality on the surface.[96]

Activated carbon materials have been known as adsorbents since the 19th century. Activated carbons are amorphous materials that are mostly composed of graphitic sheets with no regular order (Figure 2.18). The usefulness of amorphous activated carbon is due to its high surface area with large micropore and mesopore volumes. Activated carbon materials are attracted considerable interest because they can be synthesized using renewable precursors like sugars and cellulose, using relatively low carbonization

temperature, and the ease functionalization of the as-synthesized materials. Therefore, they widely used as adsorbents and catalyst supports in many industrial applications.[96]

Activated carbons are generally synthesized via either physical or chemical activation processes. In a typical procedure, the carbon precursor first pyrolyzes at a high temperature in an inert atmosphere. Then the carbon material is activated either physically, in the presence of oxidizers, such as carbon dioxide or oxygen gases, or chemically, in the presence of an acidic or basic reagents.[113] These two activation methods are not favorable due to the harsh conditions of temperature and pressure required. Therefore, the hydrothermal carbonization method evolved, and is now a well-established procedure in carbon research. In this method, hydrothermal decomposition of a carbon precursor, such as carbohydrates, takes place in an aqueous solution at low temperatures, which yields monodispersed carbon spheres. In addition, carbon materials obtained from hydrothermal carbonization of carbohydrates are rich in functional groups, such as hydroxyl, ether, and carbonyl groups.[114][115] This synthesis method features a facile, cheap, and mild general route towards the production of functionalized carbon materials, which also fits the green chemistry concept. Furthermore, adding an acid, such as acrylic or hydroxyethylsulfonic acid, to the reaction mixture yields acidic activated carbons (Figure 2.18).[113][115][116]

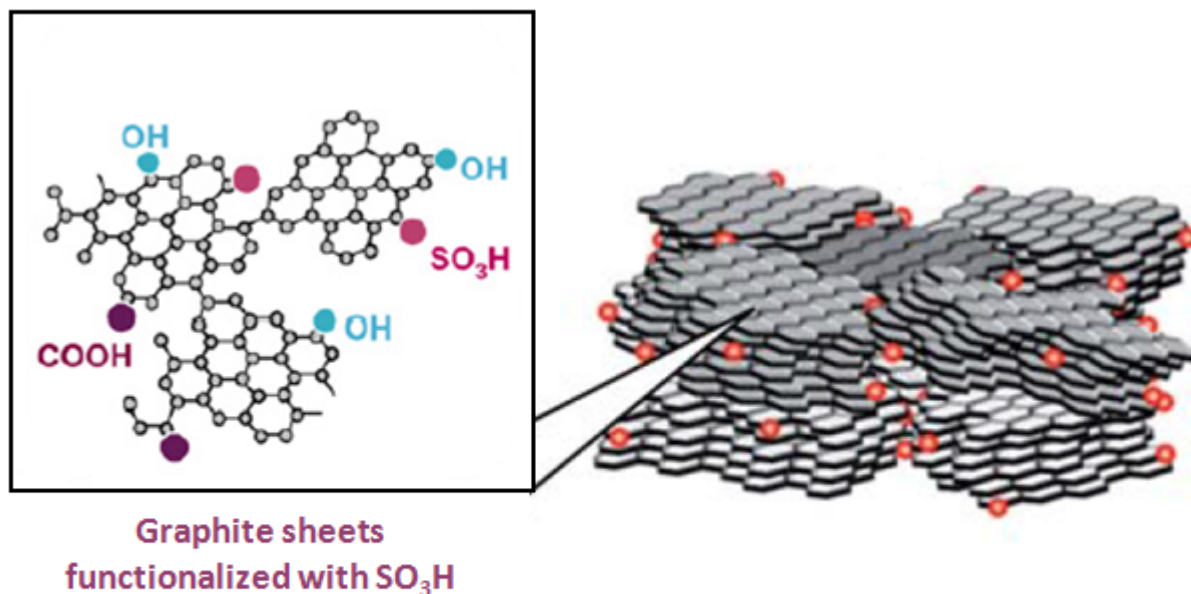


Figure 2.18. Schematic structure of sulfonated activated carbon materials.[147]

In the last decade, research on ordered porous carbons has flourished as a new form of structured carbon with tunable pore systems at the nano-scale.[96] The traditional synthesis strategies are mostly limited to porous carbon materials with irregular pore structure.[100] Recent effort using different types of ordered porous materials as a template led to the discovery of novel carbon materials with periodic pore structure. This synthesis method is called a *hard-template synthesis*, in which porous solids are used as the template instead of the surfactant. In this context, the pore system of the template is replicated as a negative image.[97] Ryoo and co-workers were the first to report this so-called hard-templated synthesis of mesoporous carbon materials, leading to a carbon denoted as CMK-1, using MCM-48 silica as inorganic template.[117] Since then, many ordered porous carbon (OMC) materials with uniform pore sizes in the nanopore range have been prepared using different inorganic templates. SBA-15 is one of the most investigated ordered mesoporous materials because it has many features, such as easy

synthesis in a wide range of temperatures (35–130 °C), controllable pore sizes (5 to 30 nm), and thick pore walls (2-6), that result in improved thermal and hydrothermal stability.[84] As described in many reports, SBA-15 is suitable to be used as a template in the synthesis of mesoporous analogs due to the occurrence of micropores that connect the mesoporous channels, allowing the structure of the analogs to be stable after removing the silica, as illustrated in Figure 2.19.[118]

Ordered mesoporous carbon materials, such as CMK, were successfully synthesized using MCM-48, SBA-1, and SBA-15 as hard templates.[100] Such materials can be used in applications where large molecules are involved, such as adsorbents for dyes, catalyst supports for biomolecules, and electrodes for biosensors.[100] Moreover, with carbon as the main component, these materials might be an alternative to the relatively expensive silica. An ordered mesoporous carbon, CMK-3, was synthesized using hexagonally ordered mesoporous silica SBA-15 calcined at 1153 K as a hard-template. The calcination temperature of SBA-15 has a great impact on the structure of the obtained carbon materials because it affects the structure of SBA-15, which will be inherited by CMK-3. The use of SBA-15 that was calcined at 1153 K as a hard-template in the synthesis of CMK-3 results in CMK-3 with uniform pores between ordered carbon rods, which are connected by thinner rods, as depicted in Figure 2.19.[112] In contrast, using SBA-15 calcined at high temperature (>1243 K) leads to disordered mesoporous carbon as a result of the loss of the interconnecting microporous bridges in the SBA-15 structure.[112] The synthesis procedure of CMK-3 may be divided into three main steps (Figure 2.19). First, the carbon/silica composite is prepared by introducing a carbon precursor into the pores of

the template. Second, the resulting composite is subjected to high temperature under inert gas to carbonize the precursor. Third, the ordered mesoporous carbon is obtained by removing the silica template by dilute NaOH or HF.

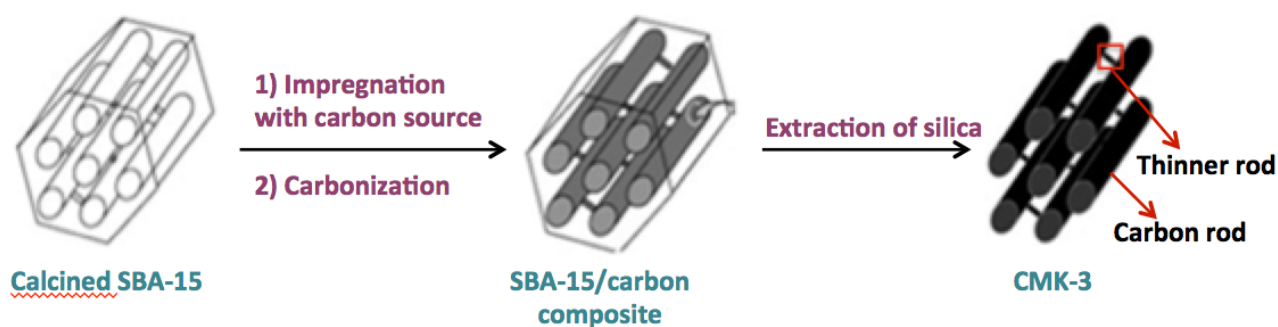


Figure 2.19. An example of synthesis of ordered mesoporous carbon using the hard-template synthesis technique.

From a chemical point of view, these ordered mesoporous carbon materials lack organic functionality, which limits their use in many applications. Xing and co-workers successfully prepared sulfonated CMK-3 through a controlled carbonization technique to control the surface composition, followed by vapor-phase sulfonation using 50 wt% $\text{SO}_3\text{H}/\text{H}_2\text{SO}_4$.^[119] This sulfonated CMK-3 exhibited high acid loading (up to 1.2 mmolg^{-1}), which makes it a very promising material to effectively catalyze many acid-catalyzed reactions, especially when bulky molecules are involved. This method of Prudent sulfonation was reported to be more effective in synthesizing high-acidic catalysts than direct submersion methods, while maintaining the mesoporous structure. In general, functionalized carbon materials are widely applied in industrial applications due to their low cost, non-toxic nature, and availability.^[100] In terms of catalysis, their catalytic activity has been investigated in many organic reactions.^[67]

2.3.5 Metal organic frameworks (MOFs)

Similarly to PMOs, metal-organic frameworks (MOFs) are a relatively new class of porous crystalline materials. MOFs commonly consist of metal cations (primary building units, PBU) or metal clusters (secondary building units, SBU), which are cross-linked by polyfunctional organic linkers.[120] Yaghi and co-workers.[121] were the first group to synthesize a prototype of this new class of hybrid materials, which was denoted as MOF-5 and was a porous cluster derived from benzenedicarboxylic acid and zinc ions (Figure 2.20). The significance of MOF-5 is that it showed high thermal stability (up to 300 °C), large surface area (2900 m²g⁻¹), and uniform pores with a volume of 0.54–0.61 cm³g⁻¹. These features led Yaghi et al.[122] to put further effort into modifying the MOF-5 structure to produce a whole new family of MOFs, namely IRMOFs, which are isostructural to MOF-5 with various modified benzenedicarboxylate (BDC) linkers (examples are presented in Figure 2.20). Since then, the MOF field has grown vastly and large numbers of new MOFs have been reported.[123] The attention given to MOFs is due to the fact that they combine the topology of inorganic materials and the versatility of organometallic chemistry, leading to remarkable properties, such as crystallinity, porosity, and the heterogeneous surface composition (metal and linkers).[120] As for porosity, the pore size, shape, dimensionality, and functionality can be altered by the choice of the building block (metal and organic components), which leads to controlling the molecule size that can diffuse into the pores, and thus modifying the host-guest interactions.[120][123] Such properties pave the way for scientists to extensively apply MOFs in many practical fields, including heterogeneous catalysis, gas storage and separation, chemical sensing,

optoelectronics (*e.g.*, LEDs), energy storage and conversion (batteries, solar cells), and drug delivery and bio-imaging.[123]

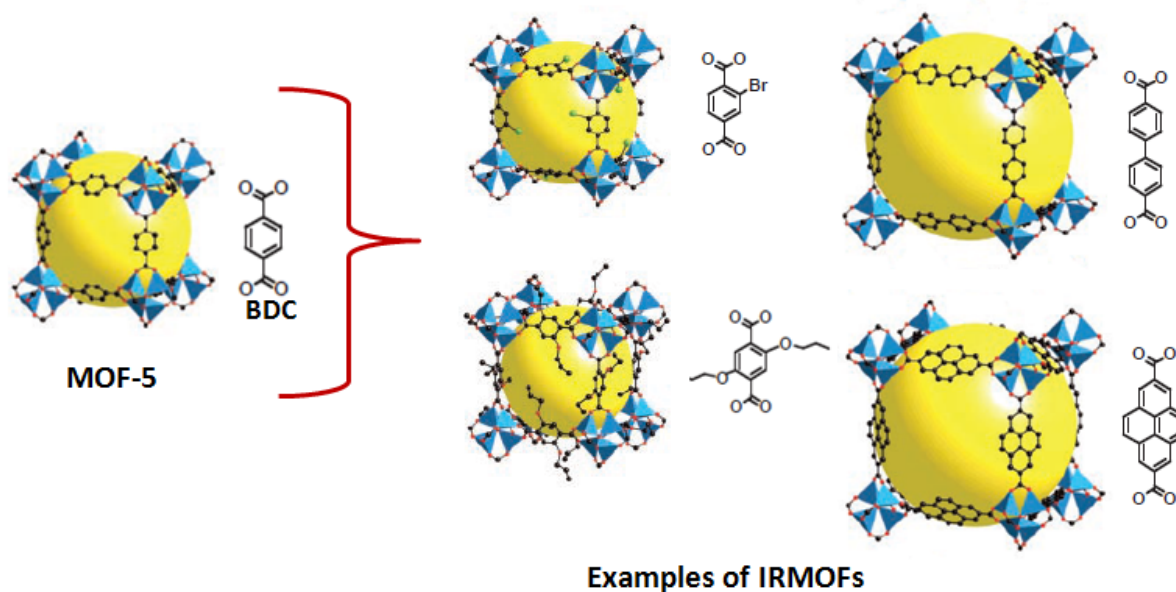


Figure 2.20. The structure of a unit cell of MOF-5 and examples of the corresponding isostructural MOFs (IRMOFs). [122]

The essential objective in MOF synthesis is to setup the reaction conditions that lead to well-defined inorganic building blocks with no decomposition occurs to the linker. Concurrently, appropriate crystallization kinetics is substantial to be established to let nucleation and growth of the required phase to take place.[124] Practically, the synthesis involves two substrates, one as a metal source and the other as a source of organic linker. Nonetheless, several synthesis methods have been reported, and this variation of methods is related to controlling the reaction parameters, including temperature, time, type of heating, and phase of reactants, which results in various MOFs, even when the same starting reaction mixture is used.[124] These procedures are usually conducted in one or a mixture of solvents at room temperature under solvothermal conditions.[120] However, a

solvent-free mechanochemical synthesis was also reported, in which the intramolecular bonds of substrates break by the mechanical force, followed by chemical transformations.[124] Overall, the crystalline framework is constructed by self-assembly of building blocks that form strong coordination bonds between the structural units. Many of the metal atoms in the periodic table can be incorporated into the structure of MOFs.[124] In terms of organic compositions, rigid linkers with an aromatic or a conjugated π system are more favorable because they simplify the formation of crystalline, porous, and stable MOFs.[125] It is worth mentioning that the final structure of the MOF is also affected by the nature of the solvent, the type of linker, and the presence of certain cations or other molecules in the synthesis batch.[124][126]

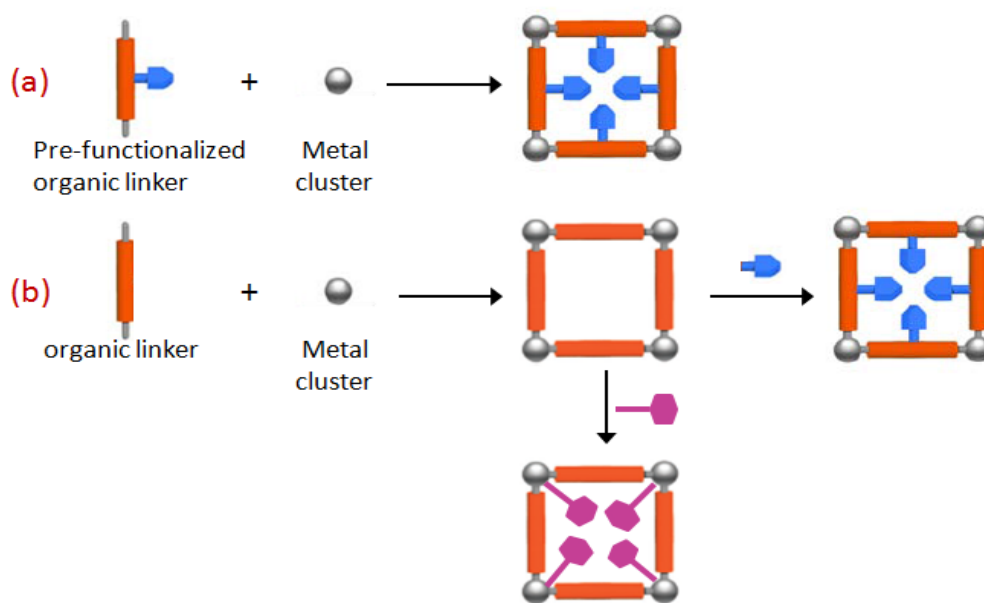


Figure 2.21. Schematic representation of MOF functionalization methods: (a) pre-functionalization, and (b) post-synthetic modification (PMS).[127]

The activity of MOFs in certain catalytic applications can be generated by the metal centers, active sites on the organic linker, or encapsulated guest molecules.[123][128] For

example, coordinatively unsaturated metal nodes generate Lewis acidity in the structure of MOFs, and can be used as an active site in applications where Lewis acids are required. However, the practical use of the unsaturated metal nodes is limited due to issues like weak acidity and difficult activation since the solvent bonded to the metal nodes in the as-synthesized MOF needs to be removed in order to expose these acidic sites, which may be a challenging process.[127] Hence, the need to functionalize MOFs is raised. MOFs can undergo functionalization on the organic linkers or the metal nodes.[127] Generally, the routes to functionalize MOFs are either to design desired building blocks or to perform a post-synthetic modification procedure (PSM), as illustrated in Figure 2.21.[126] The method involving the design of functional building blocks in the pre-synthesis step is less favored, perhaps due to the required modification of the synthesis procedure, or the possible prevention of forming the desired MOFs. This may be due to the compatibility of the new functional groups in the linker and the actual linker chalet in bonding to the metal nodes.[126] However, Lillerud and co-workers[129] were able to design a series of isorecticular MOFs by incorporating a pre-functionalized BDC linker with different substituents (NH_2 , NO_2 , Br) in the synthesis of UiO-66, which is a Zr-based MOF with high thermal and chemical stability. The obtained isorecticular UiO-66 MOFs retained the chemical and thermal stability of the pristine UiO-66, and they showed good CO_2 adsorption capacity, especially amino-UiO-66. Sulfonation of UiO-66 was also reported by Van Der Voort et al.[130] who were able to synthesize it using a pre-functionalized BDC linker ($\text{BDC-SO}_3\text{Na}$), which was protonated during the reaction in an acidic medium to form SO_3H groups. These functionalization procedures followed the approach of functionalizing the linker as a first step before incorporation into the MOF synthesis.

On the other hand, the PSM strategy enables functionalization of both ligand and metal units with moderate to high complexity and functionality, with no need for changing the synthesis conditions.[126] Examples of MOFs that can be functionalized with the PSM technique are MIL-53 (Al) and MIL-53 (Cr), which were sulfonated under mild conditions using a mixture of sulfuric acid (H_2SO_4) and triflic anhydride (Tf_2O).[131]

Metal-organic frameworks have attracted the interest of researchers in the field of catalysis due to their remarkable advantages, such as high surface areas, pore-size tunability, well-defined structures, structural diversity, and thermal and chemical stability.[73] The interest of MOFs in catalysis can be emphasized by the scope of modifying the pore environment by including active functional groups in the framework. Having said that, the number of catalytic applications of functionalized MOFs is still limited as a result of some challenges related to the structure and functionalization. For example, some of the well-established MOFs, such as MOF-5, are moisture-sensitive, which restricts their utilization in practical applications.[132] This drawback has already attracted research interest in synthesizing MOFs that are stable in water by, for example, introducing hydrophobicity into MOFs.[133] To date, a few approaches have been used MOFs in biomass conversion. To our knowledge, sulfonated MOFs have not been tested in catalyzing biomass conversion to 5-HMF, except in one recent studies where serious of MOFs were sulfonated using PSM technique and tested in fructose dehydration.[134] While other MOFs were used either without functionalization (MIL-53(Al)) or as a support (MIL-53(Cr)) for a phosphotungstic acid giving a maximum yield of 28% and 44%,

respectively.[135][136] Thus, it is essential to introduce functionality into these porous frameworks with desired sites for carrying out biomass catalytic reactions.

2.3 Scope of the study

As discussed earlier in this chapter, fructose is an important intermediate in the prevalent route for the conversion of carbohydrates to 5-HMF, and since this is mainly a comparative study to test the effect of various porous catalyst supports on the catalytic activity of the catalyst, fructose was chosen as a model feedstock because it provides a straightforward route to 5-HMF, avoiding as many side-reactions as possible.

The first essential step in heterogeneous catalysis studies is to choose the catalysts. According to the results discussed above, we believe that a promising and efficient catalyst for fructose dehydration has to bear strong acidic groups. Inomata et al.[137] assumed that the performance of hexose dehydration into 5-HMF is correlated to the strength and type of the acidic groups, which was in agreement with the high yield of 5-HMF accomplished by using sulfonic acids (Table 2.2) or sulfated materials, such as zirconia[74], and sulfonic acid-supported catalysts (Table 2.5). In this research, we aimed to use supported sulfonic acid as a strong acidic catalyst. Additionally, we supposed that a crucial property of efficient catalysts in fructose dehydration is the dispersion of the sulfonic acid groups on the surface of solid materials, taking advantage of their structural properties. This can be seen in the increase in the yield of 5-HMF over acidic ion-exchange resin (61%) in comparison with homogeneous H_2SO_4 (42%) under the same reaction conditions.[46]

Incorporation of sulfonic acid groups into the structure of supports is expected to provide catalysts with a high concentration of accessible, highly dispersed, and structurally confined active sites for the dehydration of fructose into 5-HMF. Moreover, the controllable pore system is expected to enhance the affinity for the reactant substrates leading to increased conversion and selectivity towards 5-HMF. Besides, solid acids are stable at high temperature, and are easily recycled, which benefits the large-scale production. In total, merging these structural and acidic properties in one catalyst is a versatile and promising approach in 5-HMF synthesis, especially for industrial-scale production. In this work, we aimed to study the effect of different supports on the catalytic activity of sulfonic acid groups.

Herein, we chose several porous materials, inspired by two main features that were illustrated above: (1) the significant structural properties, and (2) the activity of the selected supports in other applications, such as adsorption, which motivated us to study their catalytic ability in our probe reaction. The first group of catalysts is related to the periodic mesoporous organosilica materials, namely phenylene-bridged PMO with a large pore size (denoted as Ph-PMO) and biphenylene-bridged PMO with a small pore size (denoted as Biph-PMO). The second group consists of two carbon materials, mesoporous carbon (CMK-3) and amorphous activated carbon (denoted as AC). The third set of catalysts contains two MOFs, which are MIL-53(Al) and UiO-66. For comparison of the catalytic activity of these three classes of materials, we introduced the sulfonic acid groups to a phenyl ring that was either the bridge of the PMOs or the linker in the MOFs. The phenyl ring was also the building block of the two carbon materials. These similar

sulfonated phenyl rings existed in all catalysts will allow a more comprehensive study of the effect of the properties of the different supports on the catalytic activity of the sulfonic acid groups. Other benefits of using the phenyl ring in such a reaction were related to its chemical structure and activity.[67][138] Firstly, the phenyl ring is suitable for post synthesis modifications, which allows easy introduction of sulfonic acid groups into the support structure. Secondly, the phenylsulfonic acid groups has more electron-withdrawing capability than other aliphatic sulfonic acid groups which results in increasing the acidic strength of the protons, and thus facilitating the catalytic reaction.[139] Thirdly, phenyl ring generates hydrophobicity on the surface of the support. In other words, it is stable in the presence of water, which is a major concern in fructose dehydration because of its role in generating rehydration of 5-HMF. In summary, sulfonic acid anchored on the surface of porous solid materials based on silica, carbon, and MOFs was chosen to catalyze fructose dehydration to produce 5-HMF (Figure 2.22).

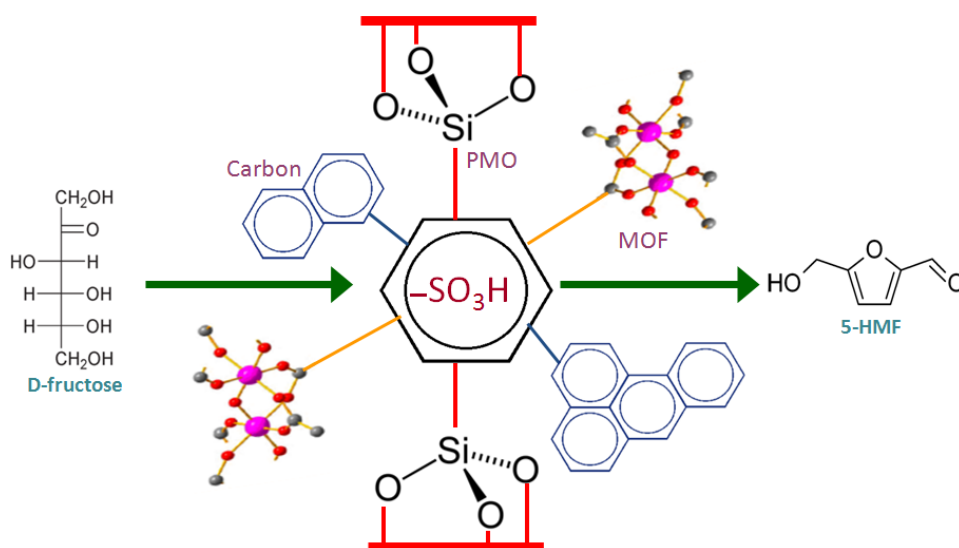


Figure 2.22. Schematic representation of the three types of catalyst supports.

