الجمهورية الجزائرية الديمقراطية الشعبية
République Algérienne Démocratique et Populaire
Ministère de L'Enseignement Supérieur et de la Recherche Scientifique

THÈSE

Présentée en Cotutelle entre
l'Université Ferhat ABBAS Sétif1 - Algérie
Faculté de TECHNOLOGIE
et l'Université de SEVILLA - Espagne

Pour l'obtention du diplôme de

DOCTORAT

Domaine : Sciences et Technologie

Filière: Génie des Procédés **Option: Génie Chimique**

Charf Eddine BOUNOUKTA

THÈME

Valorization of a platform chemicals issued from sugars hydrogenation reactions over supported metal catalysts on functionalized carbon materials.

Soutenue le 20/12/2021 devant le Jury:

Benachour Djafer	Professeur	Univ. Ferhat Abbas Sétif 1	Génie des polymères
Ammari Fatima	Professeur	Univ. Ferhat Abbas Sétif 1	Génie chimique
Ivanova Svetlana	Professeur	Univ. Séville-Espagne	Chimie inorganique
Rendon Marquez Nuria	Professeur	Univ. Séville-Espagne	Chimie inorganique
Reina Tomas Ramirez	Maitre de conférences	Univ. Séville-Espagne	Chimie inorganique
Bencheikh Lahcen	Professeur	Univ. Ferhat Abbas Sétif 1	Génie chimique

Preface

The present work is carried out in cotutelle between the University of Seville in Spain and University Ferhat ABBES, Setif-1-in Algeria. The research is a part of the activities of the Surface chemistry and Catalysis group, University of Seville and Laboratoire de Genie des Procedes chimiques, University of Setif -1.

The financial support from Algerian ministry in the form of P.N.E followship is gratefully acknowledged. I am also thankful to the Department of Chemical Process of the University of Setif-1- in Algeria and University of Seville for the initiation of the research program between both university and trimestral scholarships.

I would like to thank Professor Fatima AMMARI for introducing me to the world of biomass and catalysis and following me during all the period of the realization of this thesis. I would like to express my most sincere gratitude to my advisor Professor Jose Antonio Odriozola for giving me the opportunity to do a PhD and to work in the Institute of Material Science (mixed center CSIC-University of Seville) also for sharing his scientific enthusiasm and experiences. I would like to express my profound gratitude to my supervisor Professor Svetlana IVANOVA, for all she has done for me and is still doing in science and much beyond ”it was a pleasure to work with you”. I would like to acknowledge Professor Djafer Benachour for accepting to be the president of the jury of my work. I would like to give special thanks to Doctor Thomas Ramírez Reina for accepting to be my examinator. I would like also to take the opportunity to acknowledge the help for organic synthesis received from Professor Nuria Rendon Marquez and accepting the examination of my work. I remain thankful to Professor Lahcen Becheikh for teaching me in the master carrier and for being a member of the tribunal of my work.

Acknowledgements

I’m deeply grateful to my big family, especially to my Grandfather “thank you MouMou for the biggest part of the scholarship”, as well as to my sweet Mom, Dad and my two brothers Yahia and Farid, for their understanding, support and unconditional love during my whole life.

I’m also using this pages to express my sincere appreciation for all the people of “Laboratoire de Génie des Procédés Chimiques” especially to, “Fatima Team” members Chenouf, Banou, Ayoub and Mahdi and, Professor M. BOUTAHALA, Doctor C. TYAR, Khalil and Chouaib, with whom I initiate my investigation carrier in chemical engineering.

I also want to thank to the Odriozola’s lab society. To all Staff member, Luis, Maribel, Marcela, Luis, Laura, and Anna Penkova. Special acknowledgement to Professor Miguel Angel Centeno, for all his help during my PhD stay. I really appreciate all the ancient PhD students, my co-author Cristina, el Alto jeringa Jose Louis “good helper in carbon and characterizations understanding”, Viki “típica cara sevillana mentalidad árabe”, Nuria “first Spanish contact in French language”, Sara and Rafa which welcomed me and supported me since I’ve landed to Spain. Special thanks To “Fartas” JC, Lola “dolor del agua”, Gabi” remolacha”, Pablo and Marta to the open hands and hearths that made me feel like being at home and changed my way to see catalysis and investigation. I hope to meet you back in Algeria as postdoc or at least in few day vacation stay.

With high regards I would like to thank the new colleagues and all the people in post-; doctorate, master or license in Algeria or Spain” Jesus, Ligia, Estela, Debora, Juan Luis, Sergio, Guille, Maria $^{1\ 2\ 3}$, Bea $^{1\ 2}$, Ikram, Ibtissem, Walid…” for the nice working atmosphere and help.

Finally, I would like to thank all the people that participate and help me from far or nearby in the realization of this thesis.

TABLE OF CONTENTS.

Chapter I. General introduction

Chapter II. Experimental techniques.

Chapter III. Fructose dehydration reaction over acidic carbonaceous catalysts.

Chapter IV. Glucose dehydration to valuable products.

CHAPTER V. Hydrodeoxygenation of levulinic acid to γ-valerolactone over Ruthenium based functionalized carbonaceous catalysts

Chapter VI. 5-hydroxymethylfurfural hydrodeoxygenation to 2,5-dimethylfuran over mono/bimetallic supported carbon catalysts.

General conclusions and perspectives

General introduction

I.1. Background and motivation

Energy is the art of civilization and a key pilot of many economy sections, electricity, industry, commerce, domestic, and transportation. With the demographic growth, advances in technology and the increasing need for higher productivity, most of these sectors are becoming more and more energy intensive.