CHAPTER 3 – EXPERIMENTAL AND INSTRUMENTATION

3.1 *Materials and Instruments*

All chemicals were reagent grade and were used without further purification. D-glucose and sucrose (99%), P123 (polyethylene oxide – polypropylene oxide – polyethylene oxide) triblock copolymer), octadecyltrimethylammonium chloride (ODTMA), BTEB (1,4-Bis(triethoxysilyl)benzene), BTEBP= 4,4'-Bis(triethoxysilyl)-1,1'-biphenyl, TEOS (tetraethylorthosilicate), MIL-53(Al), and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, were purchased from Sigma-Aldrich. D-fructose (99%), 5-HMF (98%), and vinyl sulfonic acid sodium salt were obtained from Alfa Aesar. BDC-SO₃Na (2-sulfo-1,4-benzenedicarboxylic acid monosodium salt) was supplied by TCI, and H₂SO₄ (98%), DMSO, acetone, and acetonitrile were from Fisher.

3.2 *Synthesis of Sulfonated Porous Catalysts*

3.2.1 *Synthesis of sulfonated phenylene periodic mesoporous organosilica (Ph-PMO-S)*

Generally, periodic mesoporous organosilica synthesis involves a supramolecular structure-directing agent and a silica source. According to the Goto and Inagaki synthesis procedure[107], represented in Figure 3.1, large-pore phenylene-bridged PMO was synthesized by adding 0.99 g of P123, 36 mL of distilled water, and 200 μL of hydrochloric acid (36 wt%) in a Teflon vessel, and stirring at room temperature until the P123 is completely dissolved. Then, 1.01 g of BTEB was added before the vessel was transferred

into an ice bath and stirred for 1 h. The molar composition of the synthesis mixture was as follows: 1 BTEB : 0.068 P123 : 2.28 HCL : 800 H₂O. The mixture was heated to reach 40 °C and kept for 20 h under stirring. After that, the vessel was sealed in an autoclave and then heated in an oven at 100 °C for 24 h. The resulting white powder was filtered and washed with water to obtain large-pore phenylene-bridged PMO. To remove the surfactant, the product was immersed in ethanol to allow solvent extraction, then calcinated at 250 °C in air yielding Ph-PMO. Sulfonation of Ph-PMO was carried out following the procedure of Molnar et al.[140] In a reflux system maintained at 55 °C, 1.5 g of Ph-PMO was dissolved in 25 mL of dichloromethane. Then, 5.2 mL of chlorosulfonic acid (ClSO₂OH) was added and stirred. After 1 h, the mixture was cooled to room temperature. The product was filtered and washed with water to remove all weakly absorbed acidic molecules. Further washing was carried out using THF and diethyl ether. This was followed by drying in a vacuum oven at 100 °C for 3 h to yield Ph-PMO-S.

3.2.2 Synthesis of sulfonated biphenylene periodic mesoporous organosilica (Biph-PMO-S)

Biphenylene-PMO was prepared following the same general concept of synthesis of periodic mesoporous organosilica, but in basic condition (Figure 3.1).[141] Typically, ODTMA (0.835 g) was added to 25.16 g of distilled water and 0.40 g of NaOH. Then, the mixture was stirred at 35 °C until the ODTMA was completely dissolved. After adding 1 g of BTEBP, the mixture was stirred overnight, followed by heating at 100 °C for 20 h. The mixture composition was as follows: 1 BTEBP : 1.5 ODTMA : 5 NaOH: 698 H₂O. The obtained solid was filtered, washed, and dried. In order to remove the surfactant, 1.0 g of

the as-synthesized product was stirred in 150 mL of methanol and 5 g of concentrated HCl aqueous solution at room temperature for 5 h. This procedure was performed one more time to remove all the surfactant. The Biph-PMO was sulfonated according to the aforementioned sulfonation procedure used in Ph-PMO.

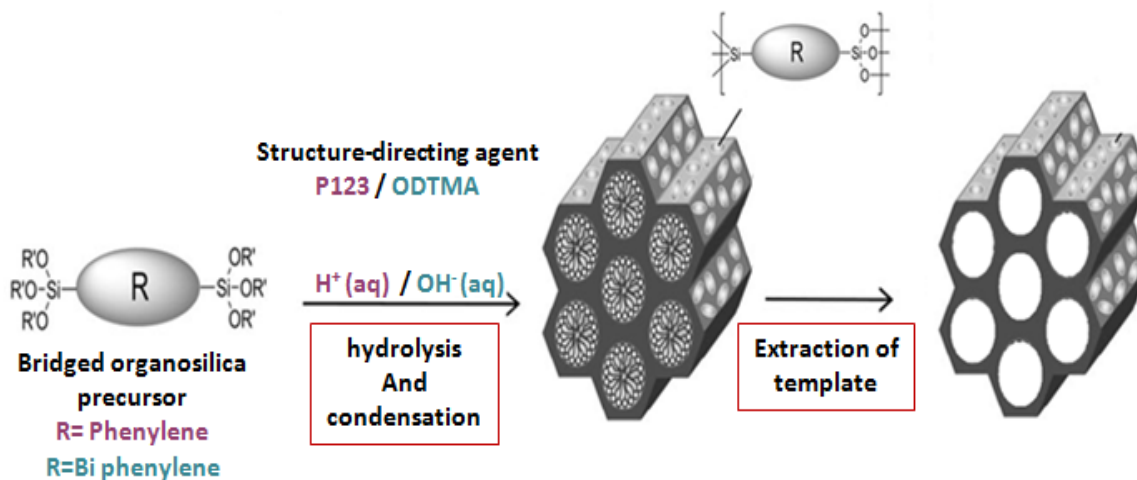


Figure 3.1. Synthesis of phenylene-PMO (purple) and biphenylene-PMO (green).

3.2.3 Synthesis of sulfonated mesoporous carbon (CMK-3- S)

Mesoporous carbon material (CMK-3) was prepared through the hard-template synthesis procedure using SBA-15 as the template.[119] Firstly, SBA-15 was synthesized following the Sayari et al.[142] procedure, in which 4 g of P123 was added to a solution of 120 mL of HCl (2M) and 30 mL H₂O, and stirred at 35 °C overnight. Then, 8.5 g TEOS was dissolved in the mixture and stirred for a few minutes. The mixture (1 SiO₂ : 0.017 P123 : 83.7 HCL : 40.7 H₂O) was kept under static conditions for 20 h at 30 °C, followed by 24 h at 80 °C. The obtained SBA-15 powder was filtered, washed with water, and calcinated in air at 500 °C.

Secondly, CMK-3 was prepared using the following procedure: 2.6 g of sucrose was dissolved in 0.25 g of H₂SO₄ (98%) and 4.2 g of deionized water. To this mixture, 2.1 g of calcined SBA-15 was added, and the mixture was heated at 100 °C for 6 h. Then, the temperature was gradually raised to 160 °C and kept for 6 h to allow partial carbonization. The obtained material was impregnated again in a solution containing 1.7 g of sucrose, 0.2 g of H₂SO₄ (98%), and 3.2 g of ionized water, then carbonized at 160 °C. The SBA-15/carbon composite was pyrolyzed under a stream of N₂ at 550 °C for 6 h to achieve deep carbonation. Then, the silica was removed from the mesoporous carbon by immersion of the material in a 5 wt% HF solution. After filtration and washing with deionized water, the material was dried at 100 °C to yield CMK-3. The sulfonation step was carried out using a vapor-phase procedure, which is schematically presented in Figure 3.2. H₂SO₄ (5 ml; 98%) and 0.3 g of CMK-3 were individually added to a Teflon container and a thick-glass tube, respectively. The glass tube was inserted inside the Teflon container, which was then sealed and heated at 60 °C for 48 h. The resulting CMK-3-S product was washed with deionized water to remove any excess acids, and dried at 100 °C overnight in air.

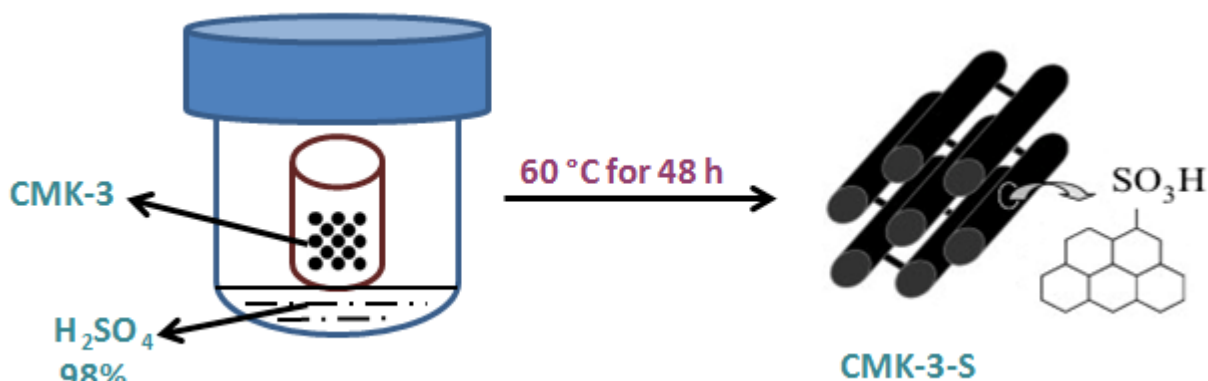


Figure 3.2. Schematic representation of the vapor-phase sulfonation procedure of CMK-3.

3.2.4 Synthesis of sulfonated activated carbon (AC-S)

Sulfonated activated carbon (AC-S) was synthesized by the hydrothermal carbonization method reported by Qi et al.[114], which was slightly modified in regard to the starting material (Figure 3.3). Typically, 6 g of glucose was dissolved in 42.5 mL of deionized water. Then the solution was transferred into a Teflon vessel containing 21.64 g of vinyl sulfonic acid sodium salt ($\text{CH}_2=\text{CHSO}_3\text{Na}$), and heated to 190 °C for 16 h. The acquired AC-S-Na product, represented in Figure 3.3, was filtered and washed with water. To exchange the Na^+ cations with H^+ , 100 mL of 0.1 N HCl was added to the product and stirred for 2–3 h, followed by washing with water to remove all excess acids, and dried in a vacuum oven at 80 °C.

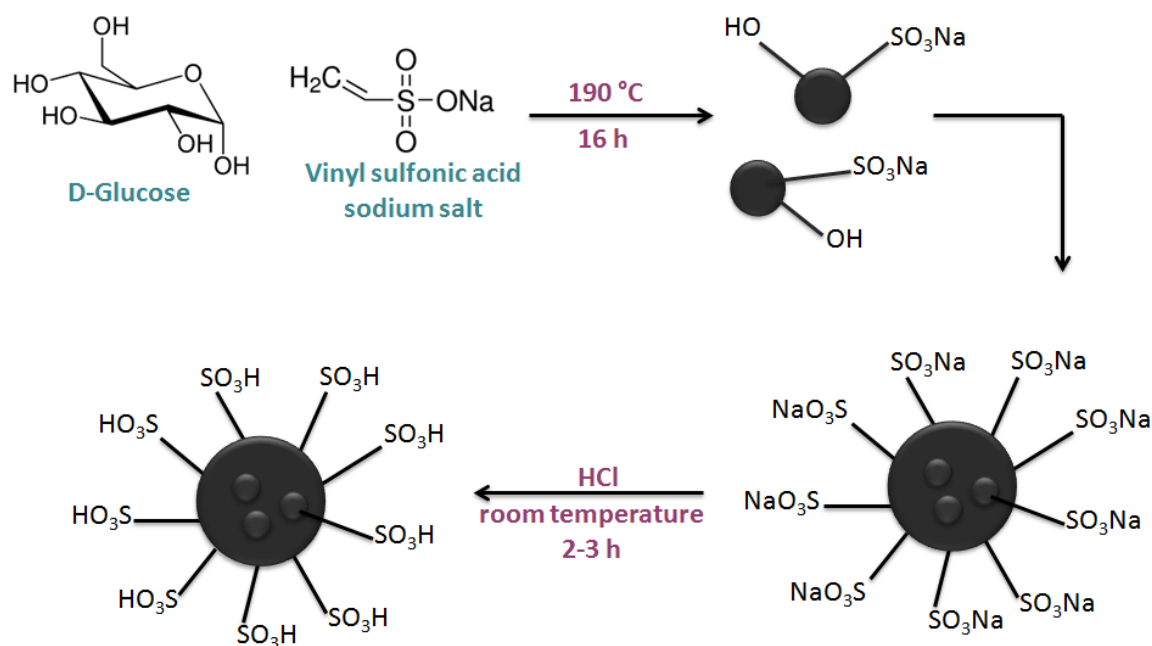


Figure 3.3. Synthesis of sulfonated activated carbon (AC-S) via the hydrothermal carbonization process.

3.2.5 Synthesis of UiO-66-S MOF

Sulfonated UiO-66 was synthesized according to the procedure published by Van Der Voot et al.[130] as schematically represented in Figure 3.4. In a Teflon vessel, 0.83 g of BDC-SO₃Na (2-sulfo-1,4-benzenedicarboxylic acid monosodium salt) was dissolved in 30 mL of dimethylacetamide (DMA). Then, 1 g of ZrOCl₂·8H₂O and 11.7 mL formic acid were added. The vessel was placed in an autoclave and heated in a programmable oven to reach 150 °C at a rate of 2.2 °C min⁻¹ for 24 h. After the solution cooled, the precipitate was collected by centrifugation, and dried in air. The as-synthesized material contains free molecules of the linker that occupies the pores. Therefore, the activated form of the material was obtained by a three-step treatment to remove the free linker molecules. Firstly, the as-synthesized compound was stirred with dimethylformamide (DMF) for 12 h to allow the free linker molecules to be exchanged with DMF molecules. Secondly, the DMF molecules were replaced by the easily removable methanol molecules upon stirring for 24 h. Thirdly, the volatile methanol was evacuated from the pores by heating at 65 °C in a vacuum oven for 24 h. The material was stored at 160 °C under vacuum.

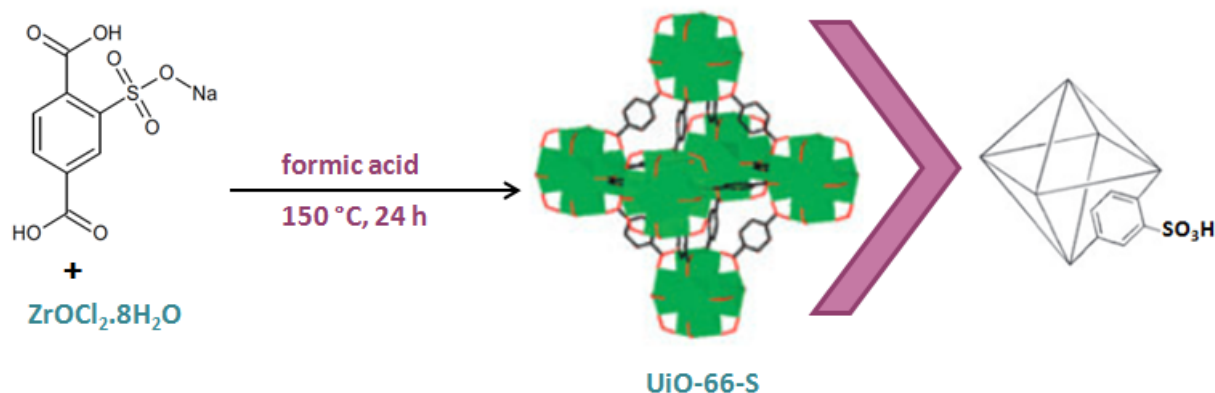


Figure 3.4. Synthesis of sulfonated UiO-66-S using a pre-functionalized BDC linker.

3.2.6 Sulfation of MIL-53(Al) MOF

The sulfonation procedure was performed in the presence of sulfuric acid (H_2SO_4) and triflic anhydride (Tf_2O) following the Gascon et al. procedure (Figure 3.5).[131] Commercial MIL-53(Al) was suspended in nitromethane (CH_3NO_2). Triflic anhydride and sulfuric acid were then added and continuously stirred for 60 min. The used molar ratio of MIL-53(Al)/ H_2SO_4 / Tf_2O was 1:1:1.5. The filtered solid was washed with deionized water and acetone, then immersed in ethanol at 70 °C for 24 h to allow activation. The sulfonated MIL-53(Al) solid was heated to 160 °C in a vacuum oven to remove ethanol molecules, and then stored at the same temperature.

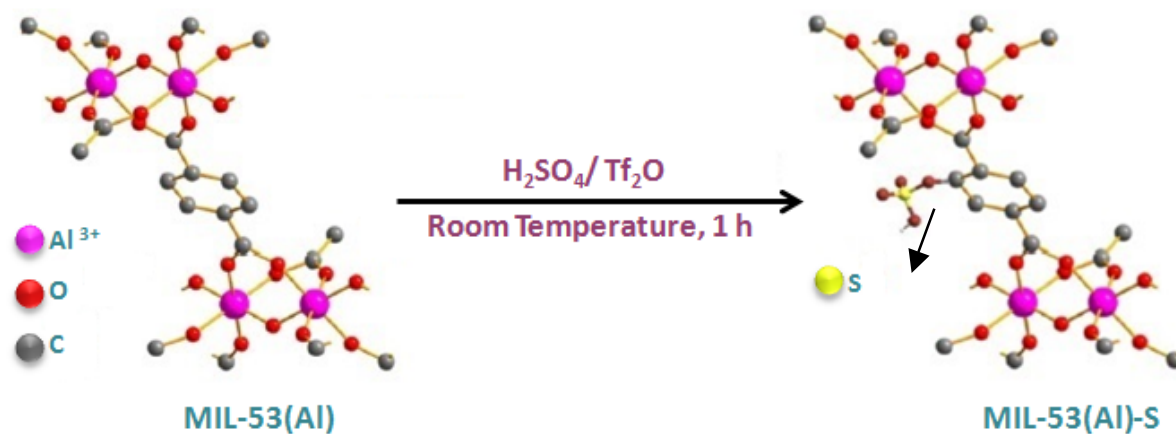


Figure 3.5. Sulfation of MIL-53(Al)-S by the post-synthetic modification procedure.

3.3 Catalyst Characterization

3.3.1 *Elemental (CHNS) Analysis*

The sulfonic acid content was measured by elemental analysis using a micro-cube elemental analyzer made by Elementar (Germany). A certain amount of sample was loaded into a tin capsule, then was inserted into the elemental analyzer. The sample was flash-combusted with O₂ at about 1800 °C, and then transferred by He through columns of reducing/oxidizing-chemicals to form N₂, CO₂, H₂O, and SO₂. The gases were separated within a single “trap and purge” adsorption column, and then detected by a thermal conductivity detector. The sulfur content was used to calculate the sulfonic acid loading.

3.3.2 *Fourier Transform Infrared Spectroscopy (FTIR)*

The ATR (Attenuated total reflectance) spectra of all catalysts were collected on a Nicolet 6700 Fourier-transform infrared spectroscopy (FTIR) instrument with a resolution of 4 cm⁻¹. Prior to analysis, the background was measured, and then catalysts were placed in a zinc-selenium plate and the FTIR was directly measured. The software used to collect the FTIR spectra was OMNIC. In the case of MOFs, the catalysts were first pretreated at 160 °C for several hours in order to remove the weakly attached water molecules.

3.3.3 *Nuclear Magnetic Resonance (NMR)*

Solid state ¹³C CP MAS NMR spectra were collected at room temperature on a Bruker AVANCE III 200 instrument in a magnetic field of 4.7 T using 7 mm zirconia rotors as sample holders spinning at MAS rate of 5000 Hz. The resonance frequencies were 50.3 and

39.7 MHz for ^{13}C and ^{29}Si MAS NMR, respectively. The chemical shift reference for C was the glycine C=O at 176.5 ppm, while for Si tetrakis(trimethylsilyl)silane Si ($\text{Si}(\text{CH}_3)_3$)₄ at 10.02 ppm was used as a reference. Recycle delay for all CP MAS experiments was about 2 s.

3.3.4 Nitrogen Porosimetry

The textural properties of all catalysts were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 volumetric apparatus. The catalysts were first degassed at 100 °C for about 8 h, except for MOFs, which were evacuated at 200 °C for 24 h. The surface area was measured by the BET method. The pore volume was calculated as the volume of liquid nitrogen adsorbed at $P/P_0 = 0.995$. The pore size and pore size distribution was calculated using the Kruk–Jaroniec–Sayari (KJS) approach.[143]

3.3.5 Thermogravimetric Analysis (TGA)

Thermal decomposition analysis was carried out by means of a Q500 thermogravimetric analyzer (TA Instruments). The samples were loaded into platinum TGA pans, then heated to 150 °C in a flow of N_2 for 2 h to remove any pre-absorbed moisture. This was followed by increasing the temperature to 800 °C at a heating rate of 10 °C/min, then to 1000 °C under the same heating rate in flowing air to insure complete decomposition of materials.

3.3.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) images were conducted using a high-resolution JSM-7500F field emission scanning electron microscope from JEOL.

3.3.7 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) images were obtained using a JEOL 2100F operated at 200 kV. Prior to screening, the materials were dispersed in anhydrous ethanol and deposited on a carbon film on a copper grid.

3.3.8 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) patterns of all catalysts were registered using X'pert instrument equipped with a solid-state detector using CuK α radiation with 0.15418 nm wavelength. The range of 2θ was below 10° for all the catalysts in a step size of 0.02 2θ , except MOFs in which the 2θ was up to 50° .

3.4 Dehydration of Fructose into 5-HMF

3.4.1 Catalytic reaction

All catalysts were used directly without pretreatment, except for the MOFs, which were treated in a vacuum oven at about 160 °C overnight. In a typical procedure[45], as schematically presented in Figure 3.6, a set of clean and labeled 5-mL microwave tubes were charged with 2 mL of solvent (DMSO/acetone; 7:3). Then, 100 mg of fructose was added to the tubes and stirred for 2–3 min at room temperature until the fructose completely dissolved. This was followed by addition of 50 mg of each catalyst into the labeled tubes. The microwave tubes were sealed with caps and subsequently inserted into a microwave reactor (Biotage Initiator Classic), which was gradually heated to reach 150 °C, then kept constant for 5 min. After completion of the reaction, a stream of N₂ cooled the reactor, and the reaction mixture was ready for analysis.

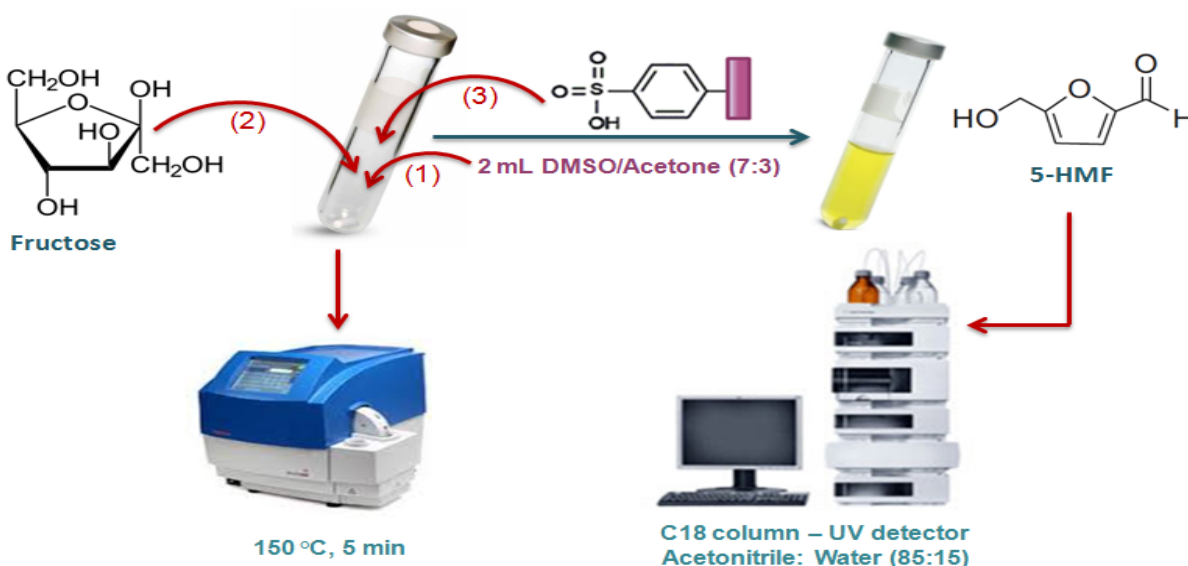


Figure 3.6. The steps of microwave-assisted conversion of fructose into 5-HMF.

3.4.2 Quantitative analysis for 5-HMF

Quantification of 5-HMF was performed using a high-performance liquid chromatography (HPLC, Agilent 1200) equipped with a UV-Vis detector and reversed-phase C-18 column at 30 °C. The mobile phase consisted of acetonitrile and deionized water (85:15 v/v) at 0.5 mL/min flow rate and the 5-HMF was analyzed at 280 nm. To prepare samples for analysis, a certain amount of the reaction mixture was transferred into a vial and diluted with deionized water. The diluted solution was then filtered through a Millipore filter (20- μ m pore size) to prevent any solid residues from entering into the separation column during HPLC analysis. The yield of 5-HMF was determined using an external standard calibration curve (Figure AI.1, Appendix) from which we calculated the actual weight of 5-HMF as follows[144]:

$$W_{5-HMF} (mg) = C_{5-HMF} (mg/ml) \times V_d \times \left(\frac{W_m}{W_d} \right), \text{ where;}$$

W_{5-HMF} = the actual weight of 5-HMF in the reaction mixture at the desired temperature.

C_{5-HMF} = the concentration of 5-HMF calculated based on the external standard calibration curve.

W_m = the total weight of the reaction mixture (the result of subtracting the weight of the empty microwave tube from its weight after the reaction).

W_d = the weight taken from the reaction mixture for dilution.

V_d = the volume of the diluted sample.

The yield of 5-HMF was calculated by dividing the actual weight of 5-HMF by the theoretical maximum weight, which is 70 mg for 100 mg fructose:

$$\text{5-HMF yield \%} = \frac{\text{Experimental weight of 5-HMF (}W_{5\text{-HMF}}\text{)}}{\text{Theoretical weight of 5-HMF (70 mg)}} \times 100$$

3.4.3 Recyclability of sulfonated porous catalysts

The catalysts were separated from the reaction mixtures by filtration. Next, they were washed with distilled water to recover the acidity and dried in air, except for the MOFs. UiO-66-SO₃H, and MIL-55 (Al)-SO₃H were washed with methanol. All MOF catalysts were activated in a vacuum oven at 160 °C. The catalysts were added to a solution of fresh fructose and solvents, and the reaction was carried out using the same conditions for three cycles.

CHAPTER 4-RESULTS AND DISCUSSION

4.1 Characterization of Catalysts

In catalysis research, studying the composition and textural characteristics of the synthesized catalysts is an important first step before going on to investigate their catalytic activity. To best address the aim of our study, namely to comprehensively compare three types of catalyst supports, it is critically important to characterize the surface area and the type of porosity in the structure, the pore system, evidence of acid existence, and the stability of each of the catalysts. The three groups of catalysts were therefore characterized by means of XRD, N₂ adsorption-desorption, NMR, FTIR, elemental analysis, SEM, TEM, and TGA. The obtained results will now be presented individually for each group.

4.1.1 Composition and textural analysis of periodic mesoporous organosilicas (PMOs)

Both phenylene and biphenylene-PMOs were synthesized for their catalytic activity to be investigated. The large-pore Ph-PMO was prepared using BTEB as precursor and P123 as supramolecular structure-directing agent under acidic conditions, while the synthesis procedure of small-pore Biph-PMO involved BTEBP as precursor and ODTMA as structure-directing agent in basic conditions. The introduction of sulfonic acid groups was accomplished using chlorosulfonic acid. The characterizations of the as-synthesized phenylene-PMO and biphenylene-PMO were carried out first to study the structure using XRD, N₂ adsorption-desorption, SEM, and TEM analysis techniques. Then the sulfonated

forms were tested in order to ensure the occurrence of acid sites using the data obtained from elemental analysis. The TGA analysis was used to study the stability of the catalysts structure.

The X-ray diffraction (XRD) patterns of phenylene- and biphenylene-PMO are presented in Figure 4.1. Phenylene-PMO exhibited two-dimensional hexagonal symmetry as inferred from the three signals in the low angle diffraction region ($2\theta < 5$), which were assigned to (100), (110), and (200) diffractions. In addition, the molecular scale periodicity of the organic bridges within the pore walls was proved by additional peaks at a diffraction angle ($2\theta = 12^\circ$) with d-spacing of around 0.8 nm as reported in previous works.[107][140] The XRD analysis showed that Ph-PMO exhibited an ordered mesostructure indicated by the well-defined XRD pattern. Similarly, Biph-PMO displayed a mesostructure assigned to the clear peak at 2θ equal to 2° , with no additional peaks detected related to the mesophase structure. According to Sayari and Yong[141], there is a lamellar structure within the pore walls which is proved by a broad peak at $2\theta=7.5^\circ$ corresponding to a d-spacing of 1.1 nm. This was proved by the regularly spaced diffraction peaks at d-spacings of 11.6, 5.9, 3.9, 2.9 and 2.4 Å.

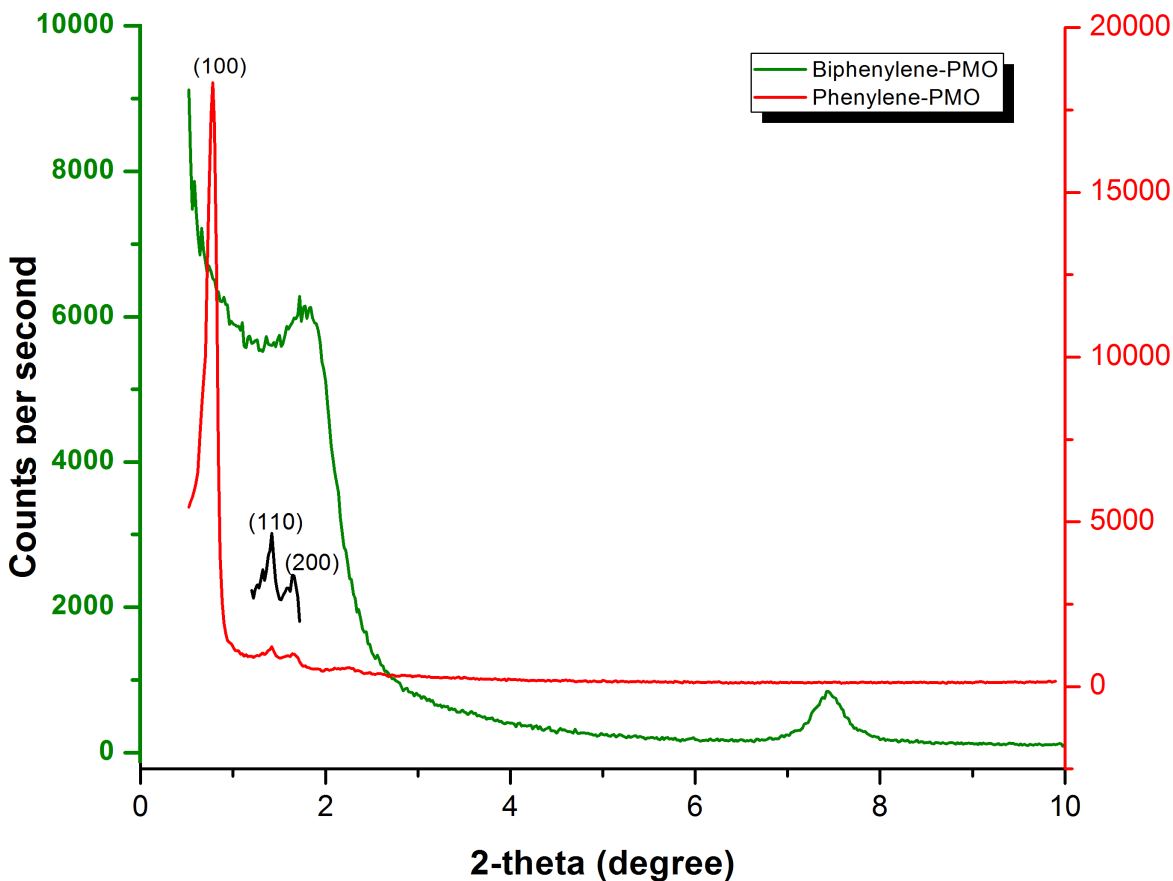


Figure 4.1. XRD profiles of phenylene- and biphenylene-bridged PMOs.

The characteristic nitrogen adsorption-desorption isotherms of phenylene-PMO and biphenylene-PMO are shown in Figure 4.2. Both isotherms feature a capillary condensation of nitrogen at $p/p^{\circ}=0.4-0.8$ indicating the occurrence of mesopores. The microporosity also occurs in the pore walls of Ph-PMO corresponding to the pore-filling step at very low pressure. It has been reported that this microporosity is a result of penetration of polyethylene oxide chains of the P123 into the pore walls during the synthesis procedure.[107] Both PMOs clearly have a mesostructure, with some microporosity generated within the pore walls.

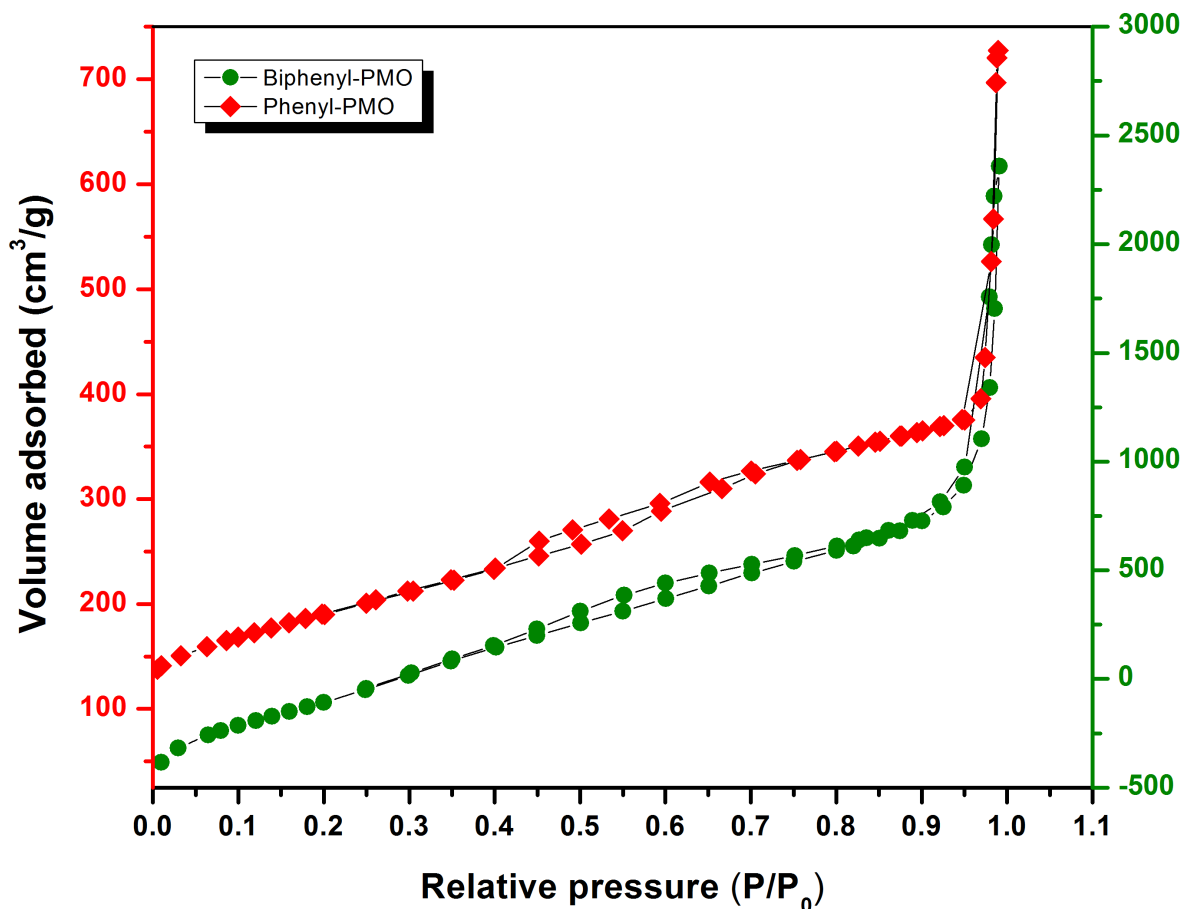


Figure 4.2. Nitrogen adsorption-desorption isotherms of phenylene- and biphenylene-bridged PMOs.

Data with respect to the textural properties (specific surface area, pore diameter and pore volume) derived from the nitrogen adsorption measurements are summarized in Table 4.1. As can be seen, phenylene-PMO has a high surface area of 1265 m²/g and a large pore size of 7.9 nm, both of which were slightly decreased upon sulfonation to 1040 m²/g and 7.5 nm, respectively. This decrease in surface area and pore size is in agreement with the majority of the published works where organosilica are sulfonated by a post-synthesis procedure[140], and indicates the occurrence of sulfonic acid groups within the pore channels. Biphenylene-PMO, has a lower surface area (462 m²/g) with an average pore size of 3.4 nm, which were also reduced after sulfonation took place by 200 m²/g in surface

area and 0.5 nm in pore size. The differences in textural properties between Ph-PMO and Biph-PMO can be ascribed to the different surfactant and condition applied. [101]

Table 4.1. Physicochemical properties of as-synthesized and sulfonated phenylene- and biphenylene-bridged PMOs.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Elemental analysis			Acid loading (mmolg ⁻¹)
				%C	%H	%S	
Ph-PMO	1265	1.51	7.9	-	-	-	
Biph-PMO	462	0.55	3.4	-	-	-	
Ph-PMO-S	1040	1.05	7.5	30.45	4.48	1.48	0.461
Biph-PMO-S	271	0.46	2.9	50.74	4.61	0.56	0.2

Scanning electron microscopy (SEM) images (Figure 4.3) show that phenylene- and biphenylene-PMOs exhibit different morphologies. The phenylene-PMO was comprised of rod-like aggregated particles with a diameter ranging from 0.1 to 1 μm and a length of 2 to 20 μm, while the biphenylene-PMO exhibited uniform smaller particles of ca. 1 μm in length. Transmission electron microscopy (TEM) images reveal the pore structure of phenylene- and biphenylene-PMO indicating a highly ordered mesostructure with a hexagonal arrangement of mesoporous channels as presented in the bottom images in Figure 4.3.

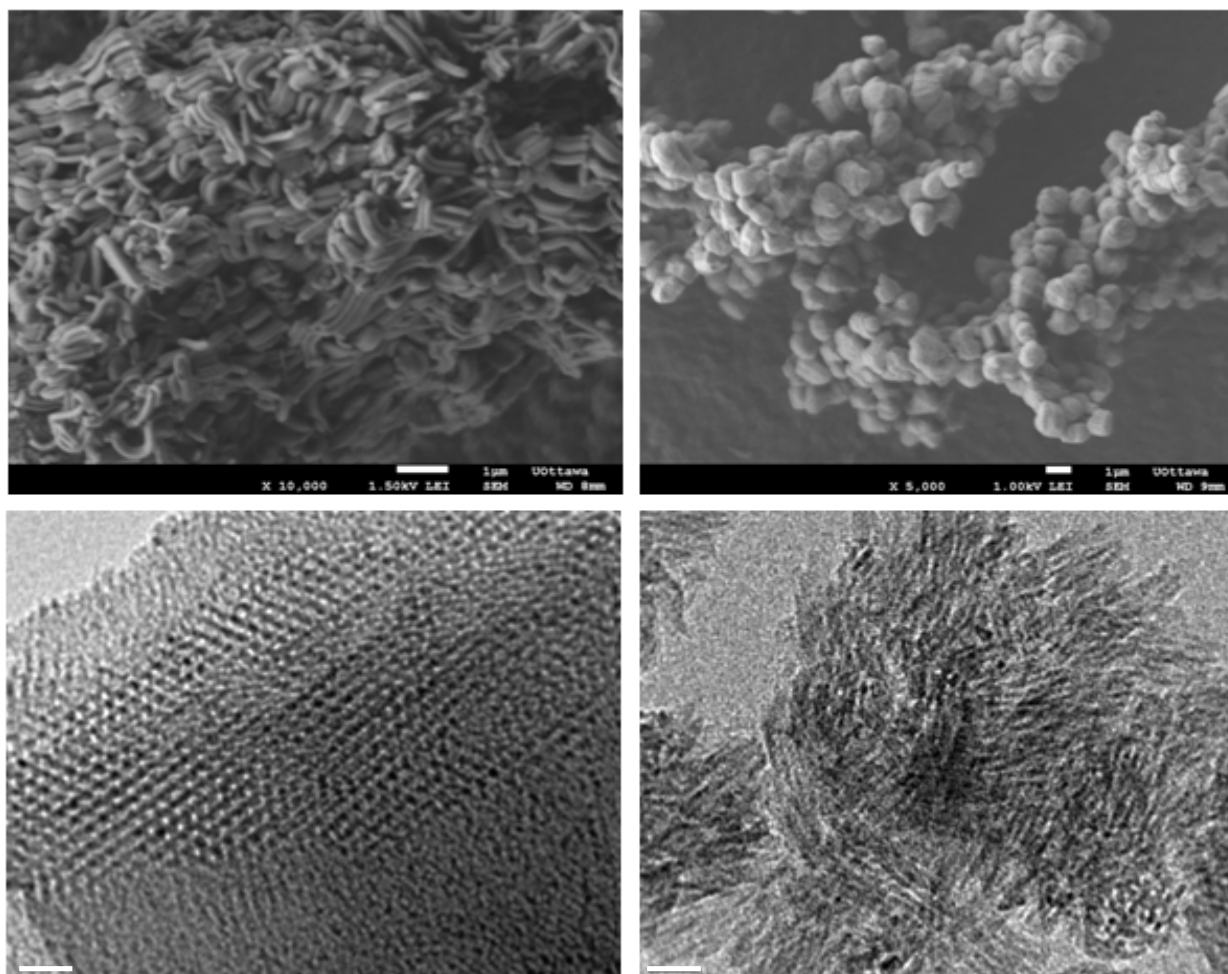


Figure 4.3. SEM images (top row) and TEM images (bottom row) of Ph-PMO (left) and Biph-PMO (right).

As for the composition analysis, solid-state ^{13}C and ^{29}Si NMR measurements were conducted to examine the appearance of organic bridges and the C-Si bonds. Further, elemental analysis was conducted to verify the occurrence of sulfur, and thus the acid loading. The ^{13}C CP MAS NMR spectrum of phenylene-PMO exhibited one peak at 133 ppm assigned to the four identical carbon atoms in the benzene ring.[107][140][141] Note that the appearance of small peaks at 17, 70, 73, 75 ppm are attributable of the residual P123 spices.[145] In the biphenylene-PMO ^{13}C NMR spectrum, four distinct peaks appeared at 125.5, 130.4, 134.0, and 141.2 ppm, and were attributed to the four different carbon atoms

in biphenyl[141] as indicated in Figure 4.4. The other peaks in the spectra of both Ph-PMO and Biph-PMO are side bands.

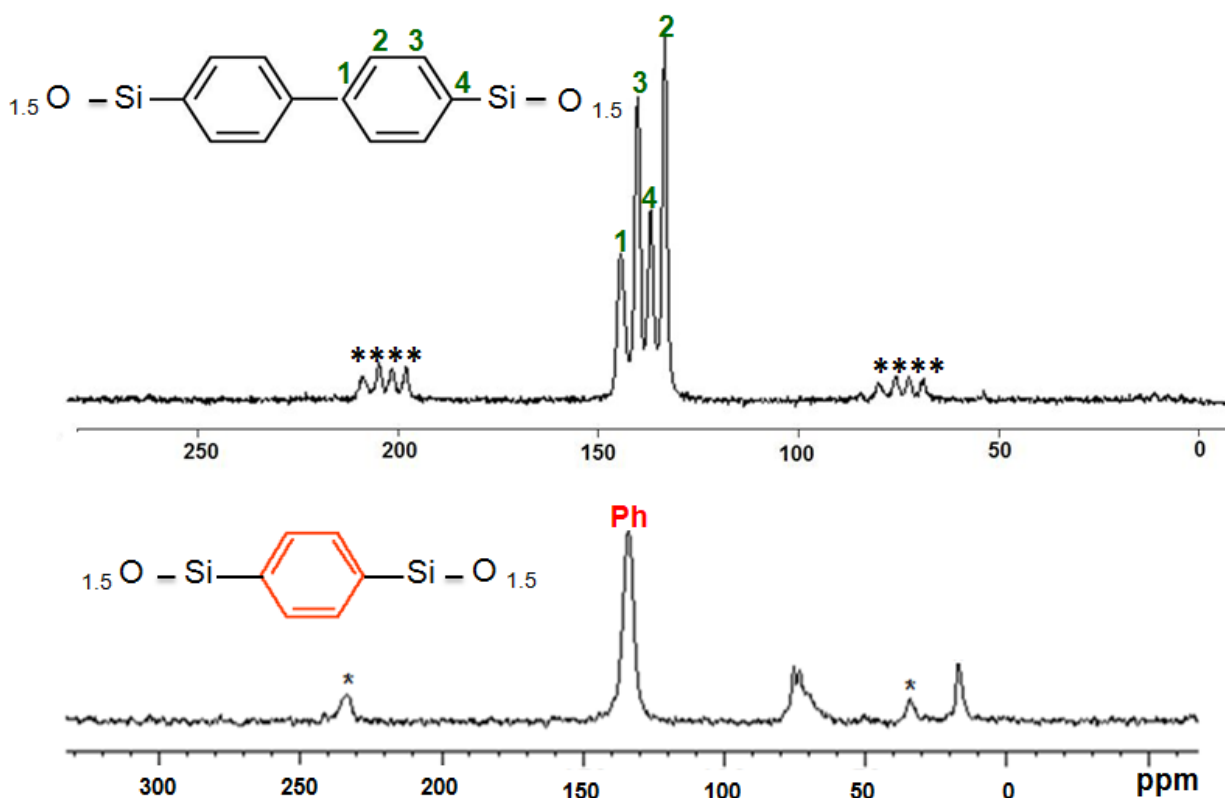


Figure 4.4. ¹³C CP-MAS NMR spectra for biphenylene-bridged PMO (top) and phenylene-bridged PMO (bottom). Note: * = spinning side bands.

As for the ²⁹Si MAS NMR, the spectra of both PMOs featured three signals at about -60.5, -70.6, and -78 ppm, attributed to the silicon resonance of T¹ [*CSi(OSi)(OH)*₂], T² [*CSi(OSi)*₂OH,] and T³ [*CSi(OSi)*₃], respectively (Figure 4.5). This result confirms the total framework linkage of these materials. It is worth to mention that the absence of SiO₄ species such as Q³ [*Si(OH)(OSi)*₃] and Q⁴ [*Si(OSi)*₄] in the range of 90 to 110 ppm confirms that no separate silica phase occurred and that all the silicon-carbon bonds were maintained during the synthesis and surfactant extraction. The combined results of ¹³C and

^{29}Si NMR illustrates the covalently bonded framework of $\text{O}_{1.5}\text{Si-C}_6\text{H}_4\text{-SiO}_{1.5}$ units with no C-Si bond cleavage.

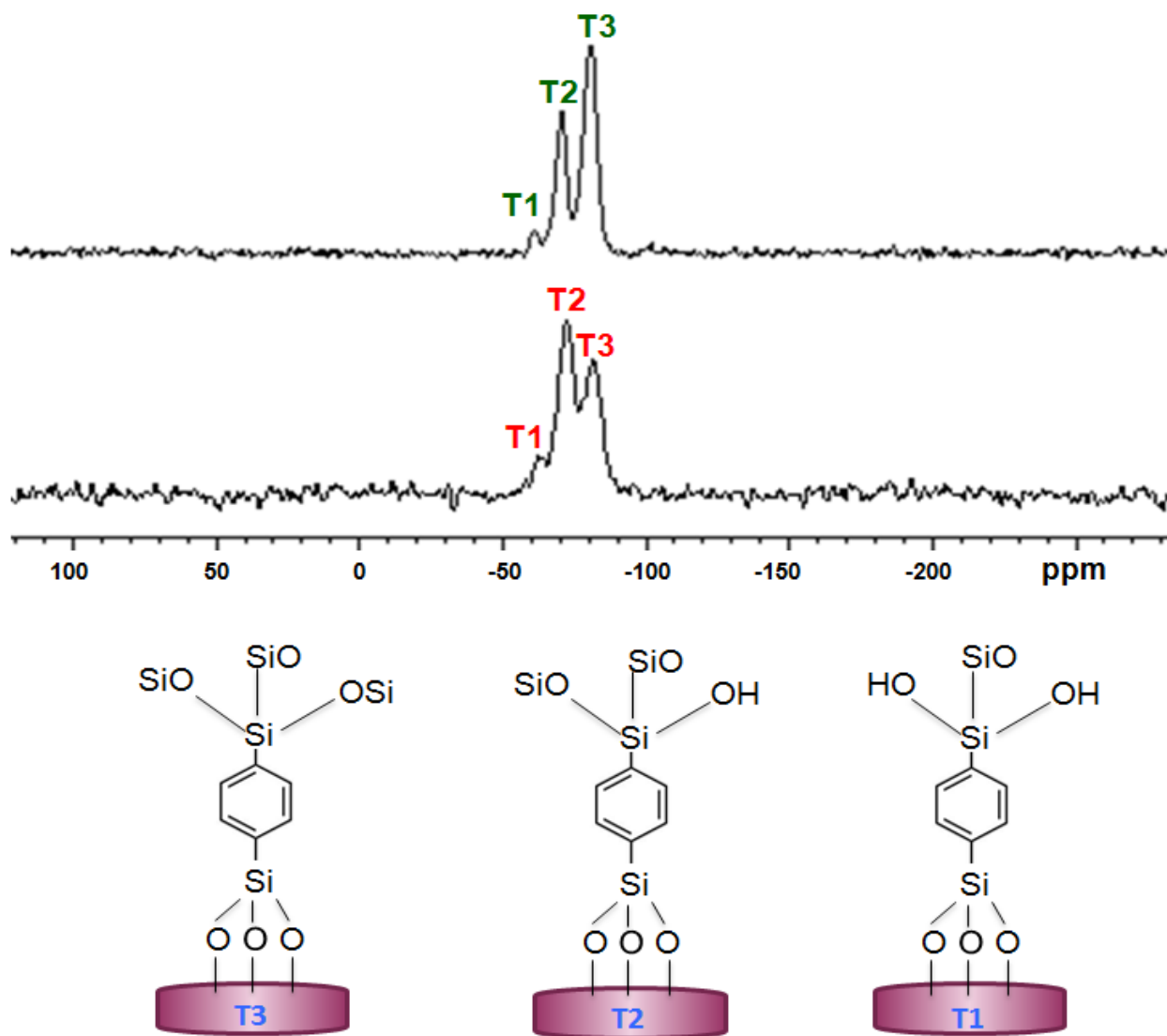


Figure 4.5. ^{29}Si MAS NMR spectra for biphenylene-bridged PMO (top) and phenylene-bridged PMO (bottom).