Global status from IAE report on energy states 76% and 12% consumption from nonrenewable fossil fuels and renewable resources, respectively (Figure I.1). The renewable energy sources include the conventional biomass, biofuels, hydropower, wind energy, geothermal heat and solar systems.

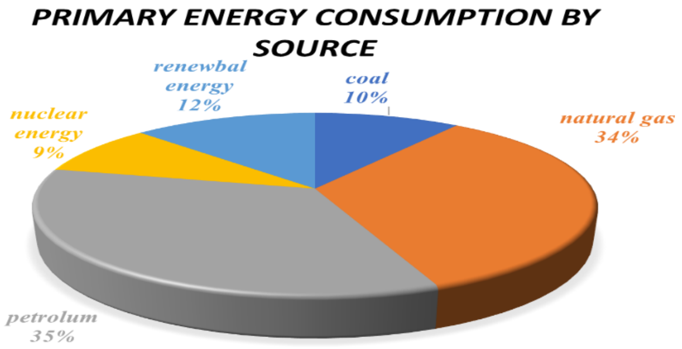


Figure I.1. *History and projections of Energy consumption primary energy.*

Indeed, the total energy supply has increased by 65 % in the last three decades, caused by the raising of the fast-growing developing economies and population with perspectives to keep growing in the next 30 years (Figure I.2). Nevertheless, switch policies, energy efficiency increase and renewable energy sources use are the key points in minimizing the harmful emissions and maintaining good overall society benefit.

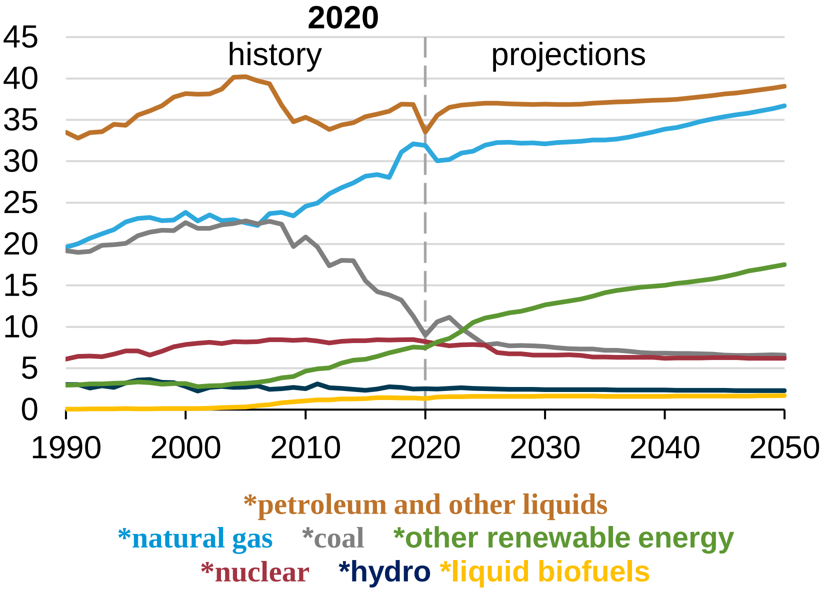


Figure I.2. *Distribution of the energy supply in the 1990-2050 from* (U.S. Energy Information Administration).

In the actual energy model, the continuous fossil fuel sources energy consumption and 90% of chemicals dependence lead to serious safety challenges [1,2]. We are speaking not only of the reserves exhaustion, petroleum prices volatility, climate change and greenhouse effect or environmental contamination, but also, we must focalize on hydrocarbon deposit concentration, the developed technology in confined part of the world, and the produced economic dependency of the underdeveloped countries. Therefore, it is extremely important to pursuit possible renewable, sustainable, and green alternatives with lower environmental and social impact for energy production.

Biomass is often shown as an example of alternative source for electricity generation, industrial and domestic calefaction, etc. with neutral CO_2 emission. Most importantly, biomass is the only sustainable resource containing carbon for chemical and fuels production. It is the ideal equivalent of petroleum for organic compounds production and in other words, the only viable answer to fulfill our future energy and materials requirements. The use of biomass feedstock and the optimization of the chemical processes for their transformation enter the so called **biorefinery** concept [3,4].

Biorefinery is a field where all type of biodegradable fraction of carbon containing matter is converted into different products, chemicals and materials, currently produced from fossil sources. For IEA *“biorefining is the sustainable processing of biomass into a spectrum of marketable products and energy”*. An integrated biorefinery englobes the cycle of biomass production and consumption, where a non-food corps are used for biofuel, biomaterials or bioenergy production respecting energy security, rural development, land use efficiency and environmental safety [5] **(**Figure I.3).