The acid loading and the organic content of sulfonic acid containing phenylene and biphenylene PMOs were determined by elemental analysis and the values are listed in Table 4.1. Since all the sulfur atoms are expected to be in the form of SO_3H in both

materials, the acid loading was calculated based on the elemental content of sulfur. For Ph-PMO and Biph-PMO, the sulfur loading was 1.48% and 0.56%, respectively, corresponding to an acid loading of 0.461 and 0.2 mmol g^{-1} , respectively. The higher acid loading of phenylene-PMO compared to biphenylene-PMO is in agreement with a previous study.[105] This behavior may be related to the higher surface area of phenylene-PMO (1040 vs. 271 m $^2/g$).

The thermal stability of the phenylene-PMO and biphenylene-PMO materials was determined by thermogravimetric analysis (TGA). Both TGA profiles (Figure AII.1, Appendix) proved that Ph-PMO and Biph-PMO exhibit high thermal stability since the decomposition of Ph-PMO starts at 480 °C, while Biph-PMO begins decomposition at 588 °C.

To sum up, the XRD and N $_2$ adsorption-desorption analysis provided direct evidence that both phenylene- and biphenylene-PMOs exhibit a two-dimensional mesoporous hexagonal structure with molecular-scale periodicity. The particle sizes and pore order were identified by TEM and SEM images. In addition, NMR data indicated that bridges occur in the materials with full organic linkage of the framework. Incorporation of sulfonic acid groups was confirmed and quantified by elemental analysis. Altogether, the similarities and differences between these two materials may lead to different catalytic activities of phenylene-PMO and biphenylene-PMO in fructose dehydration, thereby offering some insights about the important features of effective catalyst support for fructose dehydration.

4.1.2 Composition and textural analysis of carbon materials

The synthesis of sulfonated activated carbon was accomplished via a one-step hydrothermal carbonization process involving the decomposition of glucose in the presence of vinyl sulfonic acid sodium salt at a low temperature (160 °C).[114] This method was chosen in an attempt to synthesize carbon materials through mild and green method since no organic solvent or surfactants were involved. Ordered mesoporous carbon (CMK-3) was synthesized through a hard-template procedure using SBA-15 as the template in two carbonization steps; partial at 160 °C and deep at 550 °C. According to Xing et al.[119] the choice of carbonization temperature is critical in this synthesis. Their results demonstrated that carbonization at a temperature higher than 550 °C is beneficial in terms of increasing the mesostructure periodicity. However, at that high temperature, the CMK-3 obtained contained a negligible amount of polycyclic aromatic carbons that are available for functionalization. Ultimately, 550 °C was found to offer an acceptable compromise between mesostructure order and the number of polycyclic aromatic carbons. The as-synthesized CMK-3 was then subjected to sulfonation through vapor transfer process.

The XRD patterns of CMK-3-S and its template SBA-15 are presented in Figure (AIII.2 Appendix). The SBA-15 featured three well-resolved diffraction peaks, revealing a 2D hexagonal mesostructure.[119] In comparison, the CMK-3-S XRD pattern indicated that the ordered mesostructure of the parent, SBA-15, is well-maintained. The XRD pattern of AC-S demonstrated a broad peak in the region of $2\theta=10-30^\circ$, which is assigned to amorphous carbon composed of aromatic carbon sheets oriented in a random fashion.[146]

The nitrogen adsorption-desorption isotherm of CMK-3-S (Figure 4.6) showed a capillary condensation step at about $p/p^\circ=0.45$, with a hysteresis loop in the relative pressure range of p/p° (0.4-0.9) revealing a mesoporous structure. The textural properties of CMK-3-S are summarized in Table 4.2, which illustrates the high surface area ($441 \text{ m}^2/\text{g}$) and relatively small pore size (3.3 nm) in the range of mesopores. On the other hand, the data obtained from the N_2 adsorption-desorption analysis of AC-S indicated a microporous structure with typical Type I isotherm [94], which is common for amorphous carbon synthesized under the hydrothermal process.[147] The AC-S textural properties are typically similar to hydrothermally prepared carbons, having a low surface area ($12 \text{ m}^2/\text{g}$) and relatively large micropores (1.9 nm).[115]

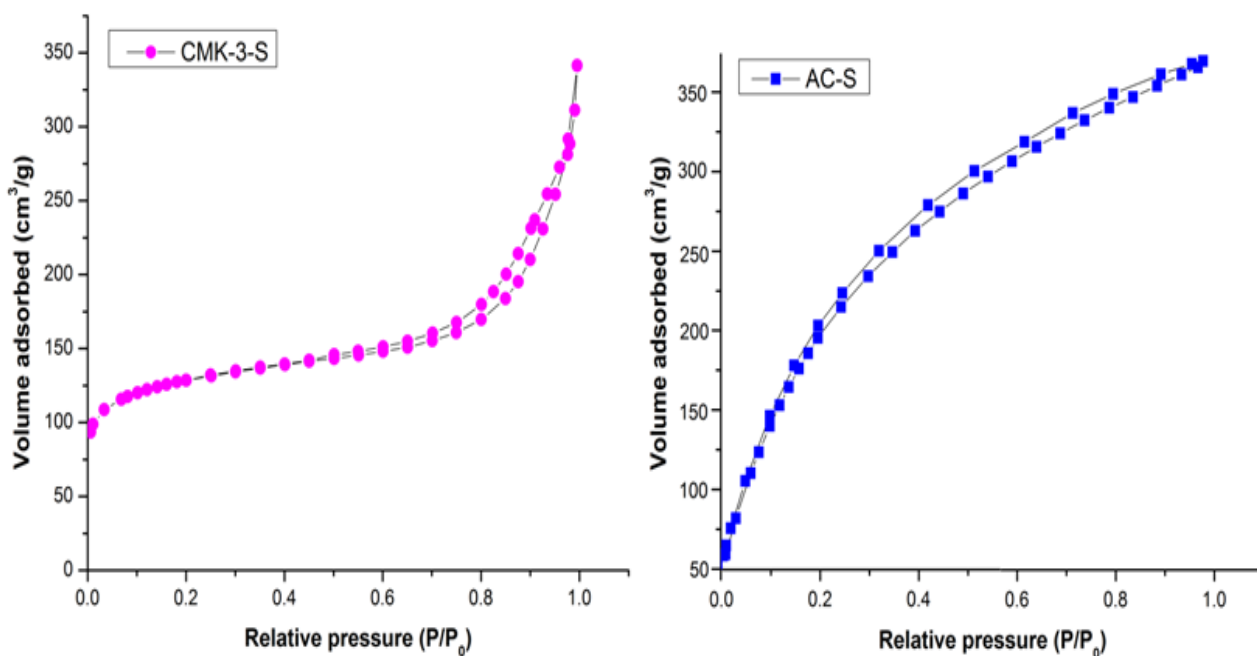


Figure 4.6. Nitrogen adsorption-desorption isotherms of CMK-3-S (left) and AC-S (right).

Table 4.2. Physicochemical properties of CMK-3-S and AC-S.

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	Elemental analysis			Acid Loading (mmolg ⁻¹)
				%C	%H	%S	
CMK-3-S	441	0.43	3.3	59.5	0.6	0.3	0.1
AC-S	12	0.01	1.9	57.5	4.1	0.57	0.18

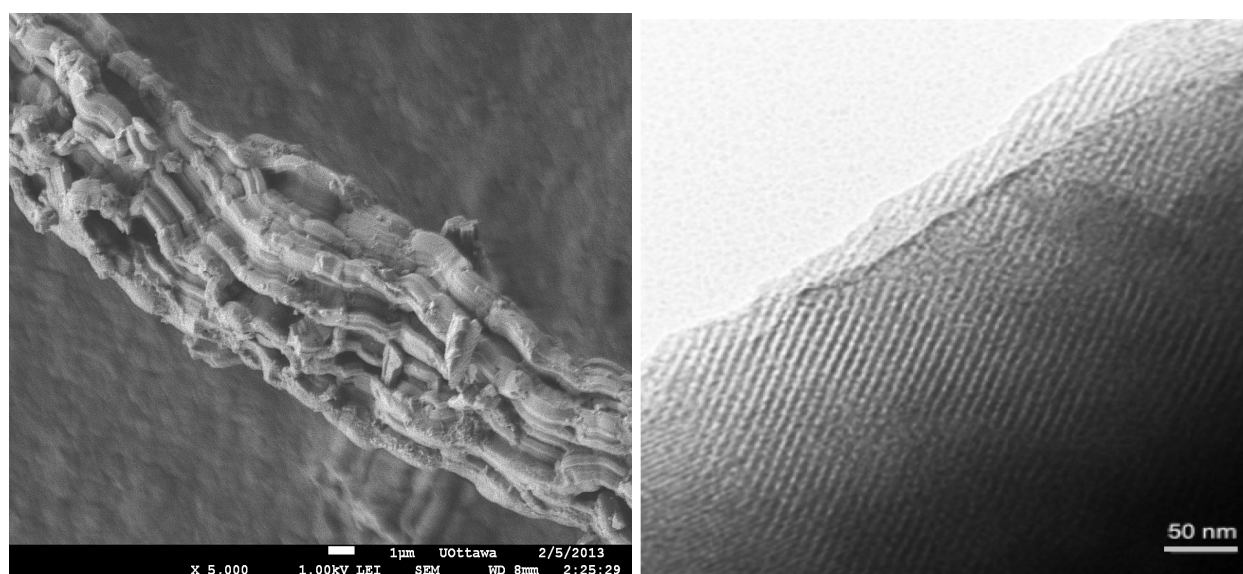


Figure 4.7. SEM image of CMK-3-S left, and TEM image right.

It can be seen from the SEM image (Figure 4.7, left) that CMK-3-S had rod-like particles, which exactly replicate the morphology of the corresponding template, while the TEM image reveals the hexagonal arrangement of the mesoporous channels. As for AC-S, the SEM image showed the formation of strawberry-like microporous carbon spheres which formed as result of the aggregation of micro-particles as represented in Figure 4.8. In addition, the random aggregation of the microporous spheres led to the formation of small

micropores between the spheres, yielding an overall amorphous structure as featured by microporosity.

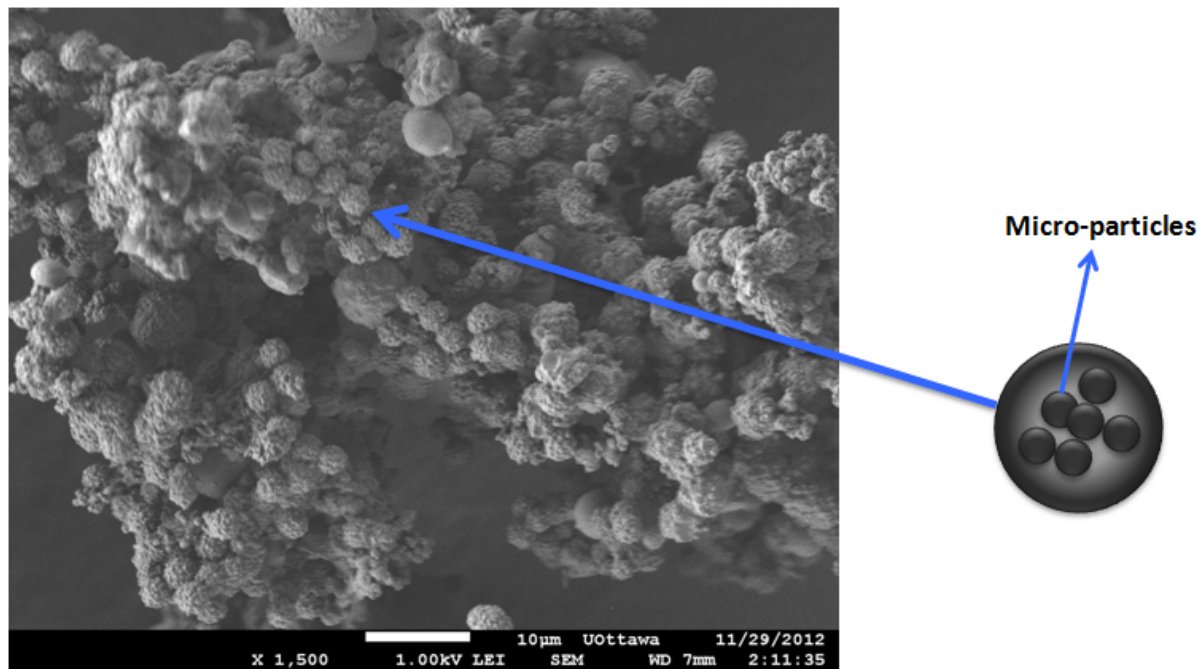


Figure 4.8. SEM image of AC-S and a schematic representation of the strawberry-like particles.

Regarding ^{13}C MAS NMR spectra, similar resonances were observed in both carbon spectra as illustrated in Figure 4.9. In the CMK-3-S and AC-S spectrum, two characteristic peaks appeared; one at about 130 ppm assigned to aromatic carbon and the other at 155 ppm attributed to the resonance of carbon in Ar-OH. A broad peak in the range of 14 to 60 ppm denotes the formation of aliphatic and ether carbons. A peak at about 170 ppm can be observed in both carbon materials, which is assigned to the $^*\text{COOH}$ groups formed during the carbonization process.[146] Regarding the occurrence of sulfonic acid groups, a peak at around 140 ppm assigned to the aromatic carbon linked to sulfonic acid groups must be formed. However, it cannot be distinguished because of the obstruction by the broad bands at 130 and 155 ppm.

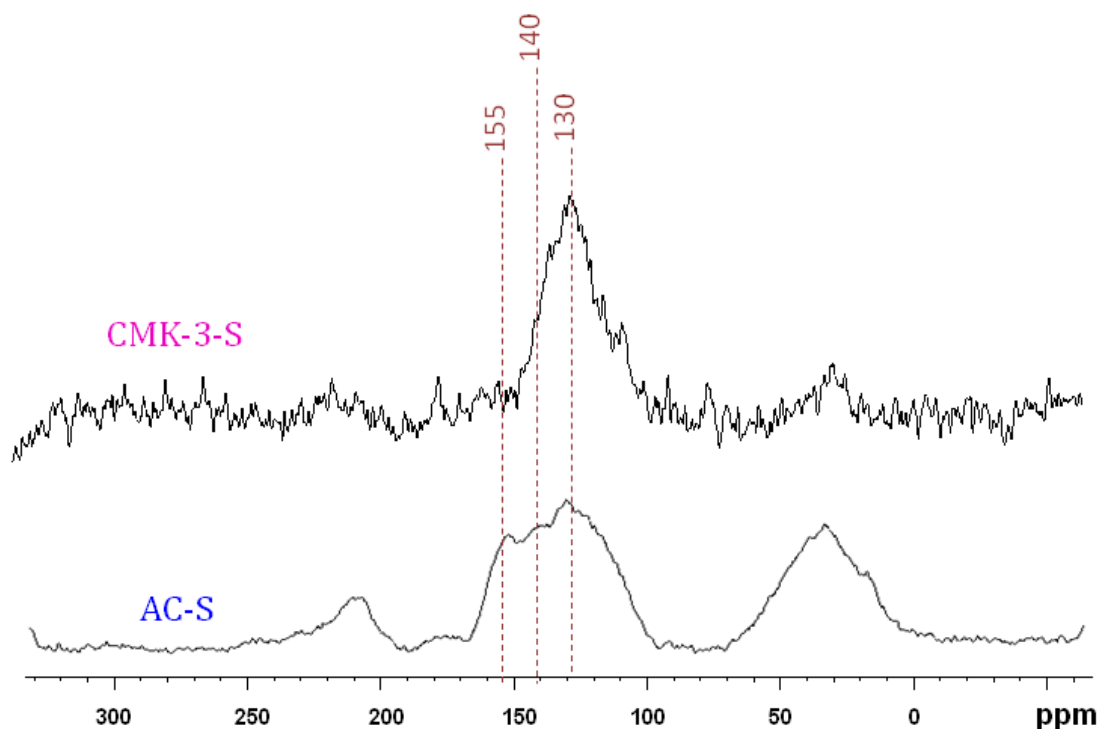


Figure 4.9. ^{13}C NMR spectra for CMK-3-S and AC-S.

IR analysis of both CMK-3-S and AC-S (Figure 4.10) was employed to confirm the occurrence of sulfonic acid groups within the carbon structure as well as the formation of some organic fragments as a result of the carbonization process. The sulfonic acid group corresponds to two characteristic absorbance bands at 940 cm^{-1} and 1032 cm^{-1} , which are assigned to the symmetric stretching of S-O and S=O bonds, respectively. In addition, a small peak at about 1377 cm^{-1} appeared, which is assigned to the O=S=O stretching in the SO_3H groups.[147] Nevertheless, these bands are of lower intensity in CMK-3-S than in AC-S due to the higher carbonization temperature that reduces the amount of polycyclic aromatic carbons available for sulfonation.[114] Other absorbances indicating the polycyclic aromatic structure of both CMK-3-S and AC-S are found in each spectrum at the range of $1466\text{-}1650\text{ cm}^{-1}$ for C=C stretching, $1209\text{-}1250\text{ cm}^{-1}$ for C-O stretching, while

2916-3030 cm^{-1} is assigned for -C-H stretching. Also, an absorbance band at around 1704-1755 cm^{-1} attributable to the vibration of C=O stretching in -COOH groups, and a band in the region of 3402-3600 cm^{-1} corresponding to O-H resonance in -COOH groups and phenolic C-OH groups generated through the carbonization process.

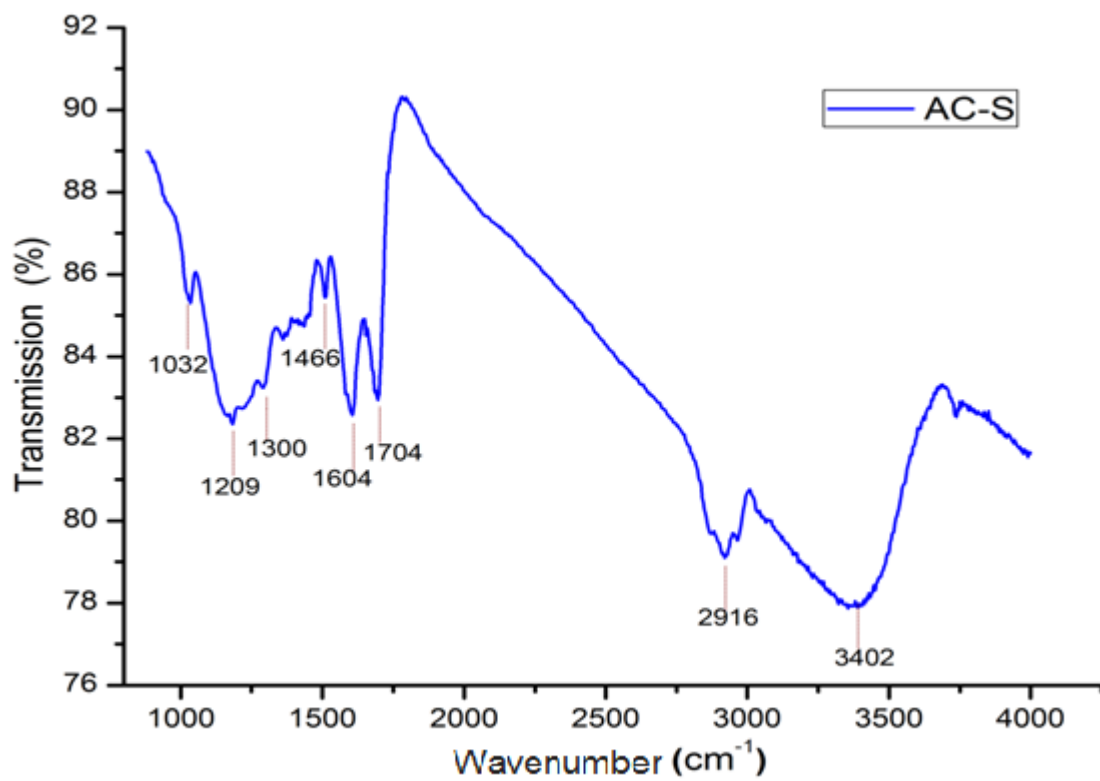
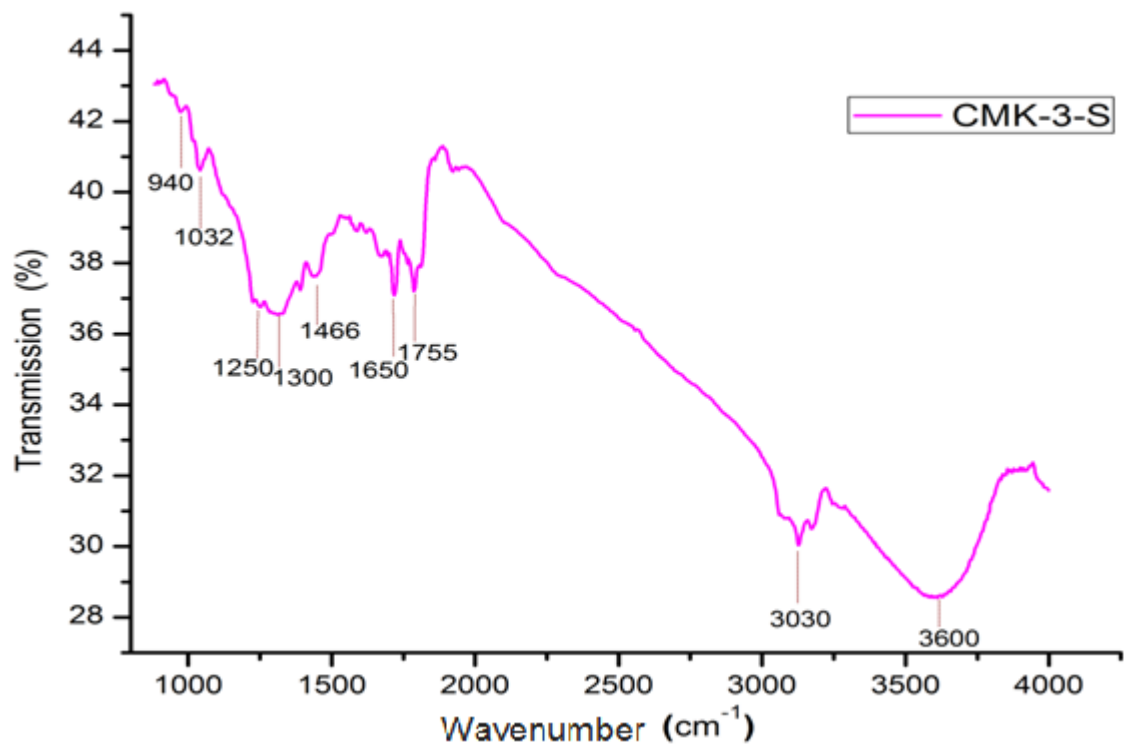


Figure 4.10. IR spectra for CMK-3-S and AC-S

The existence of sulfonic acid groups was proved by IR spectroscopy, and then quantified by elemental analysis. Elemental analysis indicated that the sulfonation reached 0.3 and 0.57 wt% sulfur in CMK-3-S and AC-S, respectively. Thus, the acid loading was calculated based on the amount of sulfur, and the results are listed in Table 4.2. Two potential reasons for the higher loading of the sulfonic acid groups in AC-S than CMK-3-S are related to carbonization temperature and synthesis method. Regarding carbonization temperature, lower temperature provided a better surface composition (OH) for sulfonic acid groups to be incorporated,[146] In addition, the one-step synthesis of the sulfonated AC-S has the advantage of incorporating sulfonate groups into the carbon structure. In this procedure, the carbonization took place slowly, and the OH groups developed during the carbonization reaction could facilitate the introduction of the sulfonate groups into the surface of the carbon products, resulting in a more efficient loading of sulfonic acid groups.[116]

As discussed above, two carbon materials with different properties were synthesized for the purpose of using them as catalysts in fructose dehydration. CMK-3-S is an inverse replica of SBA-15, which inherited its structural properties such as mesoporous structure and the rod-like morphology. On the other hand, AC-S showed an amorphous structure consisting of strawberry-like micro-particles. In addition, different acid loadings were observed in both carbon materials due to the different synthesis procedures. By testing these two carbon materials in our model reaction, we will perhaps be able to illustrate the required balance between the uniform porosity and the concentration of sulfonic acid groups, and most importantly, compare the behavior of periodic mesoporous carbon

materials with the previously discussed periodic mesoporous organosilica (Ph-PMO and Biph-PMO) under the same reaction conditions.

4.1.3 Composition and textural analysis of metal organic frameworks.

Two MOFs were used to investigate the efficacy of MOFs as catalyst supports in fructose dehydration. The first one, Zr-based UiO-66-S, was synthesized and sulfonated in one step via the solvothermal method using conventional heating.[130] The structure of UiO-66 was studied, and demonstrated a cubic 3D framework with a $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ secondary building unit (SBU) coordinated via the terminal carboxylate in the benzenedicarboxylate (BDC) linker, which forms an octahedral void in the center that connects the corner tetrahedral void. This results in the formation of two cages as represented in Figure 4.11; (a) octahedral cage of ca. 1.1 nm in diameter, and (b) tetrahedral cage of ca. 0.8 nm in size. These two types of cages are accessible through microporous windows in the range of 0.5 to 0.7 nm.[148]

The other MOF, MIL-53(Al), was obtained commercially and then sulfated under mild conditions with sulfuric acid (H_2SO_4) and triflic anhydride (Tf_2O).[131] MIL-53(Al) is comprised of the BDC linkers and corner-sharing AlO_6 octahedra, forming a 3D structure (Figure 4.11,c). Its framework contains 1-dimensional diamond shaped channels, with a free diameter close to 0.8 nm, and has a unique structure-breathing property.[149] The stability of the structure and the existence of the sulfonic acid groups is the main scope in

the following data analysis since they are the most important factors of MOFs as far as catalytic applications are concerned.

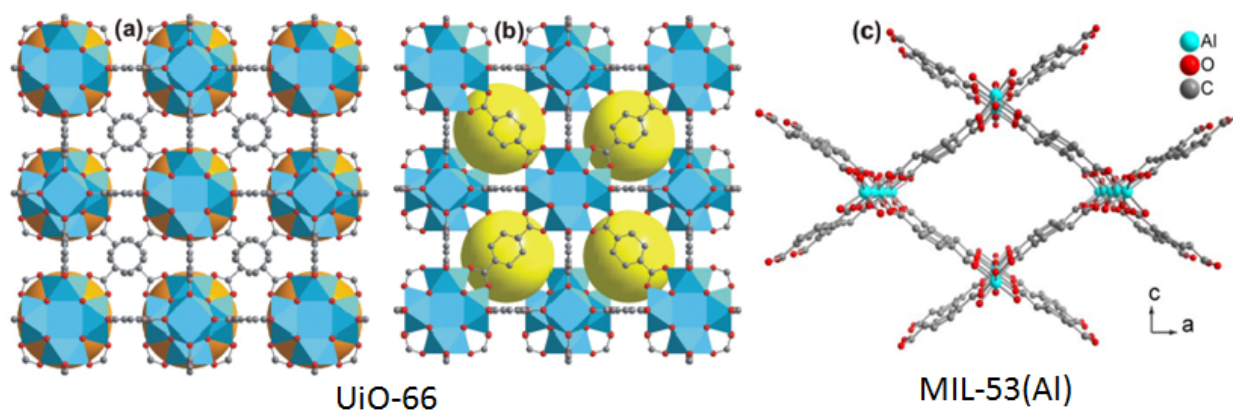


Figure 4.11. Schematic representation of the framework structure of UiO-66-S showing (a) the octahedral, and (b) tetrahedral voids represented by orange and yellow spheres, respectively, and (c) MIL-53(Al), (color codes: C, gray; O, red; blue, metal).

The XRD pattern (Figure AIII.1, Appendix) provides evidence of crystallinity and phase structure for UiO-66-S and MIL-53(Al)-S. The XRD patterns obtained for both UiO-66-S and MIL-53(Al)-S were in a good agreement with the reported data for pristine UiO-66 and MIL-53(Al) since no significant changes were observed in the diffraction peak positions and their relative intensities.[130][131][136] This result indicates that the two frameworks maintained their crystallinity after incorporating the sulfonic acid groups.

N₂ adsorption-desorption measurements were performed after thermal evacuation of the MOFs at 160 °C overnight.[181] The shape of the isotherms (Figure 4.12) was of Type I according to IUPAC classification[94], with steep increases in N₂ adsorption into micropores at low relative pressure ($p/p^\circ = 0.1$), indicating the microporous nature of UiO-66-S and MIL-53(Al)-S. The hysteresis loop in the isotherm is very commonly observed in

microporous polymers, which may indicate the existence of different micropores.[130] The surface area calculated from the N₂ adsorption data at 77.4 K using the BET equation was found to be 905 and 1015 m²/g for UiO-66-S and MIL-53(Al)-S, respectively. The other textural properties are presented in Table 4.3. Both MOFs exhibited a decrease of porosity in comparison with the pristine forms,[130][136] which may be associated with the partial occupation of the pores by the sulfonic acid groups.[73][150]

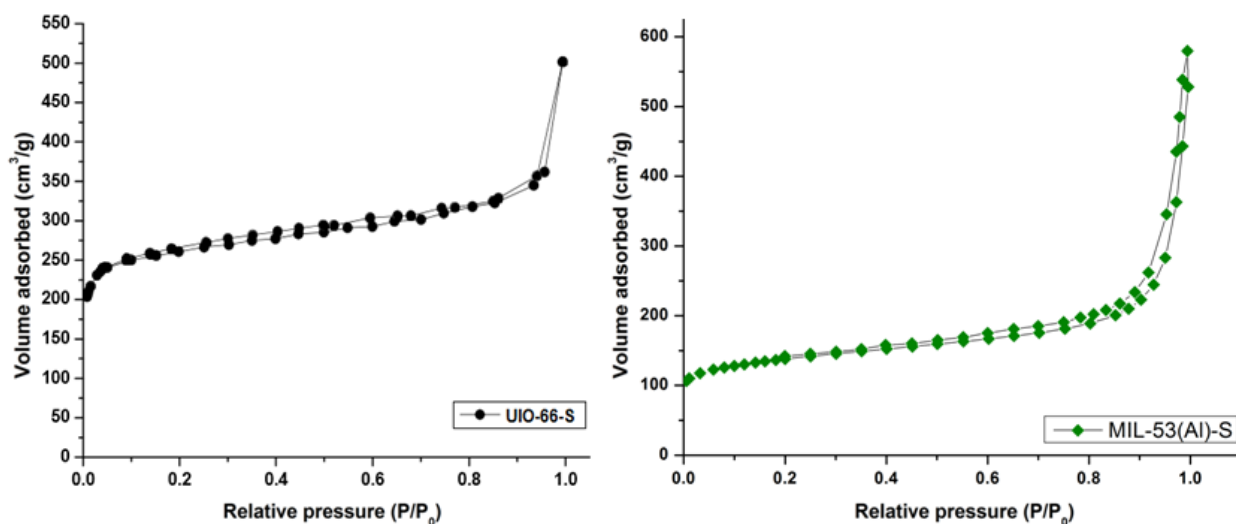


Figure 4.12. Nitrogen adsorption-desorption isotherms for UiO-66-S (left) and MIL-53(Al)-S (right).

Table 4.3. Physicochemical properties of as-synthesized and sulfonated MIL-53(Al) and UiO-66-S

Catalyst	Surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Elemental analysis			Acid loading (mmolg ⁻¹)
				%C	%H	%S	
UiO-66-S	904	0.54	0.47	22.85	3.39	6.20	1.8
MIL-53(Al)-S	1015	0.61	0.58	56.06	3.84	0.47	0.15

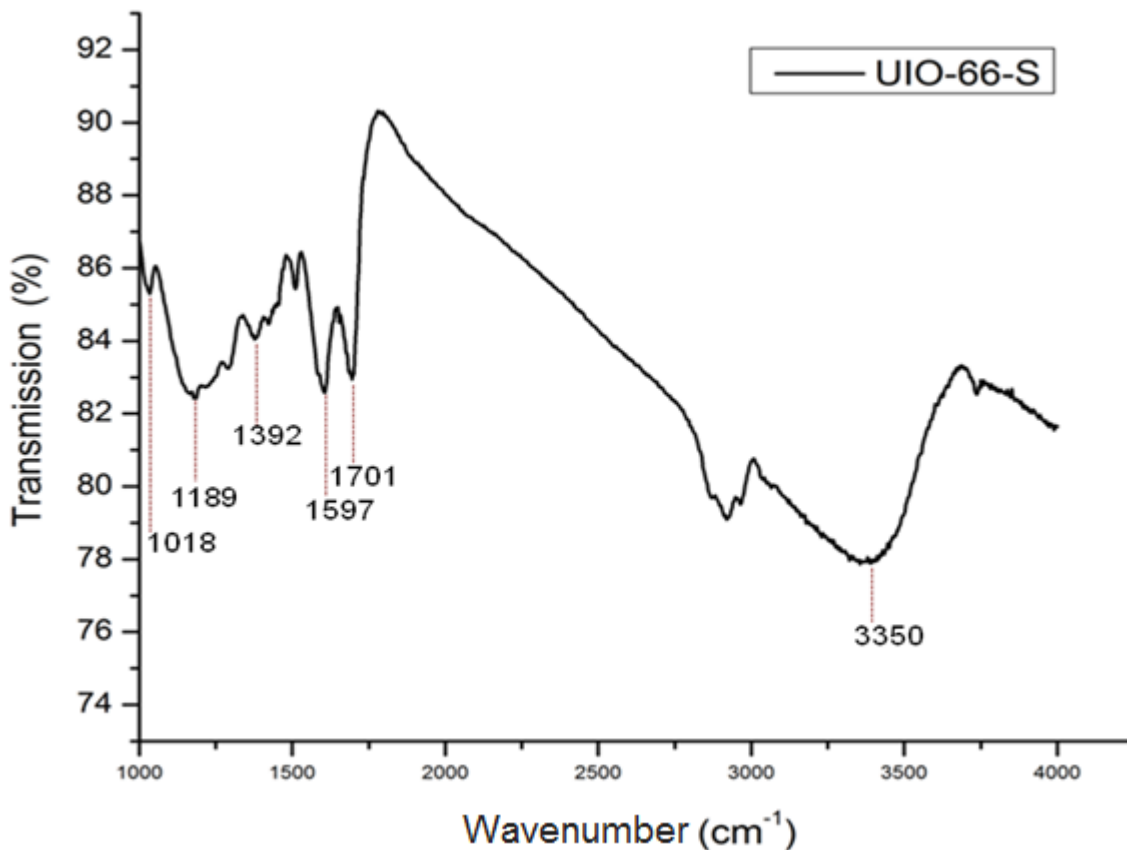


Figure 4.13. IR spectrum of UiO-66-S

Figure 4.13 presents the FT-IR spectrum of UiO-66-S, which illustrates the chemical composition and the successful incorporation of sulfonic acid groups into the framework. The coordinated BDC linker molecules showed two strong absorption bands at around 1392 and 1597 cm^{-1} , which are assigned to symmetric and asymmetric stretching vibrations of -CO_2^- . [130] Another strong adsorption band at 1701 cm^{-1} is attributable to the C=O stretching in -COOH groups of BDC linker, indicating the existence of a small number of unreacted BDC molecules occupying the pores of the UiO-66-s framework. In addition, a broad absorption band located in the region 3000-4000 cm^{-1} corresponded to the stretching vibration of OH groups, indicating that water molecules occupy a small portion of pores. In other words, the framework was easily hydrated upon the short

exposure time to air prior to the IR analysis. As for the sulfonic acid groups, there are two characteristic absorption bands situated at 1018 and 1189 cm^{-1} , which are assigned to the asymmetric and symmetric stretching of SO_2 fragments.

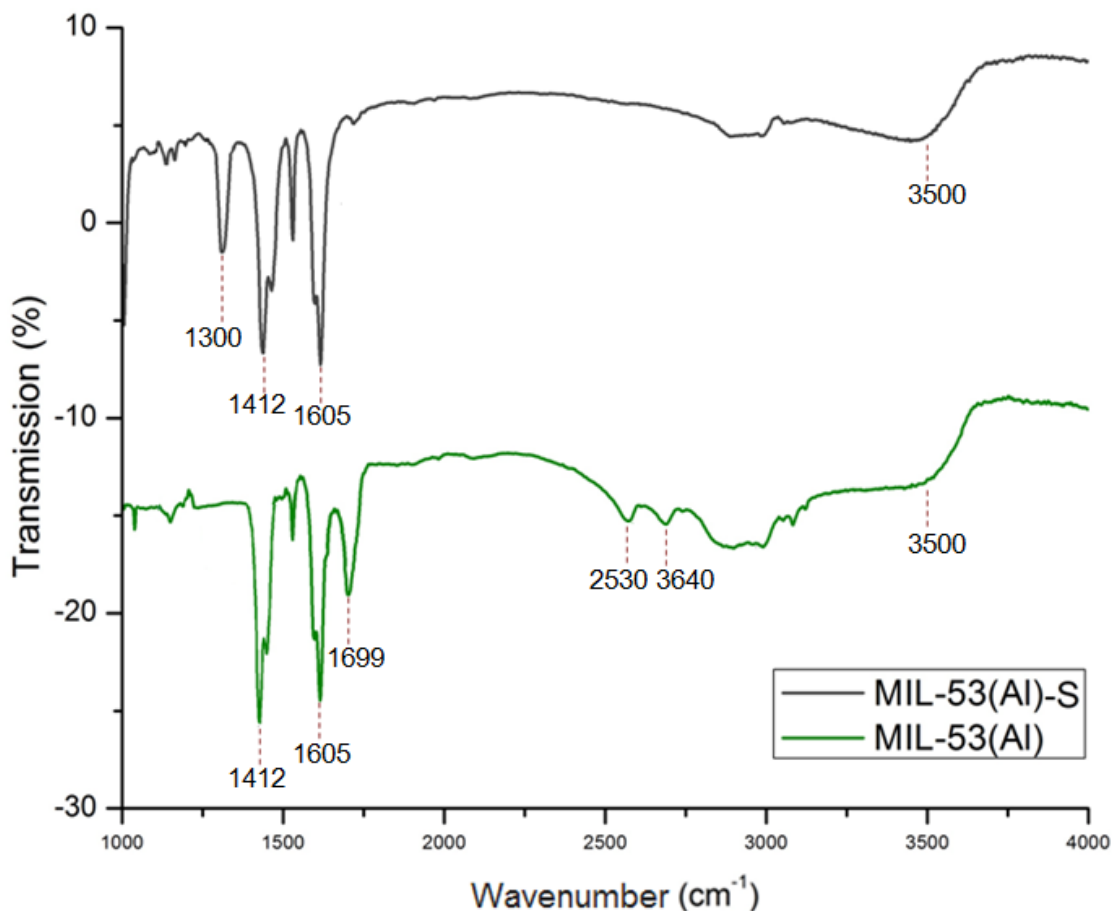


Figure 4.14. IR spectra of MIL-53(Al) and MIL-53(Al)-S.

Regarding MIL-53(Al)-S, the IR spectra were collected before and after sulfonation (Figure 4.14). Similar to UiO-66-S, vibration bands in the region of 1400–1700 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of $-\text{CO}_2^-$ of carboxylic functional groups, located at 1412 and 1605, while a specific band at about 1699 is attributable to C=O stretching in COOH group of unreacted free BDC linkers that are

trapped in the cavities of MIL-53(Al).[134][136] The sulfonic acid group vibration was associated with a sharp band at 1300 cm^{-1} , which did not exist in the unfunctionalized MIL-53(Al) spectrum. Bands in the range of $2750\text{-}3500\text{ cm}^{-1}$ are indicative of remaining water molecules in the framework of MIL-53(Al).[131] In addition a broad band at approximately 3500 cm^{-1} was observed corresponding to the stretching vibration of the OH groups. This vibration may be assigned to the hydrogen bond between the hydrogen from water molecules and the oxygen from acid groups, which may result in stabilizing the sulfonic acid groups.[131]

Looking at the ^{13}C CP-MAS NMR spectra of pristine and sulfated MIL-53(Al) (Figure 4.15), peaks appearing at $\delta=129\text{-}137\text{ ppm}$ are assigned to the resonance of aromatic carbons. The peaks observed approximately at 169 and 174 ppm are assigned to the deprotonated ($-\text{CO}^{-}_2$) and protonated ($-\text{CO}^{-}_2\text{H}$) carboxylic groups, respectively.[149] In the spectrum of the commercial MIL-53(Al), the latter two peaks were overlapped as the sum of contributions between the coordinated and free BDC linkers as illustrated in Figure 4.15. However, in the sulfated MIL-53(Al), only one sharp peak at about 169 ppm is noticed, indicating the removal of the free linker molecules represented by the protonated carboxylic groups ($-\text{CO}^{-}_2\text{H}$). Apparently, the removal of the free linkers was due to the washing, and drying process of the applied sulfonation procedure.[131]

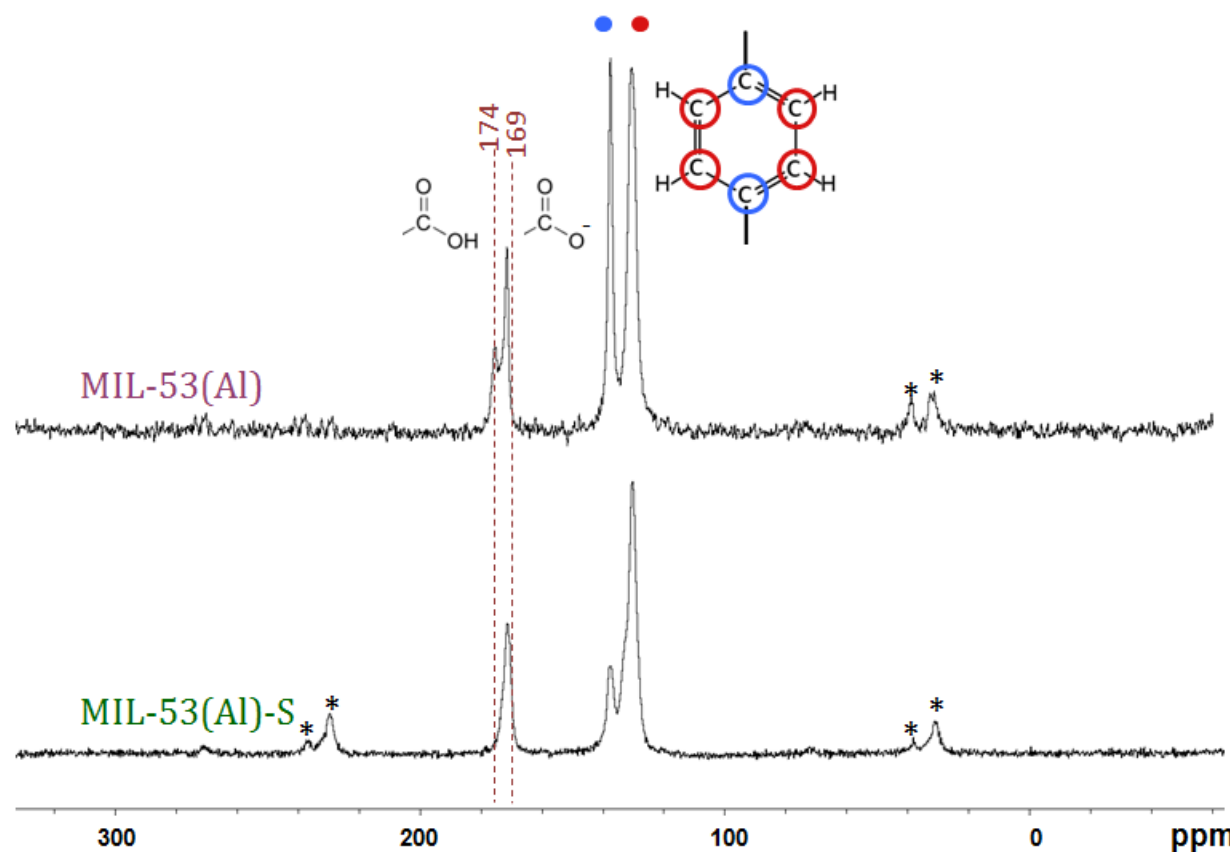


Figure 4.15. ^{13}C CP-MAS NMR spectra of MIL-53(Al) and MIL-53(Al)-S, Note: * = spinning side bands.

The thermal stability of UiO-66-S and MIL-53(Al)-S was indicated by means of TGA measurements. The pattern of TGA data was in agreement with published studies.[73][130][131] This indicates that MIL-53(Al)-S is thermally stable up to 175 °C, whereas UiO-66-S decomposition starts at 260 °C (Figure AII.2, Appendix). Two steps of weight loss were observed. The first one might be assigned to the removal of water and the free linker molecules. [131][73]On further heating, the second loss occurs and is ascribed to the release of the organic linkers leading to the decomposition of the framework structure.

The elemental analysis determined the amount of sulfur loaded onto MIL-53(Al) and UiO-66-S once the successful introduction of the sulfonic acid groups had been shown qualitatively (Table 4.3). There was a significant amount of sulfur (6.20%) successfully incorporated into the structure of UiO-66, resulting in a high acid loading of 1.8 mmolg⁻¹. However, MIL-53(Al) contained only 0.45% sulfur, corresponding to H⁺ loading of 0.15 mmolg⁻¹, which was dramatically lower than UiO-66-S. In addition, this different acidity clearly highlights the role of functionalization methods, and shows the huge advantage of using functionalized precursor instead of post-synthesis modification.

So far, the characterization results showed that six catalysts with various properties were successfully synthesized. Evidently, Ph-PMO-S, Biph-PMO-S, and CMK-3-S all have mesoporous structures. It should be stated that some differences in terms of their porous structure may lie in the textural properties and periodicity order, which is lower in CMK-3-S as a result of the synthesis conditions. AC-S activated carbon has an amorphous structure with some micropores between the particles. The surface composition of both carbon materials not only contains sulfonic acid groups, but also other weaker acids such as carboxylic acid and hydroxyl groups. On the other hand, both UiO-66-S and MIL-53(Al)-S possess a microporous crystalline structure that is highly able to contain water within the pores. This difference in the supports' structures most probably affects the catalytic activity of the sulfonic acid groups, thus shining a light on the significance of the type of porosity, periodicity, and surface composition of catalyst supports in fructose dehydration. This will be discussed further in the following section. Finally, the three main compositions

(organosilica, carbon, and metal organic frameworks) may allow us to estimate the preferred compositions of the catalyst supports for fructose dehydration.

4.2 Acid-Catalyzed Fructose Dehydration to 5-HMF

Once the characterization of all the catalyst supports had been completed, the catalytic activity of the sulfonic acid was to be examined. The objective of this examination was to compare the effect of the three main types of support for the activity of supported sulfonic acid in the dehydration of fructose into 5-HMF. Basically, the catalytic activity is determined based on the yield of 5-HMF, conversion of fructose, and the selectivity of catalysts, however due to instrumental limitation only the yield of 5-HMF will be calculated to represent the catalytic activity. From the characterization results, three main differences between the catalyst supports were observed, with regard to structural properties, porosity, and surface composition. These differences are expected to considerably affect the acid loadings, and thus the catalytic activity of the catalysts. Nonetheless, all catalysts have one common feature which is the attachment of sulfonic acid groups to aromatic rings. This design was aimed to generate hydrophobic surfaces that play an important role in limiting the deactivation of the catalysts.

4.2.1 Model reaction

In a comparative study, the selection of the model reaction is vital. The purpose of this effort is to optimize the reaction conditions to maximize the yield of 5-HMF. Therefore, the effect of variables for the dehydration process, such as reaction medium, reaction

temperature, and reaction time, must be investigated, and a reference catalyst must be chosen for these experiments to be conducted.

In order to evaluate the performance of a series of sulfonated catalysts depending on the support used, the reaction first needs to be performed in the presence of a reference catalyst. A commercially available Amberlyst-15 resin¹⁵ was found to be an excellent candidate for several reasons. First, the sulfonic acid group is attached to a phenyl ring (Figure 4.16), which is similar to the catalysts under study. Second, according to many published reports, Amberlyst-15 is capable of accommodating the highly polar fructose molecules, giving a high yield of 5-HMF.[24] Third, Amberlyst-15 has a strongly acidic character.[41][87] Together, these properties of Amberlyst-15 allow the design of a highly efficient reference catalytic system.

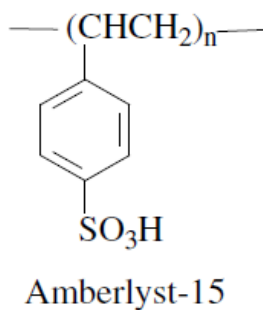


Figure 4.16. The chemical structure of Amberlyst-15 resin.

Thereafter, the first variable to be examined is the reaction medium. A system consisting of DMSO and acetone was selected based on research conducted by Qi et al.[45]

¹⁵ Amberlyst-15: sulfonated polystyrene-cation exchangeable resin with the chemical formula 2-ethenylbenzenesulfonic acid - 1,2-diethenylbenzene (1:1).