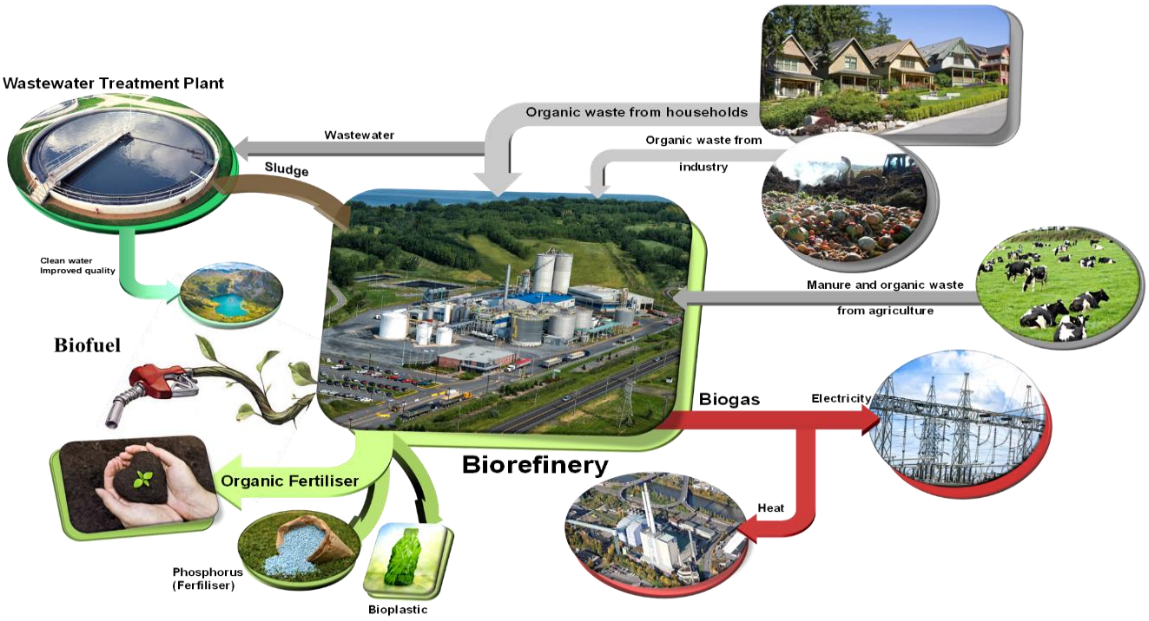


Figure I.3. *Biorefinery concept.*

The main challenge for scientist and industries is the optimization the processes and their implementation in large capacity biorefineries with a sustainable environmental and economic costs.

For instance, two approach exist for achieving alternative chemicals and energy from the biorefinery. The **direct** substitution approach with the production of the same chemicals obtained using petroleum or the **indirect** substitution approach with the development of new chemicals. Despite that indirect substitution still suffers low product yields and incapacity to fit the markets, this approach allows the elaboration of chemicals with properties superior to fossils fuel intermediates.

In contrast to the petrochemistry, that use mainly distillation, cracking and refining catalytic processes to get naphtha as starting material for polymers (ethylene, propylene, butadiene), biomass requires processes such as depolymerization, dehydration and deoxygenation reactions to produce platform molecules. As a consequence, catalyst' requirements and mechanisms for biomass transformations would be distinct from that in conventional petrochemistry [6].

So, the development of efficient processes with selective and durable catalysts provokes great interest in both, laboratory and pilot scale biorefinery approach. Many review papers summarized the challenges that is facing the design of the heterogeneous catalysts and biomass upgrading process for chemicals and fuels production [7,8].

I.2. Lignocellulosic biomass carbohydrates sources

Sugars obtained from biomass could serve as starting molecules for new benchmark generation of interesting products and molecules and in fact, they are considered as a particularly viable option for sustainable fuels and chemicals production [9].

Sugars monomers can be obtained easily from starch carbohydrates but they are considered as a non-suitable carbohydrates sources for socioeconomical process [10]. On the contrary the lignocellulosic biomass including plant biomass, waste agricultural or forestry materials, perennial herbaceous plants and short rotation woody crops appears to be the most available future sugars feedstock for the biorefinery [11]. Lignocellulosic biomass is inexpensive, price adaptable, and non-competitive raw materials of a mixture of rich sugars complex structures and polyphenolic compounds [12]. Its hydrolysis yields different monosaccharides, aromatic compounds, various organic acids, and carbon dioxide biofuels (ethanol, butanol, hydrogen) and/or added-value chemicals. The lignocellulose is composed by cellulose as main polymer, hemicellulose and lignin [13]. Cellulose is a linear polysaccharide composed of glucose units linked via β1,4-glycosidic bonds, while hemicellulose is a branched polysaccharide consisted primarily of xylose with small quantity of mannose, galactose, rhamnose, and arabinose units connected via multiple types of glycosidic bonds. Lignin is a three-dimensional amorphous polymer composed of three kinds of phenylpropanolic rings.

During lignocellulosic biomass conversion, a major part of hemicellulose and cellulose can be hydrolyzed into xyloses and glucose, the most abundant monosaccharide found in nature and fundamental source for bio-chemicals production.

Chemical routes of lignocellulosic biomass transformation

Two are the principal ways of lignocellulose biomass conversion: chemical and biological. In the latter the biomass is decomposed to sugars and converted into biofuels and valuable chemicals products by fermentation with enzymes or anaerobic digestion [14,15]. However, the strict reaction conditions, unsatisfactory efficiency and poor recyclability are serious drawbacks for a practical large-scale application of this method. That is way the chemical pathways are preferred.

Lignocellulosic biomass can be transformed to useful chemicals via three principal pathways: gasification, pyrolysis, and hydrolysis and catalytic conversion [16–18].

Gasification route

In the gasification processes, the biomass can be treated in air (for power energy generation) or in oxygen to produce a mixture of gases like CO, CO_2, CH_4 and H_2. The obtained gases can be used as precursors for methanol, dimethyl ether or liquids alkane production with similar properties to diesel via catalytic **Fisher Tropsh** reactions [19]. However, the low selectivity's to C5-C12 alkanes and the costly processes for the production of high purity final products is the major inconvenient of this way of biomass valorization.

Pyrolysis and liquefaction

On the other hand, lignocellulosic biomass could be transformed into bio-fuels, bio-char and gases through simple pyrolysis, where both liquid and syngas can be further converted into valuable fuels and chemicals [20]. However, the high oxygen content (up to 40%) of the raw lignocellulosic biomass and the low-controlled reaction process determine the poor quality of the resultant bio-chemicals, making indispensable energy consuming post treatments (*e.g.* hydrogenation, deoxygenation) for a further upgrading. All those processes decrease the efficiency of the technology and enhance the cost of the products for practical applications.

Hydrolysis and catalytic conversion route

Targeting the optimal utilization of each component of the lignocellulosic biomass for the preparation of useful biochemicals and biofuels, the chemical conversion route is considered as the most efficient approach to produce primary molecules from which an eventual of secondary products can be obtained [15]. In this approach, the major part of the cellulose and hemicellulose is hydrolyzed to carbohydrates to obtain the monomers which are then used for the productions of other different chemicals [21]. This approach commonly employs a specific heterogeneous catalyst for discrete reactions, such as deoxygenation, dehydration, hydrogenolysis, coupling reaction, hydrogenation, isomerization, or hydrodeoxygenation optimized to a maximal efficiency.

I.3. Chemical structure and transformations of lignocellulosic biomass

Lignocellulosic biomass comprises various natural polymers (cellulose, hemicellulose and lignin) with some quantities of moisture, proteins, and various minerals depending on its source (Figure I.4).

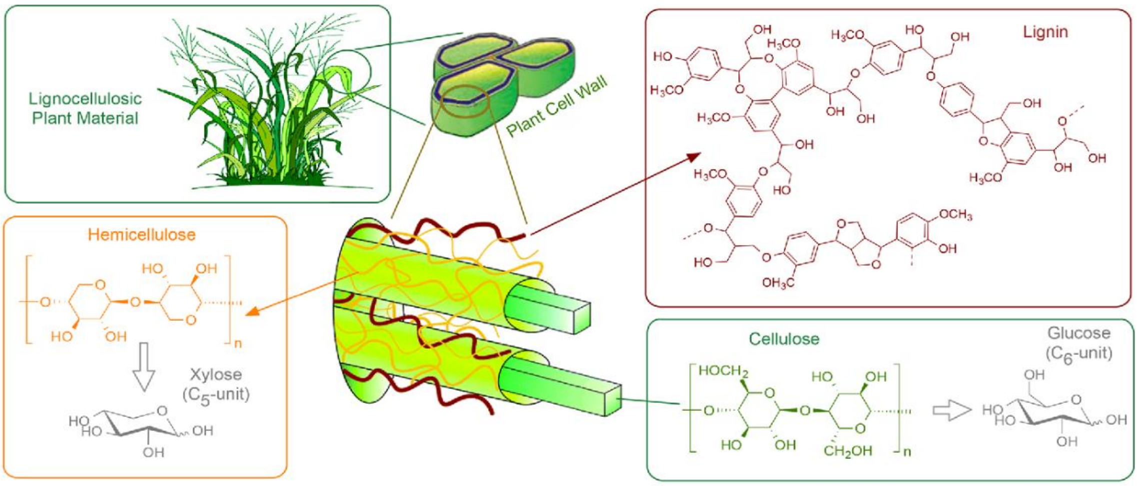


Figure I.4. *Chemical structure of the lignocellulosic biomass[22].*

Cellulose

Since about half of the organic carbon in the biosphere is present in form of cellulose, its conversion into fuels and valuable chemicals is of paramount importance. Cellulose is the major component of lignocellulosic biomass and it is composed by polysaccharides consisting of a straight chain of D-glucose molecules linked through β-(1-4) glycosidic bonds with general formula $(C_6H_{10}O_5)_n$ (Figure I.5)[23]. It is the main structural constituent of the primary cell wall of the green plants, algae, and oomycetes. Cellulose is the most common organic polymer and can be found in different proportions. For example, cotton fiber contains 90% of cellulose, the wood 40%-50% and the dried hemp approximately 57%. Cellulose depolymerization allows the production of glucose as sugar monomer and in low ratio some cellobiose as anhydride dimer. The unit of glucose in the cellulose structure is named glucan $(C_6H_{10}O_5)_n$ and can be hydrolyzed further by losing one or more water molecules in strong acid.

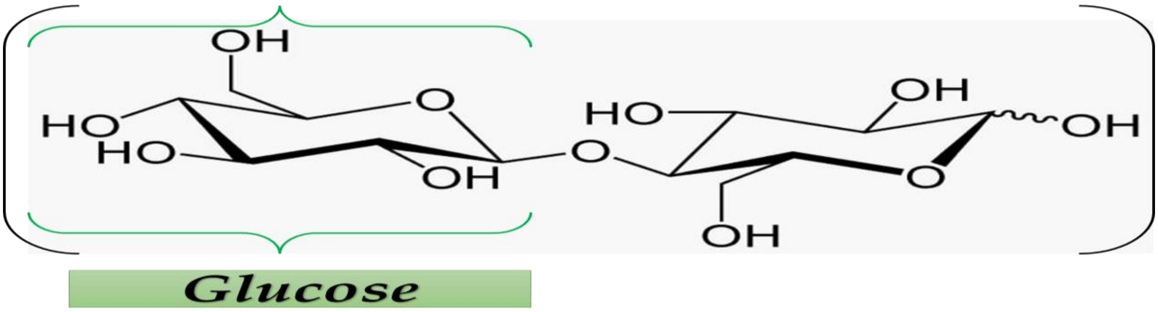


***Figure I.5.** Structure of cellulose unit.*

Hemicellulose

Hemicellulose is the second most abundant polymer. It is a branched heteropolymer containing approximately 500-3000 sugar units [24] of several types including mainly glucose, xylose and arabinose.