In solution, fructose exists in three types of structural isomers in equilibrium, which are fructoketose, fructofuranose and fructopyranose, with each of the two cyclic forms having two diastereoisomers (α and β) as presented in Figure 4.17.[42][45] Fructofuranose is an important intermediate that is protonated and dehydrated to form a fructosyl oxocarbenium ion (1 in Figure 4.17), which goes through irreversible chemical reactions to eventually yield 5-HMF.[42][44] Fructopyranose, however, leads to the formation of byproducts.[42] Therefore, controlling the relative concentration of fructofuranose and fructopyranose is of prime importance in directing the reaction towards high yield of 5-HMF. Akién et al.[42] found that the concentration of these two isomers differs depending on the solvent. For instance, in DMSO, 61.4% of the fructose isomers formed during the dehydration reaction was either one of the two diastereoisomers of fructofuranose (α and β) after 5 min of heating at 150 °C, while only 31.7% was fructopyranose (α and β). Furthermore, a high concentration of difructose dianhydrides (DFAs) intermediates (Figure 4.17) was identified in the presence of DMSO. These DFAs intermediates were found to be essential for the formation of 5-HMF, because they act as a reversible fructose reservoir to inhibit the route to fructopyranose in which fructose is converted into unwanted byproducts, such as humins.[16][42] These properties of DMSO as a solvent for fructose dehydration may explain the ability of DMSO to suppress the formation of the byproducts of 5-HMF, which was reported in many 5-HMF production systems.[77][89] Overall, the dehydration of fructose in DMSO leads to a high yield of 5-HMF, along with negligible amounts of byproducts.

In the same context, acetone was found to be able to promote the conversion of fructose into fructofuranose in a similar way to DMSO.[45][151] However, the solubility of

fructose in acetone is negligible (0.5 gL^{-1} in $25 \text{ }^\circ\text{C}$) and thus a co-solvent is needed to allow sufficient conversion. The use of water as co-solvent increased the conversion of fructose, but unfortunately triggered side reactions of 5-HMF.[151] In contrast, the use of DMSO as co-solvent was reported to improve the yield of 5-HMF and inhibit the formation of byproducts.[45] Moreover, acetone has a low boiling point ($65 \text{ }^\circ\text{C}$) compared to DMSO ($189 \text{ }^\circ\text{C}$), and thus mixing acetone with DMSO will lower the boiling point of the solvent mixture and reduce the amount of energy consumed in the separation step of 5-HMF. Therefore, a DMSO and acetone mixture is an excellent solvent system for the dehydration of fructose into 5-HMF because it increases the yield of 5-HMF, reduces byproducts, and makes the system more environmentally sound. Additionally, the ratio between DMSO and acetone was found to affect the yield of 5-HMF, and the maximum yield was obtained with a ratio of 7:3 DMSO/acetone.[45]

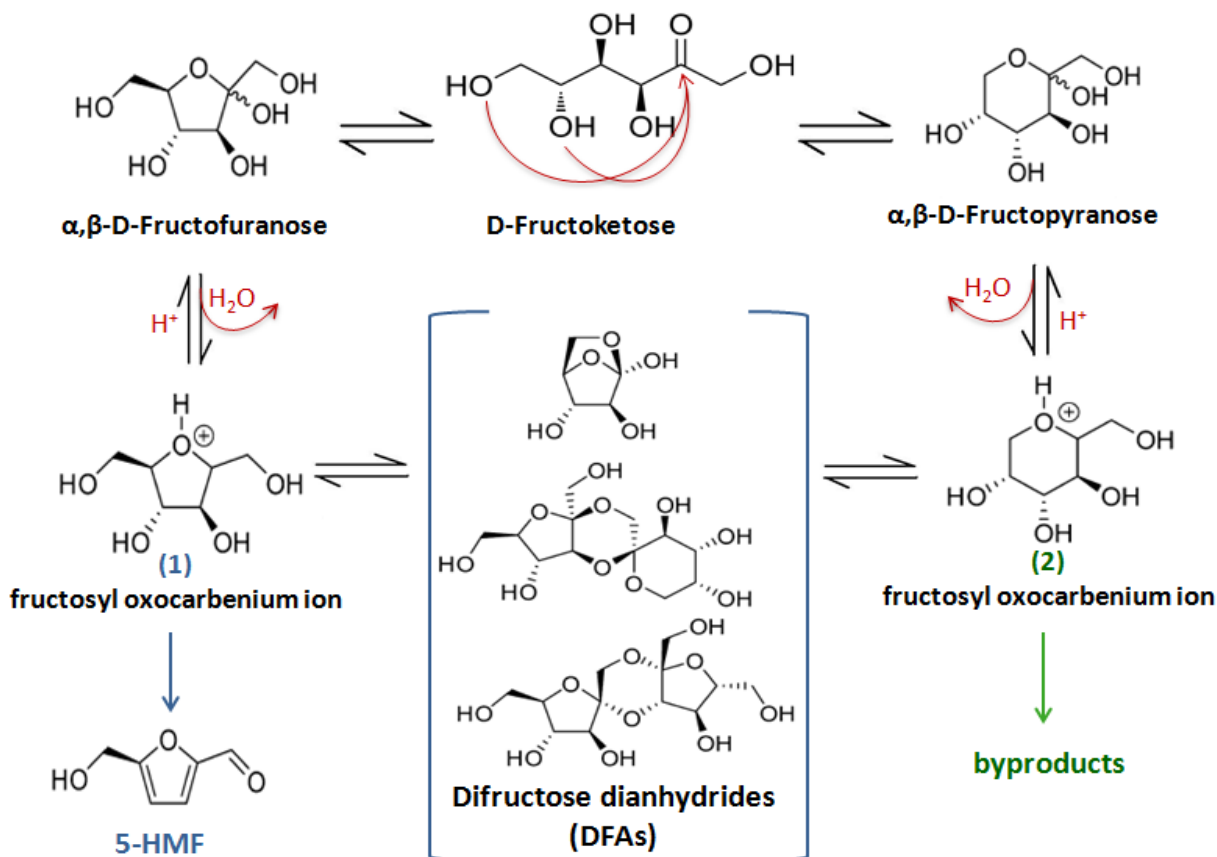


Figure 4.17. Structural isomers of fructose in solution and the main intermediates in the fructose dehydration route to form 5-HMF.[42]

The concentration of fructose is another essential factor to consider, since a higher amount of fructose in the reaction mixture, in which water molecules are generated, results in the formation of colored soluble and insoluble byproducts. This includes humins, which are insoluble brown products of the oligomerization of either fructose molecules or fructose and 5-HMF.[35][42] It was previously shown that 100 mg of fructose in 2 mL solvent (DMSO/acetone) and 50 mg of catalyst was appropriate.[45]

To further optimize the system in order to achieve maximum yield of 5-HMF, the reaction was carried out under microwave irradiation. It has been proven that microwave

irradiation is very effective at enhancing the dehydration of fructose, resulting in a high yield of 5-HMF in a shorter period of time.[152] In all of the studies using microwave irradiation[24][92], higher yields of 5-HMF were achieved in comparison with conventional heating methods. For example, Saha et al.[77] obtained a 49% 5-HMF yield by microwave heating in DMSO, while the maximum yield of 5-HMF obtained by conventional heating was only about 25%. It is worth noting that the DMSO improves the microwave synthesis system due to its high microwave absorbing ability[77]

In catalytic reactions, adequate reaction time and temperature are essential to reach sufficient mass transfer in the catalytic reactions. Therefore, several experiments were conducted using different periods of time and temperatures, and the results are presented in Figure 4.18 and Figure 4.19, respectively. In terms of the effect of reaction time, the maximum yield of 5-HMF (66%) was achieved after 5 min following reaction initiation. The 5-HMF yield decreased slightly upon increasing the reaction time, indicating that there was only a small loss of 5-HMF due to the occurrence of side reactions. Regarding the effect of temperature, an increase in the reaction temperature from 110 °C to 140 °C increased the yield of 5-HMF from 43% to 57%. This increase in the yield of 5-HMF upon increasing the reaction temperature was observed in most previously published works, and it was assigned to the fact that the rate of 5-HMF degradation is more rapid than the rate of formation in low temperature.[38][60] Further increase of the temperature to 150 °C, led to further increase of 5-HMF yield to an optimal value of 65%. However, higher temperature *e.g.* 170 °C leads to a decrease in the yield of 5-HMF due possibly to secondary reaction of 5-HMF.[57][60] In summary, we suggest that under MI, the optimum reaction

temperature is 150 °C, while the optimum reaction time is 5 min in a DMSO/acetone (7:3) solvent system.

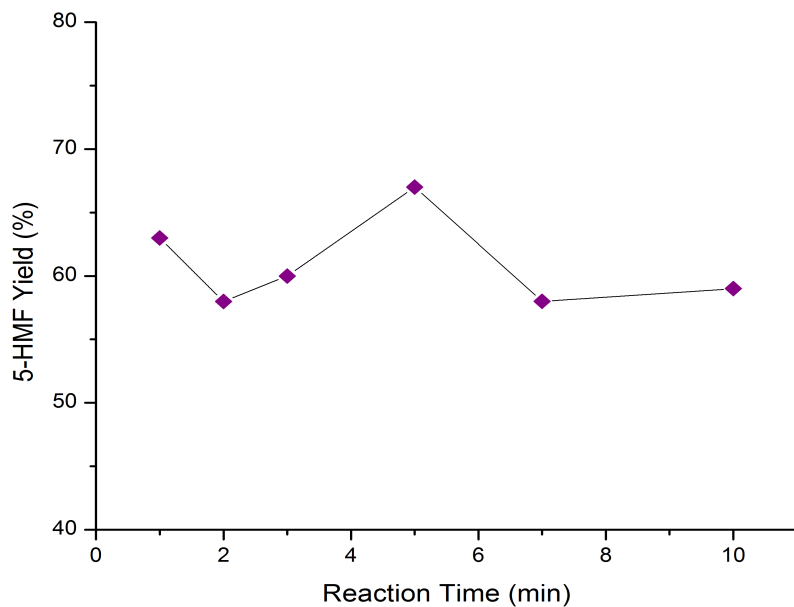


Figure 4.18. Effect of reaction time on the yield of 5-HMF. Reaction conditions: 100 mg fructose, 50 mg amberlyst-15, 2 mL DMSO/acetone (7:3), 150 °C, MI.

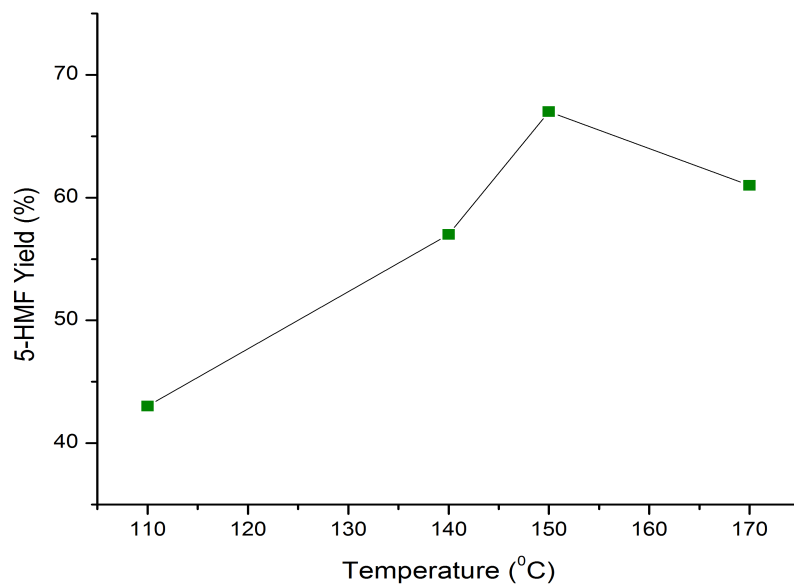


Figure 4.19. Effect of temperature on the yield of 5-HMF. Reaction conditions: 100 mg fructose, 50 mg amberlyst-15, 2 mL DMSO/acetone (7:3), 5 min, MI.

It was important to determine that the solvent is not involved in the catalytic reaction. The importance of this step is because Amarasekara et al.[43] noted the ability of DMSO to catalyze fructose dehydration at a high temperature (150 °C). It has also been reported that this catalytic activity is assigned to the decomposition of DMSO ((CH₃)₂S=O) into CH₃SO₃H and H₂SO₄, which act as autocatalysts for the fructose dehydration.[153] So that, it is essential for us to make sure that under our reaction conditions the solvent is not involved in catalyzing the dehydration of fructose. Therefore, several experiments were conducted in the absence of catalysts at 150 °C for 5 min under microwave irradiation. The dehydration reaction did not proceed efficiently with no more than 2% of 5-HMF obtained. This illustrates that under our reaction conditions, the only source of catalytic activity was the acidic catalyst.

After all the parameters were established, the catalytic activity of all the sulfonic acid containing catalysts was tested. Herein, we applied the following optimized conditions to all reactions conducted for each of the catalysts: 100 mg fructose, 50 mg catalyst, 2 mL solvent (7:3 DMSO/acetone), 150 °C, 5 min under microwave irradiation. It is worth taking into consideration that in order to deeply study the catalytic effectiveness of each catalyst in the production of 5-HMF from fructose dehydration, individual optimizations of the previous parameters is recommended, however, in a such comparative study the optimized conditions are sufficient to give an overall conclusion.

4.2.2 Acid-catalyzed dehydration of fructose over sulfonated phenylene and biphenylene-bridged PMOs.

The first group of catalysts to be investigated was the periodic mesoporous organosilica materials, phenylene-PMO-S and biphenylene-PMO-S. These two catalysts differ in terms of their porosity as indicated by the characterization results, specifically, in the pore size, and surface area. In addition, dissimilar hydrophobicity is generated on the surface of both catalysts due to the less hydrophobic character of phenylene rings than biphenylene. So that, the effect of pore size, surface area, and hydrophobicity will be tested. The catalytic reaction was carried out under the optimized reaction conditions.

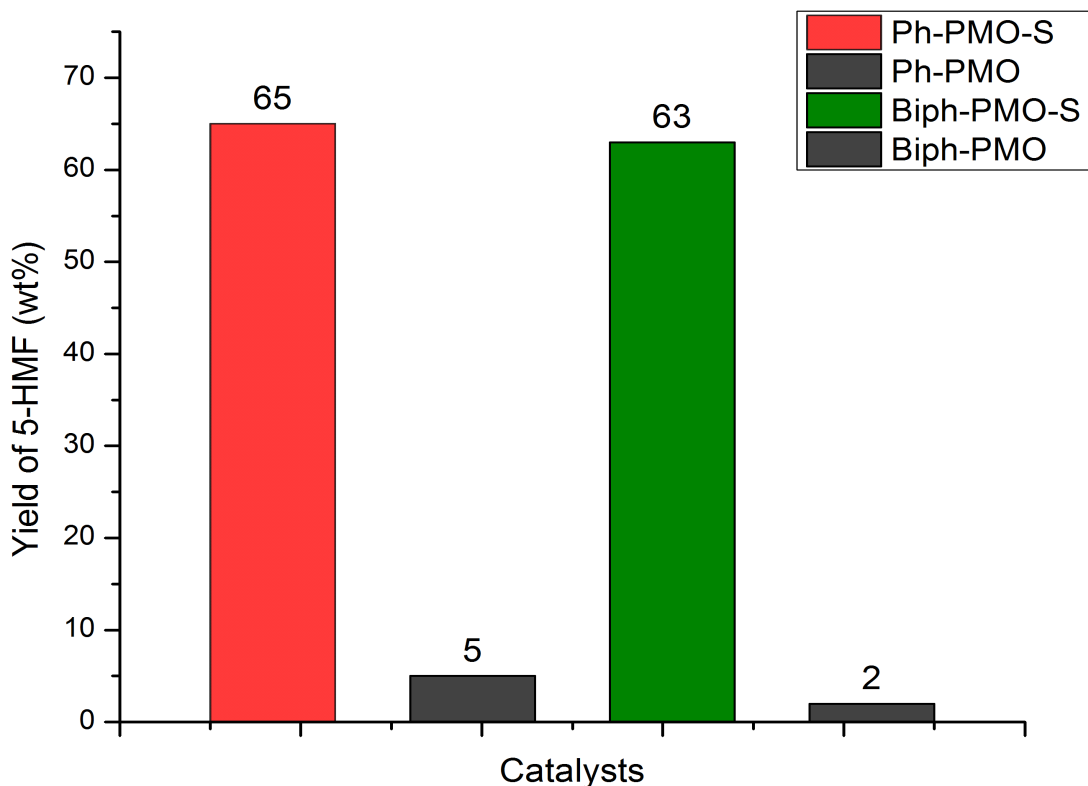


Figure 4.20. 5-HMF Yield in fructose dehydration using Ph-PMO and Biph-PMO catalysts before and after sulfonation. Reaction conditions: 100 mg fructose, 50 mg catalyst, 2 mL DMSO/acetone (7:3), 150 °C, MI.

The results in Figure 4.20 show that both sulfonated phenylene- and biphenylene-bridged PMOs are capable of promoting the dehydration of fructose with almost the same catalytic activity. However, the sulfonated phenylene- and biphenylene-bridged PMOs differ dramatically in terms of pore size (7.5 vs. 2.9 nm) and surface area (1040 vs. 271 m²g⁻¹). Due to the identical catalytic activity, one can conclude that for this particular substrate a small mesopore is as suitable as a large mesopore, both being large enough to allow the fructose and 5-HMF to rapidly diffuse through the framework.[44]

In addition, the H⁺ loading is a key factor in investigating the catalytic activity of acidic catalysts. The acid loadings in the sulfonated phenylene- and biphenylene-bridged PMOs were, respectively, 0.461 and 0.2 mmolg⁻¹, which was calculated based on the sulfur content determined by elemental analysis. However, only 0.2 and 0.17 mmolg⁻¹ of acidic sites were accessible in phenylene- and biphenylene-bridged PMOs, respectively, which was estimated based on pH measurements following the procedure published in previous work.[38] So that, the similar accessible acid sites of both phenylene- and biphenylene-bridged PMOs explain the identical yield of 5-HMF. In terms of hydrophobicity, the slight difference of hydrophobic character of the supports shows no effect on the adsorption of the fructose, the highly polar molecule, over the surface as indicated by the identical yield of 5-HMF. This may be assigned to the similar accessible acid sites of both PMOs since a previous study confirmed that the hydrophobic effect of the support is governed by the acid loading of SO₃H.[138]

A set of blank experiments was run, using acid-free phenylene- and biphenylene-PMO. The results showed that both PMOs exhibited almost no activity towards the dehydration of fructose (Figure 4.20), which indicates that the PMO supports had no catalytic role in the dehydration of fructose.

In summary, sulfonated mesoporous organosilica materials are excellent catalyst supports for the dehydration of fructose into 5-HMF. An important finding was that a small mesopore size of about 2.9 nm is as sufficient for fructose dehydration as a large mesopore.

4.2.3 Acid-catalyzed dehydration of fructose over sulfonated carbon materials (CMK-3-S and AC-S)

The catalytic efficiency of sulfonic acid-functionalized carbon materials (CMK-3-S and AC-S) in the dehydration of fructose into 5-HMF was determined under the optimum reaction conditions. These two catalysts have two main differences related to their surface area, structural properties, and acid loadings.

The results show that sulfonated activated carbon (AC-S) afforded a 60% yield of 5-HMF in contrast to the sulfonated mesoporous carbon (CMK-3-S), which gave a slightly lower yield of 55%. From these results, one can conclude that the activated carbon material is more efficient at converting fructose into 5-HMF, but this cannot be assigned to the surface area or pores structure, since CMK-3-S exhibited a significantly higher surface area ($441 \text{ m}^2\text{g}^{-1}$ compared to $12 \text{ m}^2\text{g}^{-1}$) and an ordered porous structure instead of the amorphous structure of AC-S. However, this is likely to be due to the lower carbonization

temperature and higher acid loading of AC-S. On the basis of the aforementioned characterization results, the amorphous carbon material AC-S, contains low density of polycyclic aromatic carbons and thus high amounts of hydrophilic functional groups, such as OH and COOH, which was proved by both IR and ^{13}C MAS NMR, as a result of the partial carbonization. Therefore, this carbon material is expected to accommodate a large amount of hydrophilic molecules, including fructose. This leads to better access to the sulfonic acid groups, providing high catalytic activity despite the low surface area.[146] This comparison illustrates the influence of accessible acid sites on the catalytic activity of such catalysts. On the other hand, the higher carbonization temperature of CMK-3-S results in a very low density of hydrophilic functional groups, namely phenolic OH, as indicated by the ^{13}C MAS NMR data. This is due to the fact that most of the phenolic OH groups were converted into hydrophobic polycyclic aromatic carbons during the high-temperature carbonization, leading to a low tendency towards accommodating hydrophilic fructose molecules. Overall, a better interaction of fructose molecules is provided by the AC-S catalyst than CMK-3-S, resulting in a higher yield of 5-HMF. Nevertheless, the yield of 5-HMF obtained over CMK-3-S is comparable to the yield acquired in the presence of other porous carbon materials, *e.g.* sulfated porous carbon catalyst produced a 5-HMF yield of 45 wt% in a THF:DMSO mixture.[90] In addition, the critical importance of acid loading is also observed since the AC-S catalyst that exhibits higher activity has an acidity of $0.183 \text{ mmol g}^{-1}$, while the CMK-3-S catalyst contains almost half the acidity (0.11 mmol g^{-1}).

Since the surface of carbon materials contains various hydrophilic organic groups, including COOH functional groups, it was important for us to investigate the efficiency of

the COOH acid groups in catalyzing fructose dehydration under the optimized conditions mentioned above. To approach this goal, an activated carbon material functionalized with carboxylic acid groups was prepared using a similar method as for AC-S, but in the presence of maleic acid (cis-butenedioic acid) as a source of carboxylic acid groups instead of vinyl sulfonic acid sodium salt.[115] The obtained acid loading was 0.16 mmolg⁻¹. After testing the catalyst in the catalytic reaction, the obtained yield of 5-HMF was approximately 38%, indicating the weaker catalytic activity of carboxylic acid groups compared to sulfonic acid groups (60%) with close acid loadings. These results may be explained by the different acid strength of the carboxylic and sulfonic acid groups, and it also might suggest that the total catalytic activity of AC-S is the sum of contributions between sulfonic acid and a small of carboxylic acid groups.[147]

In summary, the results indicate that the catalytic activity of the carbon materials under investigation is independent of textural properties such as surface area and pore size, but is dependent on the surface composition and acid density.

4.2.4 Acid-catalyzed dehydration of fructose over MOFs

The last set of catalysts to be examined in the fructose dehydration into 5-HMF was metal organic frameworks, *i.e.* MIL-53(Al)-S and UiO-66-S. All of the catalysts were activated at 160 °C overnight before being tested. Both UiO-66-S and MIL-53(Al)-S exhibited microporous structure with high surface area (905 and 1015 m²/g) and small pore sizes of 0.54 and 0.61 nm, respectively, that are accessible to a molecule in the size of fructose.[135][136] It is worth mentioning that both MOFs have a high tendency towards

water adsorption, yet the crystal structure is reported to be stable during the hydration/rehydration process.[133][154]

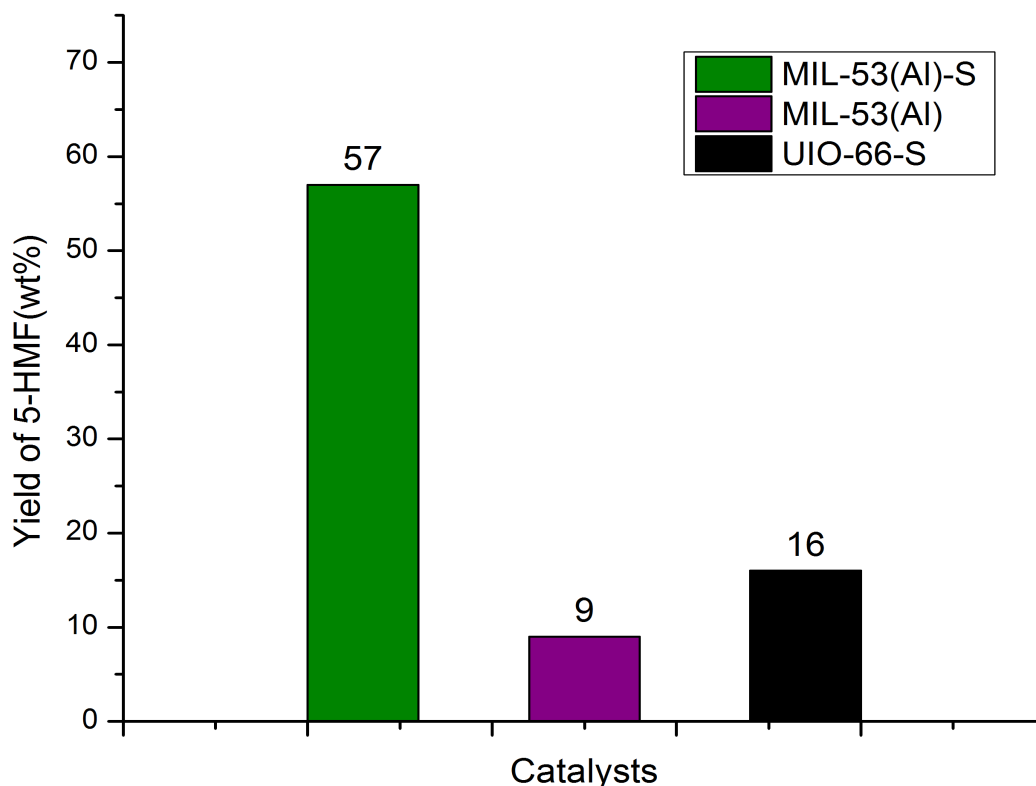


Figure 4.21. 5-HMF yield in fructose dehydration using pristine and sulfonated MIL-53(Al), and UiO-66-S catalysts. Reaction conditions: 100 mg fructose, 50 mg catalyst, 2 mL DMSO/acetone (7:3), 5 min, MI.

During the investigation of MOFs as catalyst supports, the aim was to post-functionalize MIL-53(Al) so that the catalytic activity of the pristine MIL-53(Al) could be examined. In principle, Al^{+3} sites may act as Lewis acid sites for the dehydration of fructose.[135] To investigate this hypothesis, MIL-53(Al) was activated at 160 °C for 8 h to remove water molecules bound to the Al centers.[135] Then, the catalytic activity of MIL-53(Al) was tested in the dehydration of fructose under the optimized conditions. The yield of 5-HMF obtained was negligible (9%), which proves that the Al^{+3} sites are not active in

the dehydration of fructose under the current reaction conditions. However, MIL-53(Al) was reported to catalyze the hydrolysis of carboxymethyl cellulose to produce 5-HMF, and a 28% yield of 5-HMF was obtained.[136] The authors assigned this activity to the OH groups bound to the Al centers.

As for sulfonated MIL-53(Al), a high catalytic activity was observed in the conversion of fructose into 5-HMF, with a yield of 57% (Figure 4.21), indicating the importance of the sulfonic acid catalyst in promoting the dehydration reaction. This high activity may also highlight the remarkable structure of MIL-53(Al)-S, which is known for its reversible large breathing ability between the hydrated and the dried forms, as presented in Figure 4.23. [133] In other words, the MIL-53(Al) cell volume shrinks or expands depending upon the polarity of the guest molecule due to host-guest interactions.[128][149] Hence, a good confinement of fructose molecules inside the pores is expected due to its polar character, leading to better access to the sulfonic acid groups. Furthermore, the expected shrinkage of the cell volume upon interaction with fructose or the polar 5-HMF as depicted in Figure 4.22, may limit the possible side-reactions of 5-HMF.

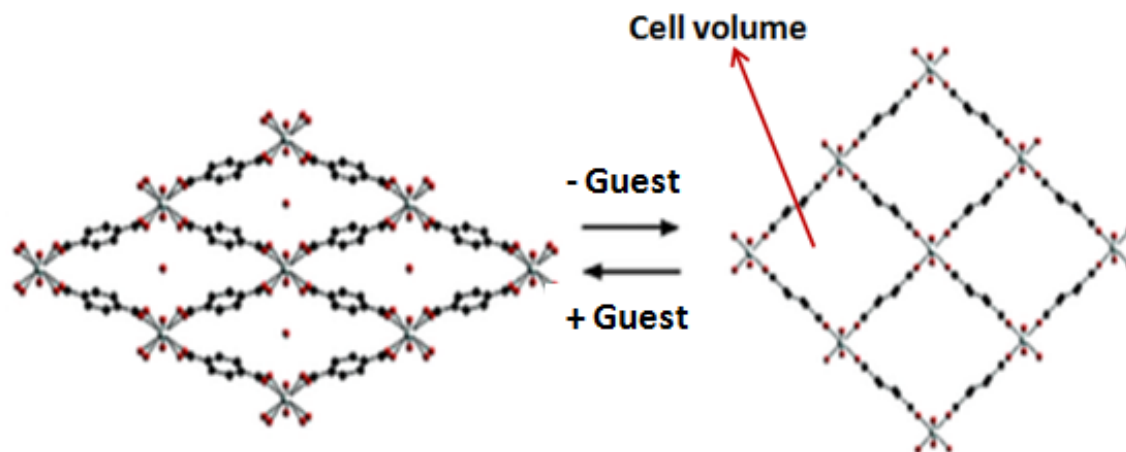


Figure 4.22. The breathing effect of MIL-53.[133]

On the other hand, UiO-66-S unexpectedly exhibited very low activity in this reaction, producing only a 16% yield of 5-HMF under the same optimized conditions. However, UiO-66-S seems suitable for fructose dehydration not only because it has two types of large cages (0.8 nm and 1.1 nm), accessible through microporous windows (0.5 to 0.7 nm)[148], but also it exhibited high acid loading of 1.8 mmol g^{-1} , which was expected to result in high catalytic activity. Additionally, UiO-66-S was reported to have a good catalytic activity as a support for phosphotungstic acid.[73] The low activity of UiO-66-S in the dehydration of fructose may be explained by the appearance of brown materials in the reaction mixture, which are likely to be condensation byproducts, *i.e.* humins. Although, it is difficult to identify humins using the current analysis techniques[131], their formation was proved by the deep brown-colored materials, which precipitate in water.[60][82] The formation of humins is a result of condensation reaction between two molecules of fructose. This led to an assumption that fructose molecules are participating in the condensation reaction instead of the dehydration reaction with the catalyst, which caused the low yield of 5-HMF. There are two possible reasons that may explain why fructose is not participating in the

dehydration reaction: one may be assigned to the small micropores of UiO-66, which may be significantly reduced owing to the sulfonation process. It has been reported that the introduction of the SO_3H functional groups into the UiO-66 frameworks leads to a substantial reduction in the pore size and, consequently, lower activity of UiO-66-S.[150] The small micropore size possibly inhibit the diffusion of fructose into the pores and thus the interaction with the sulfonic acid groups as noticed with microporous ZSM-5 zeolite that has a slightly smaller pore size (about 0.5 nm)[71] than UiO-66-S (0.54 nm). Another possible reason of limited activity of fructose may be related to the occupation of the micropores with guest molecules. It was reported that UiO-66 exhibited high water uptake, although it maintained its crystal structure after water had been removed, as evidenced by the powder X-ray diffraction results.[154] Hence, one of these two assumptions is expected to be responsible for the hindering of dehydration reaction. We first investigate the possibility of pores occupation so that the UiO-66-S was evacuated at various temperatures for 24 h before being tested in fructose dehydration. Evidently, the results show a clear relationship between the yield of 5-HMF and the evacuation temperature. As presented in Figure 4.23, the yield of 5-HMF was dramatically increased from 4% without evacuation to 51% upon evacuation at 200 °C. This finding clarifies that the micropores are accessible for fructose, yet the pores were occupied with water, and perhaps solvent molecules. Ultimately, the yield of 5-HMF increased over UiO-66-S upon raising the evacuation temperature to higher than 160 °C. The evacuated UiO-66-S materials at 200 °C denoted as UiO-66-S(200).

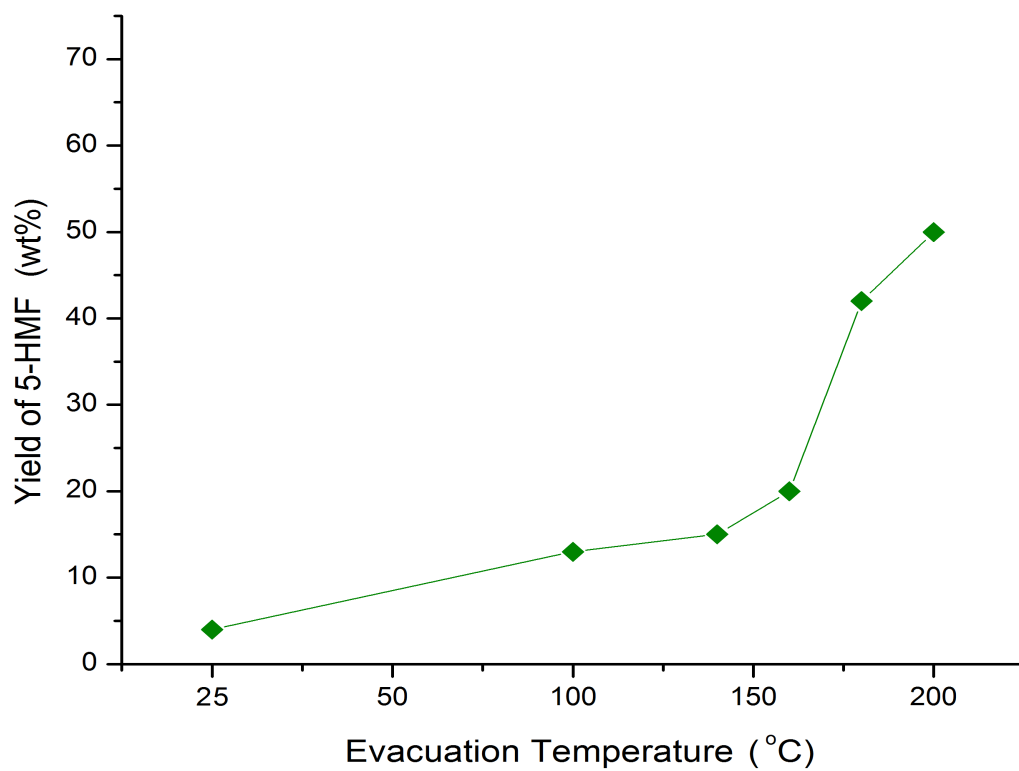


Figure 4.23. 5-HMF yield obtained over evacuated UiO-66-S at different temperatures. Reaction conditions: 100 mg fructose, 50 mg catalyst, 2 mL DMSO/acetone (7:3), 5 min, MI.

4.2.5 Comparison of the catalytic efficiency of all three types of catalysts.

All catalysts with different supports under study were shown to possess different levels of dehydration activity for the conversion of fructose into 5-HMF, which was mainly associated with their acid loadings, pore structure, and surface composition. A comparison between the catalytic activity of the catalysts based on their structure and acidity will be discussed in detail hereafter.

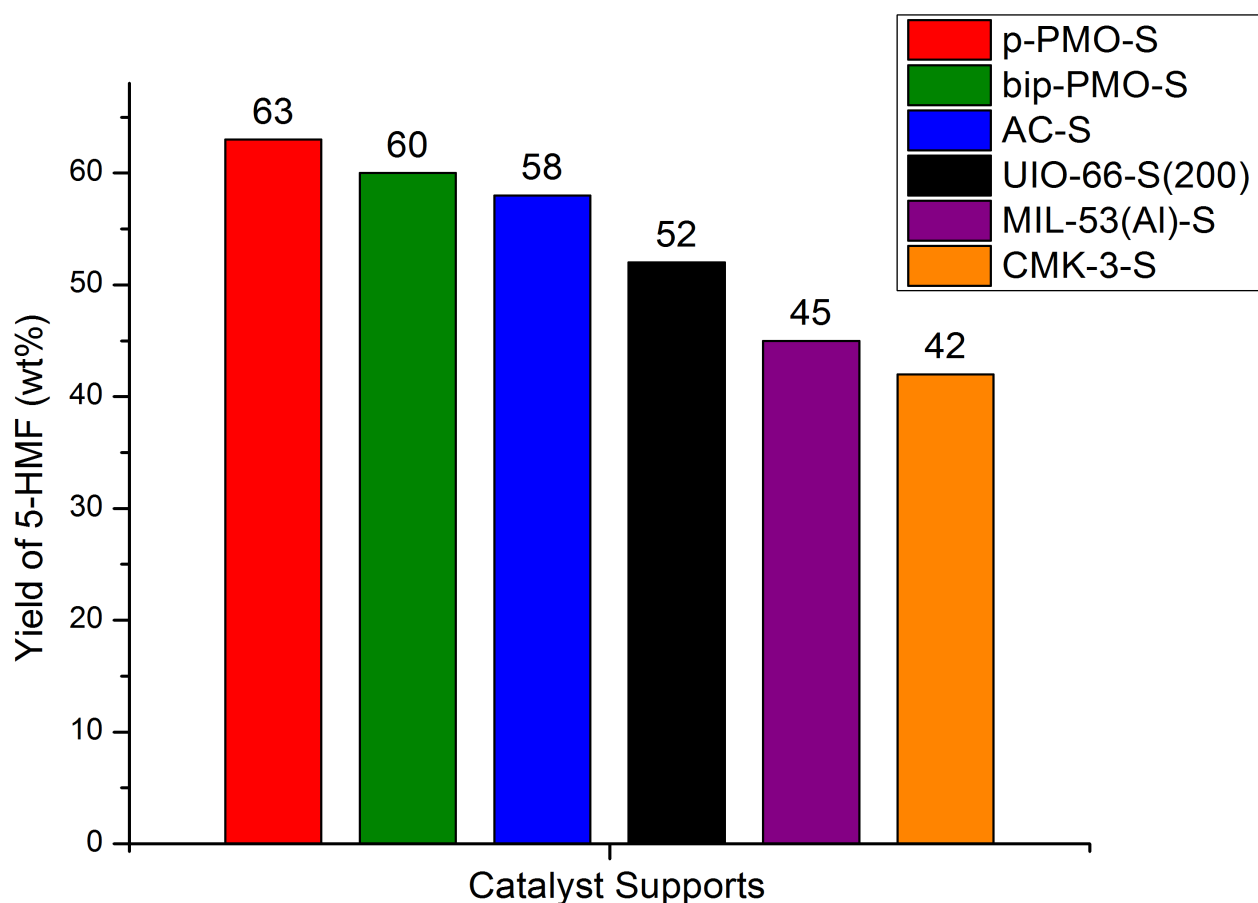


Figure 4.24. 5-HMF yield in fructose dehydration over porous catalyst supports.

Looking at the trend in Figure 4.24, sulfonated periodic mesoporous organosilica with phenyl and biphenyl bridges are the most effective catalysts compared to the others under study. This may be due to the very well-ordered structure giving rise to a high content of organic groups that can bear sulfonic acid species[39], leading to high acidic concentration, which was in the range 0.2–0.45 mmolg⁻¹. Moreover, their molecular-scale periodicity perhaps provides a uniform dispersion of sulfonic acid groups on the surface and thus structural orientation of substrate molecules results in enhancing the selectivity and activity. In addition, their suitable mesopore size, in the range of 2.9-7.5, probably permits faster migration of fructose molecules into the pores. Regarding mesoporous CMK-3-S carbon, the catalytic activity of SO₃H was lower (42% yield of 5-HMF) in comparison to Ph-PMOs (63%), and Biph-PMO (60%), with the latter exhibited a smaller pore size than CMK-3-S(2.9 nm vs. 3.3). This can be mainly assigned to high carbonization temperature that led a highly hydrophobic surface, and thus lower loading of acidic sites (0.11 mmolg⁻¹).

In terms of microporous supports, although both MOFs have a good crystalline structure, their impact on the activity of the SO₃H was less effective than the PMOs. This may be attributed to the smaller pore size of MOFs since either lower (in MIL-53-S) or dramatically higher (in UiO-66-S) acid loading did not positively affect the yield of 5-HMF compared to PMOs with larger pore size. Even after extensive evaporation the microporous MOF UiO-66-S(200) provided lower catalytic activity than mesoporous materials Ph-PMO-S (52% vs. 63%). In contrast, amorphous activated carbon with micro-sized particles showed a very good influence on the catalytic activity of SO₃H with a 58% yield of 5-HMF, which is comparable with the yield obtained in the presence of well-ordered PMO materials. Yet, it

must be stated that the activity of activated carbons is essentially related to another factor *i.e.* surface composition than structural properties as discussed earlier.[147]

Altogether, the effect of supports that exhibit highly ordered structure on the catalytic activity is mainly ascribed to the pore size, however, when the support is composed of carbon, the surface composition plays the key role.

The acid density is a crucial factor in this acid-catalyzed reaction. Despite all the differences in structure and composition between the catalysts, their catalytic activity follows the order of acid loading (Table 4.4). This means that the acid loading is the key factor of the catalytic activity, while the role of structure and the composition of the supports is to control the acid loadings. For instance, the well-ordered mesostructure of sulfonated PMO supports led to increase the acid loading of sulfonic acid groups, while in AC-S catalysts the composition of the surface was the reason that facilitates the incorporation of sulfonic acid groups into the surface.

Furthermore, it can be noted that, generally, a decrease in the amount of acid loading reduces the yield of 5-HMF, which is due to the fact that decreasing the sulfonic acid sites reduces hydrophilicity of the surface, and thus increases the effect of hydrophobic phenyl rings. This results in a more hydrophobic structure, and may make it difficult for the polar fructose molecules to diffuse into the pores.[138] Apart from this, the catalytic activity of UiO-66-S(200) does not follow its acidity since it has a higher acid loading (1.8 mmol g^{-1}), yet apparently has catalytic activity of 52% yield of 5-HMF which is lower than Ph-PMO-S with lower acid loading (0.45 mmol g^{-1}). This catalytic activity of UiO-66-S(200) may indicate that a high degree of evacuation is essential for all the pores to be evacuated and thus the acidic sites to be accessible. Overall, These results indicate that the yield of 5-HMF

is strongly dependent upon the content of the sulfonic acid groups incorporated into the framework of the supports, and the properties of the supports direct the loading of the acid.

Table 4.4. Effect of acid loading on the activity of different catalysts.

	Ph-PMO-S	Biph-PMO-S	AC-S	MIL-53(Al)-S	UiO-66-S(200)	CMK-3-S
Acid loadings (mmolg ⁻¹)	0.45	0.2	0.18	0.15	1.8	0.11
Yield of 5-HMF	63	60	58	54	52	42

The good overall activity of all catalysts may be ascribed to the favorable environment surrounding the sulfonic acid groups. In other words, the hydrophobic character of phenyl rings compensates for the hydrophilic character of the sulfonic acid groups, resulting in a well-balanced surface that favors the production of 5-HMF due to the capability of phenyl rings to partly limit the solvation of sulfonic acid sites with water. However, certain structural properties, such as a large pore size and a highly flexible structure, are required to allow high loadings of acid sites and sufficient diffusion of fructose into the pores. To study the effect of the phenyl rings in preventing water molecules from interacting with SO₃H and, thus enhancing the reaction productivity, a set of experiments was conducted using a molecular sieve (3 Å)¹⁶ to remove the water generated during the reaction. The results showed no dramatic changes in the yield of 5-HMF with a molecular sieve in comparison to that acquired without a molecular sieve for periodic mesoporous materials and carbon-based catalysts (Table 4.5), indicating that the

¹⁶ Molecular Sieve (3 Å) is a zeolite compound with SiO₂/Al₂O₃ ratio of ≈2, and a small pore size of 0.3 nm. It only allows smaller molecules like water (0.19 nm) to pass through and so blocks larger ones.

hydrophobic character of phenyl rings prevents water molecules from deactivating the catalytic sites the same as the molecular sieve does. In the case of the MOF supports, as expected, a noticeable enhancement of their catalytic activity was observed in the presence of the molecular sieve. The yield of 5-HMF increased from 53% to 59% and 52% to 55% over MIL-53(Al)-S and UiO-66-S(200), respectively, in favor of the molecular sieve. In addition, the yield of 5-HMF significantly improved to reach 30% in the case of UiO-66-S. This enhancement is largely due to the removal of water molecules from the pores which emphasizes the negative effect of water occupying the pores in MOFs for their efficiency as catalyst supports. Additionally, this overall strong catalytic activity may be explained by the formation of strong hydrogen bonds between the sulfonic acid groups, or sulfonic acid groups and OH from the surface of the supports, resulting in strong and thus stable acidity.[147]

Table 4.5. Effect of molecular sieve on the activity of different catalysts.

5-HMF Yield (%)	Ph-PMO-S	Biph-PMO-S	AC-S	UiO-66-S(200)	MIL-53(Al)-S	CMK-3-S	UiO-66-S
Without molecular sieve	62	61	58	52	53	51	14
With molecular sieve	62	63	59	55	59	52	30

In conclusion, the catalytic activity of the sulfonic acid groups supported on phenylene- and biphenylene-PMOs, mesoporous and amorphous activated carbon materials, and MOFs is promising. There are three main factors leading to this activity: the appropriate acid density, the adequate hydrophobicity of the support framework, and the type of porosity. Although sulfonated phenylene/biphenylene PMOs are the most active

catalysts, the overall differences between the catalysts' activities are quite small (3–8%). Despite the low initial activity of UiO-66-S, a high activity was achieved upon the evacuation of the pore residues under high temperature.

4.2.6 Recyclability of the catalysts.

The stability of the pore structure and the active sites with respect to leaching or other transformations is a fundamental requirement for heterogeneous catalysts. Therefore, four consecutive cycles of experiments examining the dehydration of fructose were performed. All of the cycles were carried out in a DMSO/acetone (7:3) mixture at 150 °C for 5 min, with 50 mg catalyst and 100 mg fructose, under microwave irradiation. Except for MOFs, the catalysts were filtered, washed with water, and dried in air after each run, then directly used for the next run. In the case of MIL-53(Al)-S and UiO-66-S, washing with methanol and drying in a vacuum oven, at 160 and 200 °C, respectively, were performed prior to reusing them in the next run.

As can be seen in Figure 4.25, no significant changes in catalytic activity were observed after four cycles. For example, a 5-HMF yield of 65% was obtained for the first cycle of phenylene-bridged PMO, and then slightly increased to 66% in the fourth cycle. However, all of the other catalysts showed good stability of their catalytic activity with a slight decrease in the yield of 5-HMF observed between the first and the last cycles. It is worth mentioning that this slight loss of catalytic activity is possibly due to the leaching of acid groups and the deposition of humins or other organic residues on the catalyst supports. However, the yield of 5-HMF slightly fluctuated in between runs, which may be

assigned to the experimental errors. Another reason for this fluctuating yield of 5-HMF may be that some of the 5-HMF molecules are retained in the pores from the previous run. These results suggest that the catalyst supports function as stable and efficient catalysts with a stable catalytic activity over four cycles.

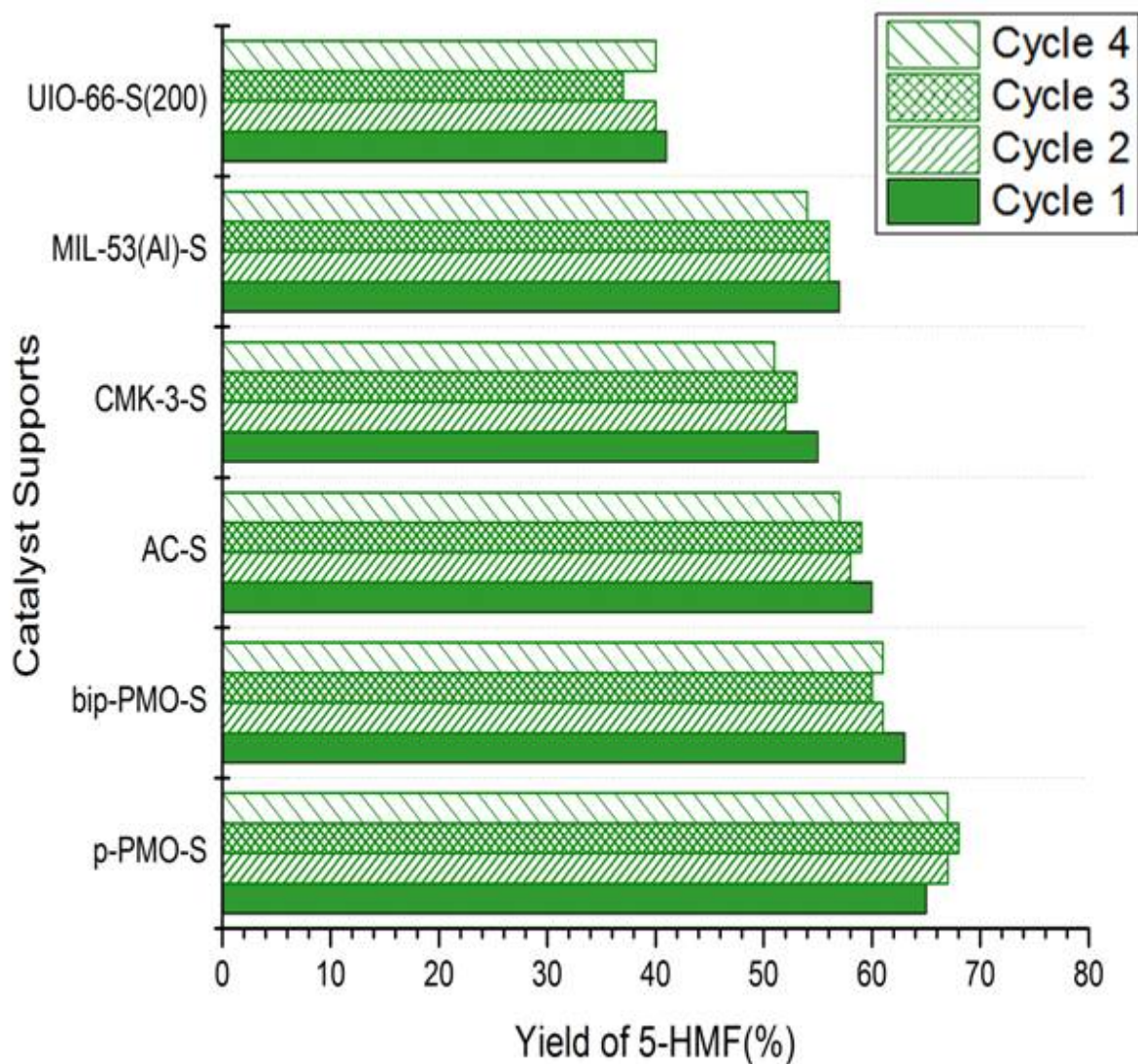


Figure 4.25. Recyclability of the catalyst supports for the dehydration of fructose.