The hemicellulose cross-links with either cellulose or lignin usually to strengthens the plant cell wall (Figure I.4). Although widely available, hemicellulose utilization is more difficult in comparison to cellulose, due to its structural diversity and difficult enzymatic hydrolysis. However, hemicelluloses offer more possibilities for regioselective chemical and enzymatic modifications in comparison to cellulose, due to the variability in sugar constituents, glycosidic links and structure of glycosyl side chains [22].

Lignin

Lignin is an aromatic heteropolymer, relatively difficult to degrade chemically or enzymatically [25]. It is a three-dimensional polymer of phenylpropanoid units, such as primarily three-dimensional polymer of 4-propenyl phenol, 4-propenyl-2-methoxy phenol, and 4-propenyl-2.5-dimethoxyl phenol (Figure I.4).

Lignin has the potential to be converted into fuels and high value chemicals, but the complexity of its structure and non-uniformity of its composition make difficult its processing. The hydrothermal degradation of lignin need high temperature of 350 – 400 °C, and the main products are catechol, phenols and cresols [26]. However, it can be catalytically hydrolyzed into various phenols and methoxy phenols by cleavage of the ether-bonds under alkaline environment.

I.4. Monosaccharaides

The monosaccharide cellulose and hemicellulose (polysaccharides) are of high importance, since they can be treated as a carbon source for biorefinery purposes. Generally, sugars (carbohydrates) are defined as polyhydroxy aldehydes or ketones or as polyalcohols containing acetal (aldose) or ketal (ketose) group. The monosaccharide is a simple monomer issued from sugars that cannot be hydrolyzed into smaller units and classified by the number of carbon atoms that presents (hexoses and pentoses with six and five atoms de carbon respectively) [27]. The usual way of representation of the monosaccharides is the Fischer projection (Figure I.6). Carbon atoms are numbered consecutively from the top to the bottom, being ***n*** the number of carbon atoms. Aldoses have an ***n*** minus 2 and ketoses an ***n*** minus 3 chiral (asymmetric) substituted carbon atoms. The stereochemistry of the farthest chiral carbon from the anomeric carbon determines whether the monosaccharide is designated as D- or L-. The most naturally occurring monosaccharides are members of the D-series.

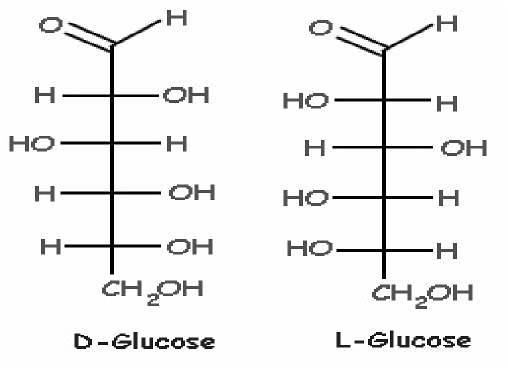
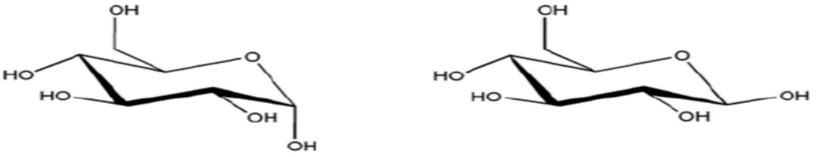
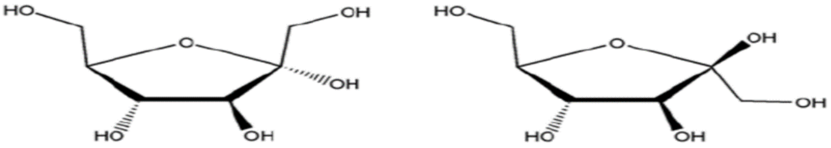


Figure I.6. *Fisher projection of glucose molecule.*

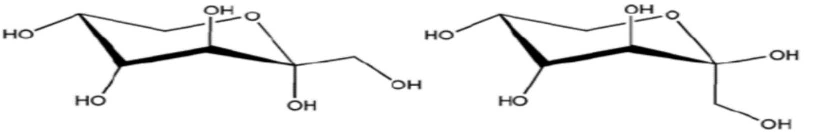
In solution, monosaccharaides do not remain as aldehydes and ketones but form hemiacetal and hemiketal bonds, respectively. Usually a five-member ring (furanose) or a six-member ring (pyranose) is formed, after a reaction of the hydroxyl group at C-4 or at C-5 position, respectively, reacts with the aldehyde group. The pyranose form is more common than the furanose but for some monosaccharides, both pyranose and furanose co-exist in equilibrium. Because stereochemistry is introduced at the aldehyde carbon atom (becomes asymmetric), there are two possible products, called anomers, for the pyranose or furanose. The carbon atom of the aldehyde or ketone is termed as anomeric carbon atom. The equilibrium between these possible forms (tautomer’s) depends on the stereochemistry of the monosaccharide, the composition and temperature of the solution and on the solvent (Figure I.7). The reaction between one anomer into its equilibrium mixture of anomers is called mutarotation and is accompanied by the change of its optical rotation.