CHAPTER 5 – CONCLUSION AND FUTURE WORK

5.1 Conclusion

Issues like the depletion of fossil fuels and their harmful effect to the environment is no longer the concern of individual nations. The entire global community is responsible for the future of energy supplies, which are the engine of modern life. Therefore, the responsibility for replacing fossil fuels with renewable sources has become a major global challenge to preclude the most disastrous scenarios of energy crises in the future. Biomass has shown a great potential as an alternative source of energy. 5-HMF is one of the important intermediates in the production of liquid fuels and valuable chemicals. Consequently, considerable efforts have aimed to design a sustainable catalytic system for the synthesis of 5-HMF from biomass-derived substrates, *i.e.*, carbohydrates.

As a modest contribution to achieve the best catalytic system for the production of 5-HMF from fructose, our work was devoted to compare the effect of porous supports, namely PMOs, carbon materials, and MOFs on the catalytic performance of supported strong sulfonic acid groups. This is an important topic in the production of 5-HMF from biomass-derived carbohydrates, because porous catalyst supports have shown high efficiency in the production of 5-HMF, yet the work conducted in this area is still growing. Additionally, comparative studies are crucial in terms of providing comprehensive data about the most promising catalyst supports, and thus may lead to the development to even more powerful catalysts. The characterization of the selected porous supports illustrates

the diverse properties, including pore sizes in the meso- and micro-pore range, degree of periodicity, and acid loading.

The first step to achieve the goal of this thesis was to test the catalysts under similar conditions to achieve a comprehensive comparison. All the reaction conditions were optimized to maximize the yield of 5-HMF using a reference catalyst, namely Amberlyst-15. The influence of these supports on the catalytic activity of SO_3H was investigated in the dehydration of fructose under the following conditions: a medium that consisted of 7:3 DMSO : acetone mixture, reaction temperature and time of 150 °C and 5 min, respectively under microwave irradiation. The catalyst supports had a very good impact on the activity of the SO_3H catalyst indicated by the high yield of 5-HMF, and the main findings are listed below:

- **Catalytic activity is dependent on the acid content of the catalysts.** There was a striking relationship between the acid loading on the surface of the supports and the corresponding catalytic activity. More specifically, the accessible acid sites are the key factor in directing the reaction towards a higher yield of 5-HMF. While the structural properties of supports are to be adjusted to enhance the acidity. In addition, a decrease in the sulfonic acid sites negatively affects the balance of hydrophilicity and hydrophobicity of the surface of a hydrophobic support.
- **The pore size of the supports influences the catalytic activity of SO_3H groups.** The results showed that both large and small mesopore-containing materials, represented by PMOs, are suitable for the production of high yields of 5-HMF.

Materials containing micropores, represented by MOFs, showed a good potential in achieving a high yield of 5-HMF.

- **The composition of the supports plays a role in enhancing the catalytic activity of SO₃H groups.** In the supports that were composed of carbon materials, the surface composition was found to be an effective factor since its functional groups possibly participated in catalyzing the reaction, and most importantly affected the acid loadings of SO₃H.
- **The synthesis and functionalization process affected the final acid capacity of the supports.** The higher catalytic activity of AC-S over CMK-3-S was found to be unrelated to the structure, yet it was strongly affected by the synthesis procedure. The lower carbonization temperature was beneficial for the introduction of a high number of acid sites into the framework. Moreover, the role of the sulfonation process was clearly observed by the different amounts of acid loading in UiO-66-S and MIL-53(Al)-S frameworks.
- **The catalytic activity is well maintained over several cycles.** All the catalysts were reused in the dehydration of fructose for four consecutive cycles, which featured their application in large-scale production. However, slight fluctuation in their catalytic activity between the runs is attributable to deactivation of the catalytic sites or losses of the catalysts after separation and wash cycle, within experimental error.

5.2 Future Work

Even though extensive work has been conducted using various catalysts in the production of 5-HMF, a lot of work remains to be done in terms of comparing their catalytic

activity in similar conditions. Based on the findings of this study, some recommendations are made to guide future efforts in research and development:

- Optimizing the reaction conditions for each catalyst supports individually may be the first essential recommendation for this system to be improved. For example, MIL-53(Al)-S may give a higher yield of 5-HMF upon increasing the reaction time since the possible side-reactions of 5-HMF, that occur in a long reaction time, are expected to be at a very low level due to the breathing effect of MIL-53(Al)-S. This step might also provide more detailed information about the efficiency and stability of each catalyst support in various conditions. For example, the individual optimization of the reaction conditions for each catalyst may show higher activity of one of the catalysts at lower temperature, which is more environmentally friendly.
- As part of the optimization process, it would be interesting to study the catalyst activity in various solvent systems, especially biphasic systems, which are of great importance to industrial applications. In this context, using a different substrate would also be a good step forward to highlight the ability of these catalysts to be applicable in large-scale operations, which is the ultimate goal of such research.
- One of the important data to be acquired in such a comparative catalysis study is the conversion of substrates and the selectivity of the product in order to understand the catalytic activity of each catalyst. Although the yield of 5-HMF is a good indication of the efficiency of the catalytic performance, it needs to be complemented by the conversion and selectivity results. In principle, an efficient catalyst must be able to convert all the substrates into the desired product.

Therefore, the amount of substrate that is converted to the desired product is of crucial importance to enable a fair judgment of the catalytic efficiency.

- As a good performance of the series of catalysts under study was achieved, further modifications of the supports would be interesting. It could be useful to use different organic groups in the PMO supports, or even to apply different carbonization temperatures in the synthesis of carbon materials to study their effect on the catalytic activity.
- The relatively high activity of SO_3H over MOF paves the way for further investigations related to the sulfonation method since it was noticed to be effective factors on the acid loadings. For instance, use of already sulfonated organic linker, for the synthesis of UiO-66 gave very high acid loadings in the final product in comparison to post-synthesis sulfonated MIL-53(Al). More effort should be made to determine an effective method to sulfonate MOFs either through one-pot synthesis using sulfonated linkers, or by post-synthesis sulfonation in order to increase the acid loadings in a way that will practically increase the catalytic activity. This would help to highlight the potential and limitations of further work on MOFs as a catalyst support for 5-HMF production. In addition, the high sensitivity towards water is a major challenge, which must be mitigated, for example, using specific metal centers for synthesized hydrophobic MOFs.

APPENDIX I: 5-HMF CALIBRATION CURVE

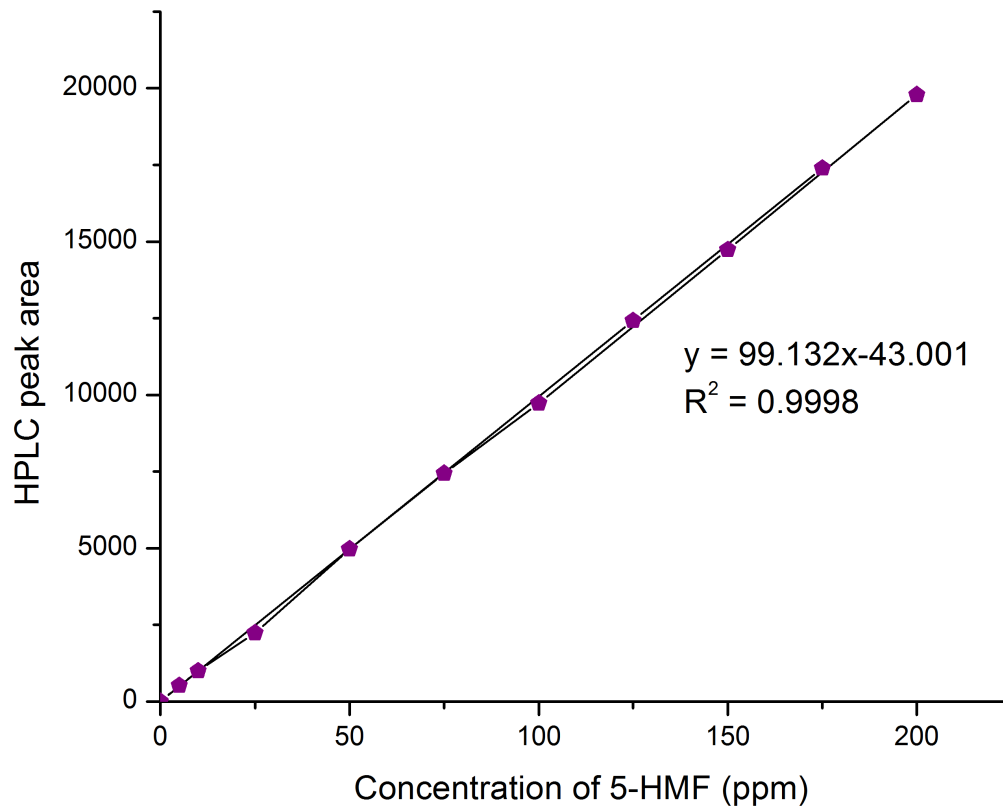


Figure AI.1. Calibration curve of 5-HMF

APPENDIX II: TGA ANALYSIS

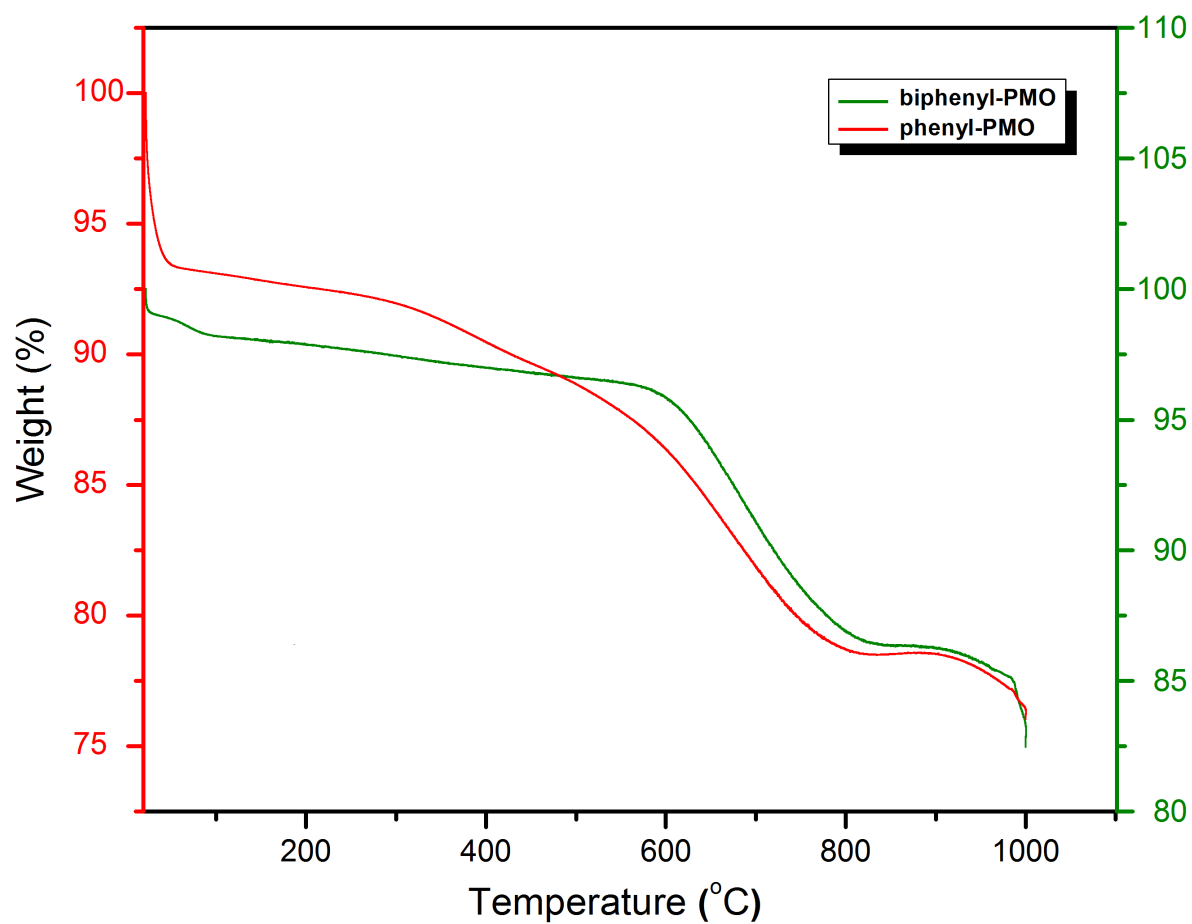


Figure AII.1. TGA analysis of phenylene-PMO and biphenylene-PMO.

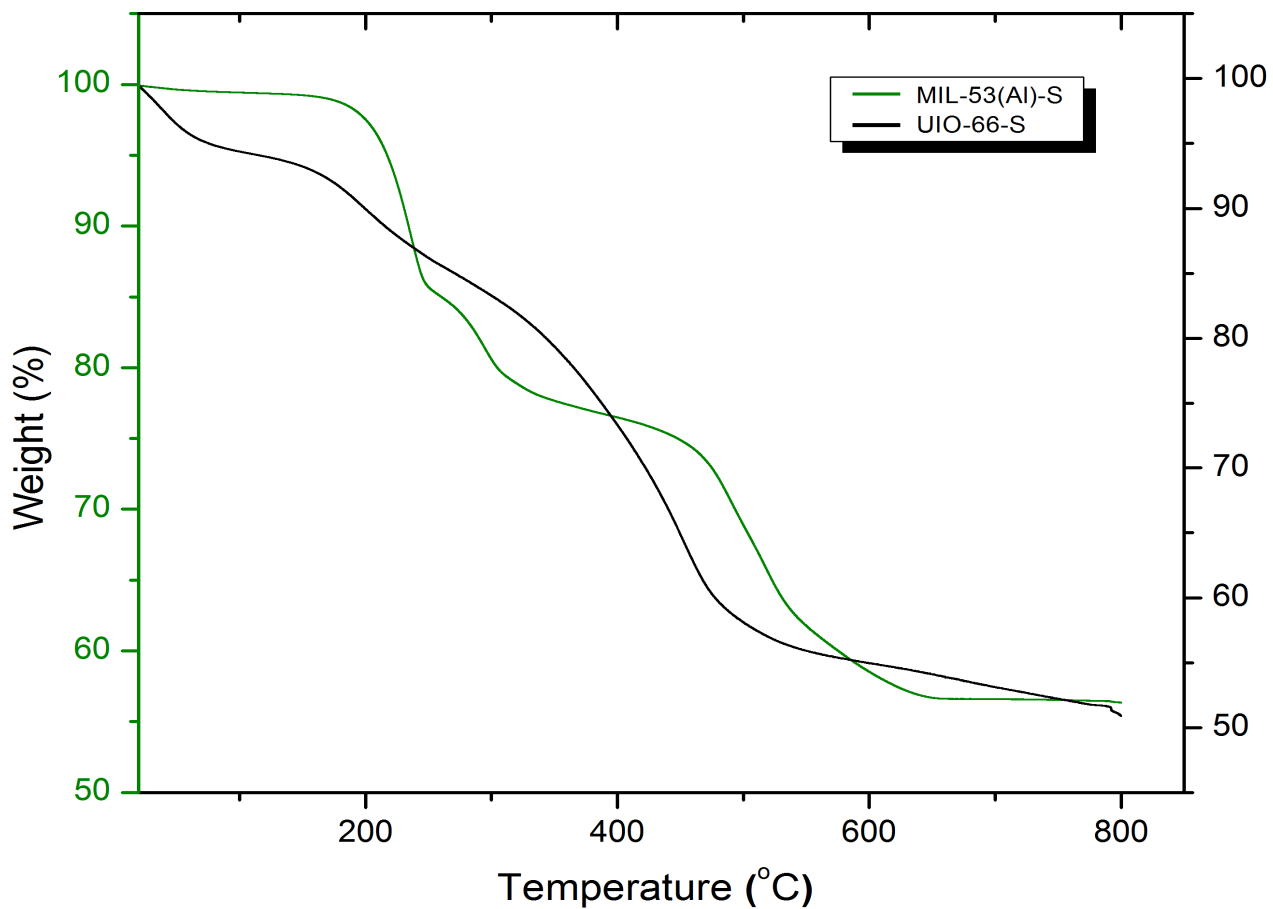


Figure AII.2. TGA analysis of UiO-66-S and MIL-53(Al)-S.

APPENDIX III: XRD ANALYSIS

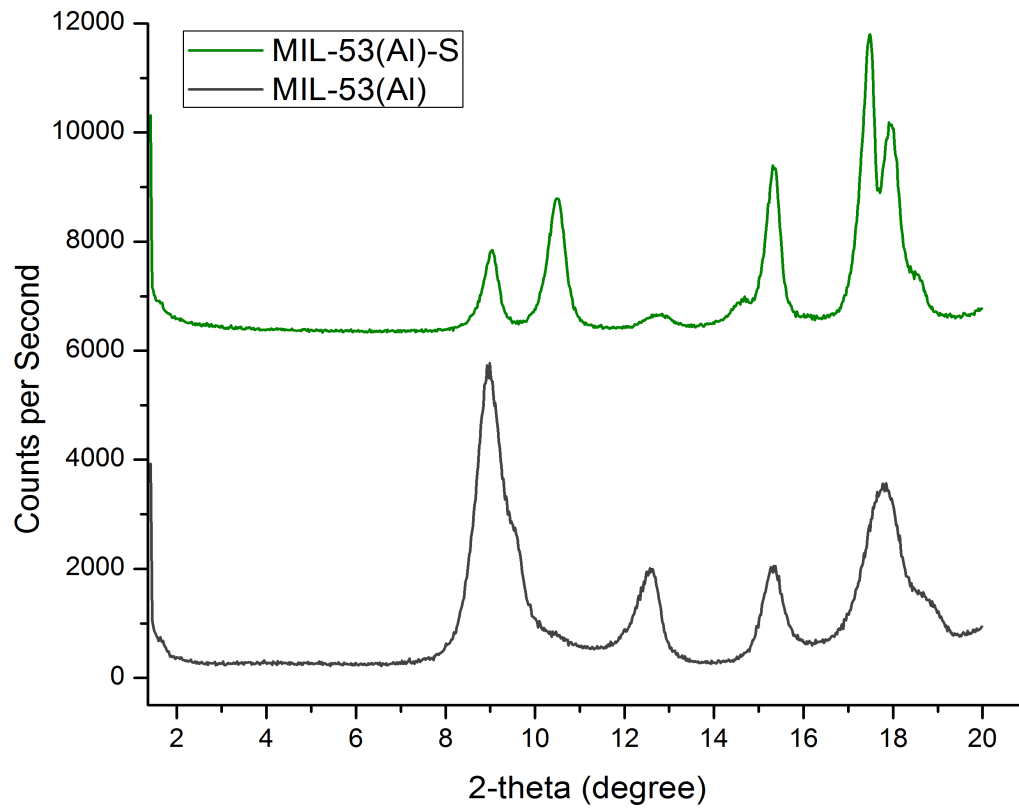


Figure AIII.1. XRD patterns of MIL-53(Al) and MIL-53(Al)-S.

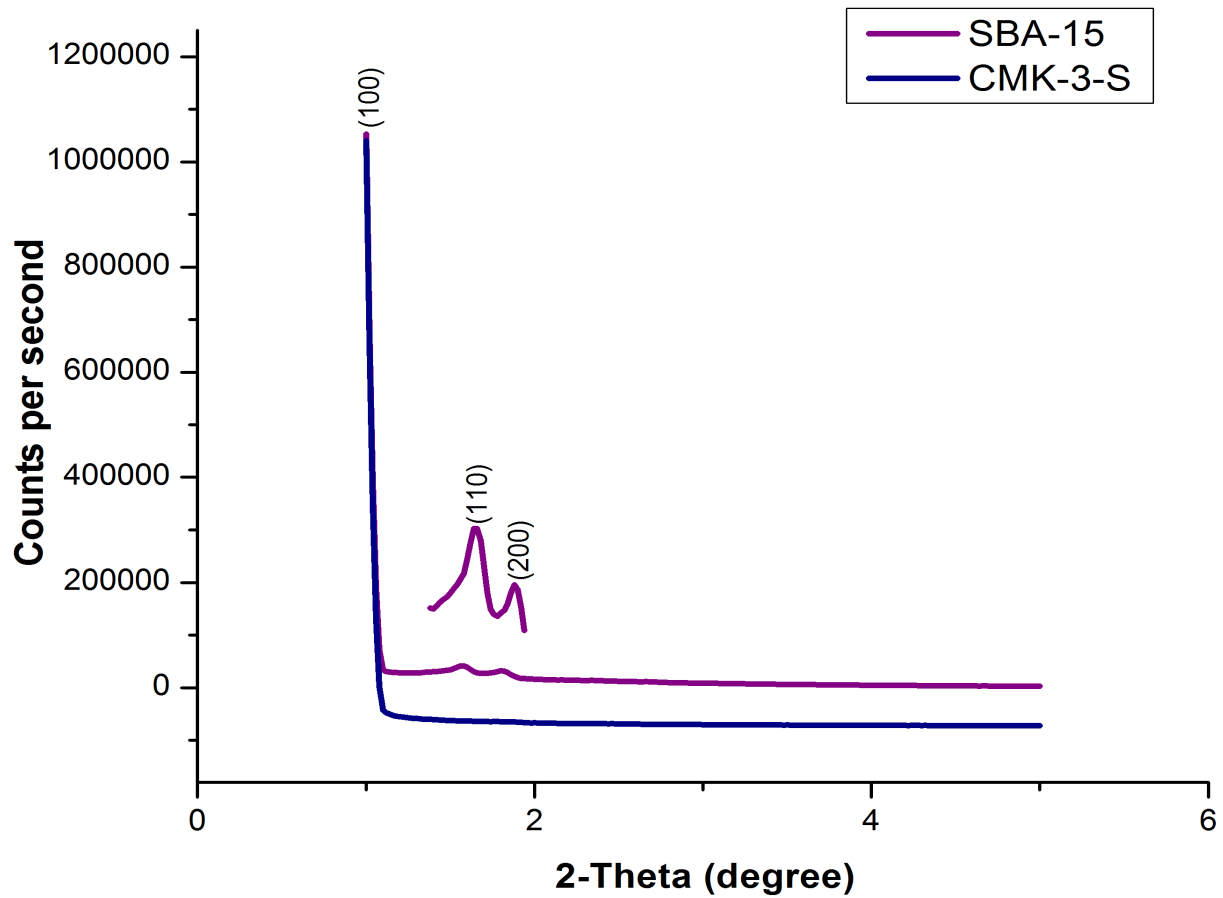


Figure AIII.2. XRD patterns of SBA-15 and CMK-3-S. Note: the (100) peak is not well-resolved due to the limitation of the XRD instrument at a very low diffraction angles.

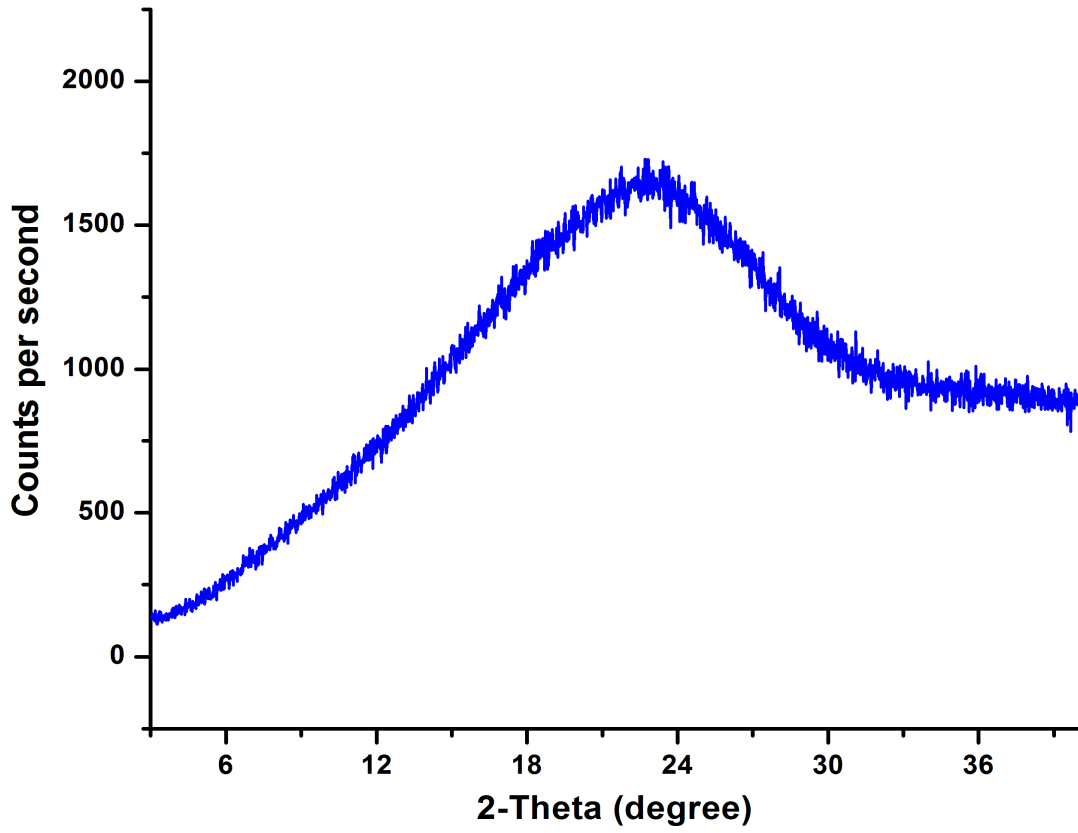


Figure AIII.3. XRD patterns of AC-S.

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