α-D-glucopyranose (35%) β-D-glucopyranose (65%)



α-D-fructofuranose (5.2%) β-D-fructofuranose (20%)



α-D-fructopyranose (2.3%) β-D-fructopyranose (72%)

Figure I.7. *Different form of glucose tautomer in solution.*

I.5. Chemicals platform molecules derived from sugars

The key of the platform chemical technology is the creation of opportunity to generate a diverse array of chemicals, rather than having a single compound. The traditional refinery is based mainly on platform chemicals like ethylene, propylene, and BTX, a non-functionalized molecules and can be converted to a diversity of organic chemicals and materials for wide range applications [28]. In analogy, for the biorefinery, the US Department of Energy (DOE) in 2004/NREL in a report, called "Top Value-Added Chemicals from Biomass" identified twelve top chemical candidates, that can act as chemical intermediates to produce a wide variety of new chemicals. Bozell and Peterson, in 2010 updated that evaluation and extended the platform chemicals for biobased products issued from biorefinery carbohydrates [29]. Among these chemicals, 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) appears as building compounds

[30]. The most versatile chemicals with high industrial potential that can be generated from LA and HMF are listed in Figure I.8.

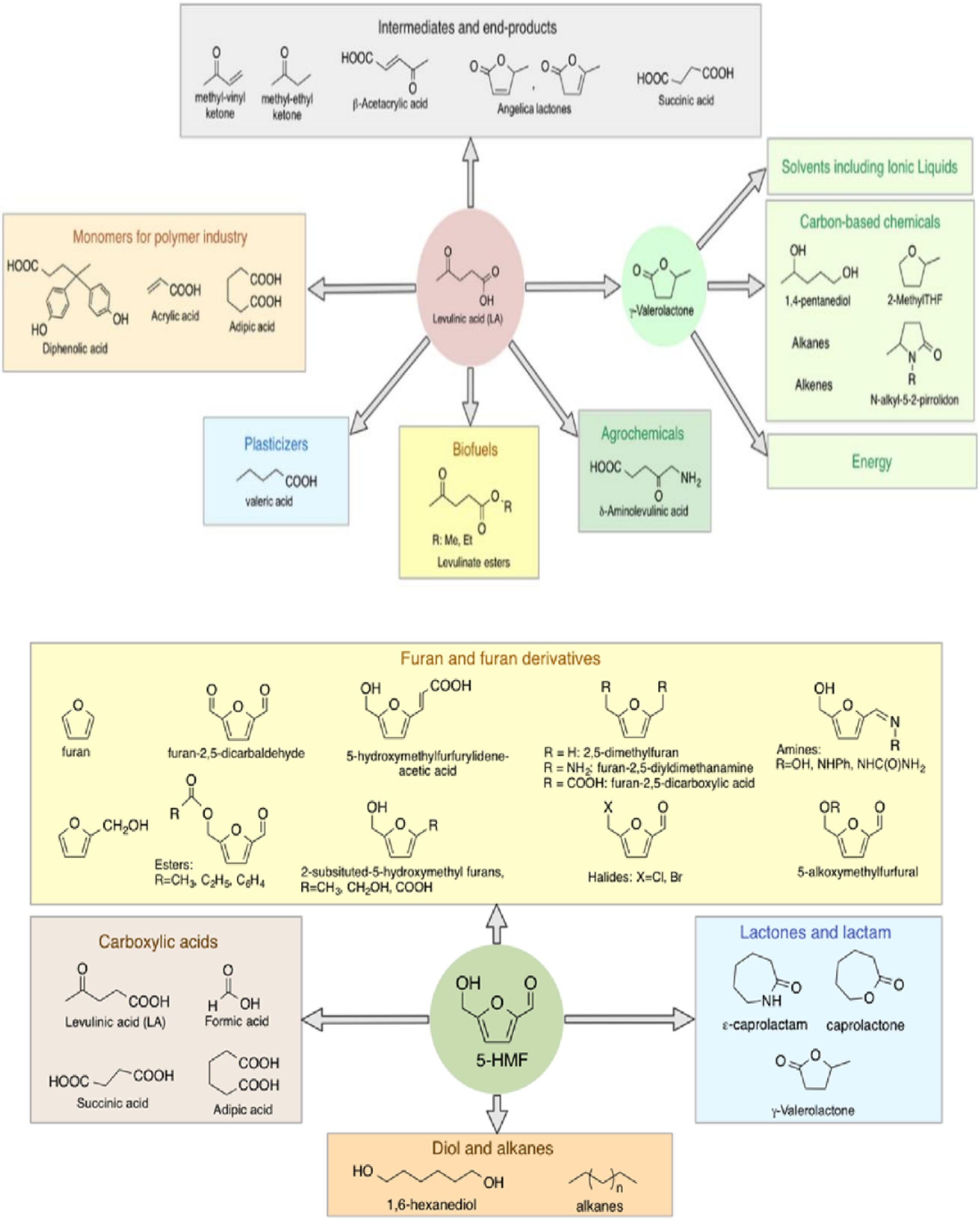


Figure I.8. *HMF and LA platform*[31].

HMF and LA bifunctional molecules with carbonyl, aldehydes and carboxylic groups are fundamental building blocks for organic synthesis. Their high electrophilicity makes them appropriate for reactions with a variety of nucleophiles, allowing the formation of single, double or triple carbon-carbon bonds or carbon-heteroatom bonds through condensation reactions. The HMF and LA can be also oxidized or reduced for polymers synthesis. The oxygen removal by hydrogenation or hydrodeoxygenation reaction could produce liquid alkanes for biofuel.

The significant interest in using HMF and LA is clearly evidenced by the increasing numbers of publications dealing with their productions and utilizations (Figure I.9).

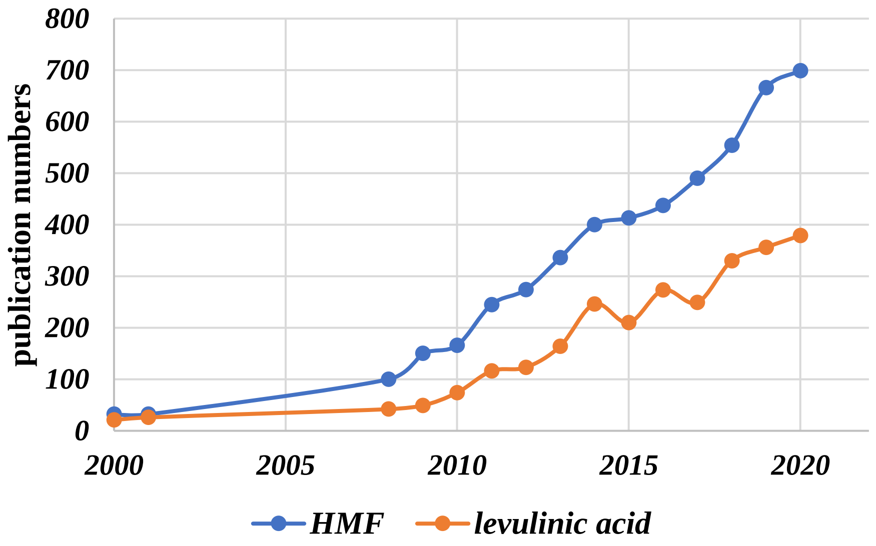


Figure I.9. *Number of publications using keywords 5- hydroxymethylfurfural or levulinic acid annually from 2000 to 2020. Source: Web of Science.*

The most effective protocol to obtain HMF and LA is the multistep acid-catalyzed dehydration of hexoses, preferably fructose and glucose representing the C6- fraction of the biomass.

I.6. Controlling of the reaction of sugars dehydration to HMF and LA

The C5 and C6 sugars can be converted selectively to furfural, hydroxymethylfurfural (HMF) or levulinic acid (LA) depending on the reaction media and type active catalytic sites [32]. HMF and furfural are the direct dehydration products of glucose and xylose, while LA is produced from rehydration of the dehydrated products or direct transformation of carbohydrates monomers. Thus, after the separation and hydrolysis of the lignocellulosic structure, the dehydration appears as the first step of biomass-derived carbohydrates upgrading to platform molecules.

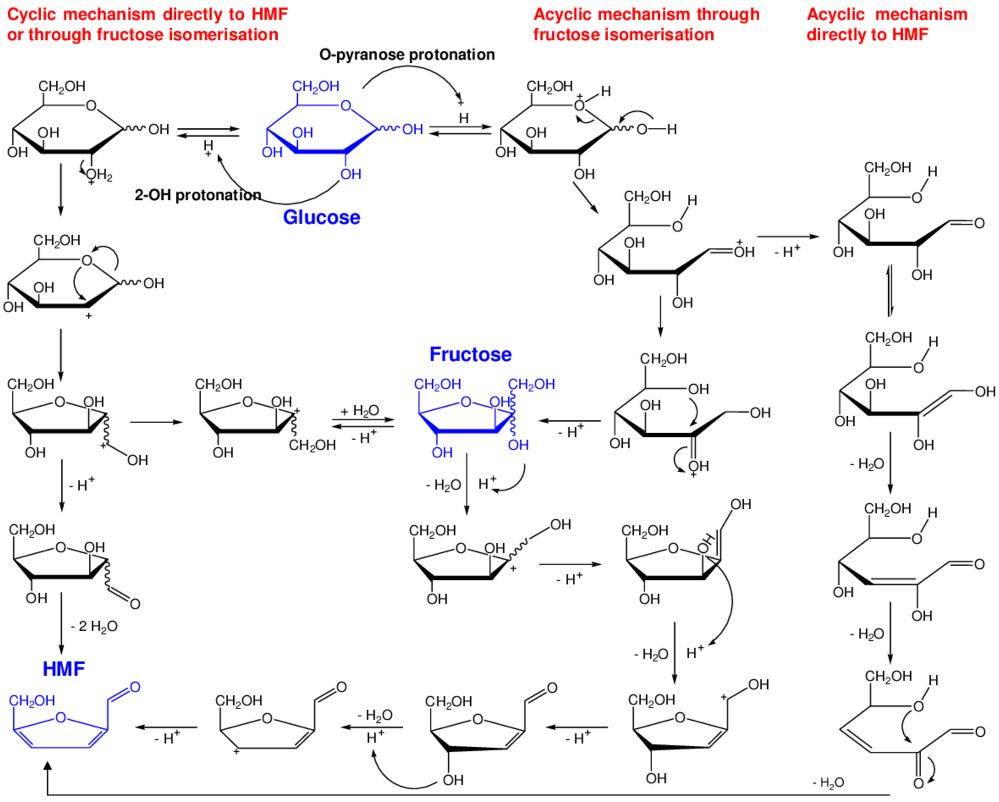


Figure I.10. Cyclic and acyclic pathways for glucose dehydration to HMF [33].

Generally, the dehydration of hexoses, glucose as main representative and his isomer fructose, is initiated by the activation at hydroxyl oxygen over an acid or base site.

Nevertheless, the mechanism of dehydration reaction is still not clearly defined and could comprise several steps of the as called cyclic and acyclic pathways (Figure I.10.).

Although with great potential as a feedstock, glucose and its configuration, in particular, does not allow a direct transformation to HMF under mild reaction conditions. The most suitable starting molecule seems to be the fructose. This is related to the main existing form in solution, six or fiver-membered ring cyclic hemiacetal for glucose and fructose respectively [34]. The dehydration of the 5-membered ring appears faster while for the dehydration of 6-membered ring the aldose to ketose isomerization is required for successful glucose transformation process.

The dehydration reaction commonly occurs on Brønsted acid sites, where the proton converts the leaving hydroxyls in water (Figure I.11). The protonation at the glucopyranose’ O1H hydroxyl group is thermodynamically the most favorable, leading sometimes also to glucose ring-opening and formation of humins and other reversion products.

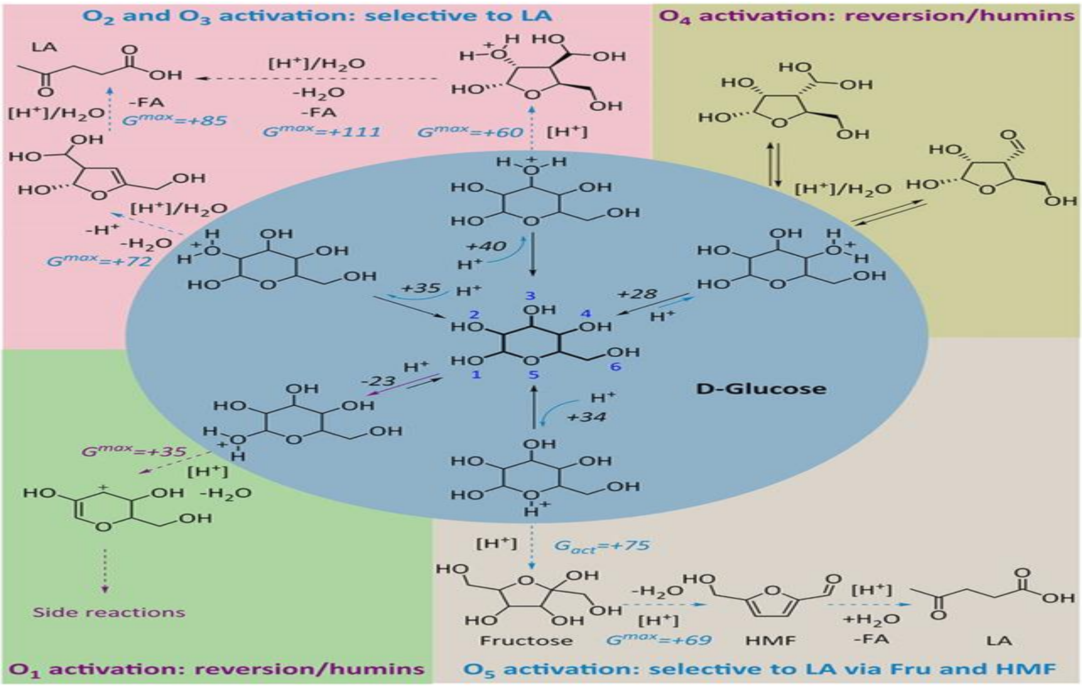


Figure I.11. *Different possible protonation of glucose[34].*

The protonation at O2H, O3H, O4H, and O5 (pyranoid ring oxygen) groups are also possible. The acyclic pathway protonations at O2H and O3H groups result in direct formation of LA without passing through HMF intermediate while the protonation at O5 promotes the tandem reactions of isomerization and dehydration of glucose to HMF. Moreover, the intramolecular dehydration of glucose induces the formation of levoglucosane (LGA) and its continuous dehydration results in LGO and even in HMF. On the other hand, fructose shows different reactivity in acidic aqueous solutions. The protonations of O2H and O5 (furanic ring oxygen) are thermodynamically favorable. The preferred protonation of O2H group at the anomeric carbon of α-D-fructofuranose and β-D-fructofuranose results in HMF formation whereas the protonation of the furanic O5 leads to the mutarotation of fructose to glucose.

Extensive research efforts have been dedicated to the choice of catalytic systems and solvent medium [35–43]. The catalysts can be homogeneous or heterogeneous and the solvent includes water, polar aprotic solvents (e.g., dimethyl sulfoxide, tetrahydrofuran, and methyl isobutyl ketone) and inorganic ionic liquids salts (i.e., liquid salts), all found as mono or biphasic system. Many active investigations on system components, reactors type and separation of the products are still underway in order to address the persisting challenges that hamper the mass production of HMF and LA with low undesirable product formation.

Once formed, HMF and LA could participate in variety of reaction to generate many new chemicals. One example of this kind of reaction is hydrodeoxygenation reaction.

I.7. Hydrodeoxygenation reaction for biorefinery purpose

Hydrodeoxygenation reaction is a chemical process where the substrate undergoes oxygen atoms removal by addition of hydrogen sources in presence of a catalyst. In this reaction a part of the added protons reduce the unsaturated structure and the substrate undergoes oxygen removal via dehydration, decarboxylation, hydrogenolysis and hydrocracking reactions [44].

The aim of the utilization of the HDO process for biorefinery construction is the reduction of the oxygen content of the biomass and the reduction of the unsaturated bonds [45]. HDO transformation is very useful for the preparation of liquid alkanes from highly oxygenated molecules in order to produce biofuel and chemicals [46]. HMF and LA HDO leads to liquid fuel alkanes via gamma valerolactone (GVL) intermediate and dimethyl furan.

The biggest challenge of the HDO process is to achieve high degree of oxygen removal at low hydrogen pressure. The catalyst usually contains active metal and acidic sites to facilitate the process. The active sites for HDO reaction are organized over the presence of unpaired *d*-electron of the metal site while a support must ensure active sites dispersion and reactive/products adsorption-desorption and C-O bond cleavage. The usual metal sites are noble metal and the best-judged support carbonaceous materials [47].

References

[1] R. Ahorsu, F. Medina, M. Constantí, Significance and Challenges of Biomass as a Suitable Feedstock for Bioenergy and Biochemical Production: A Review, Energies. 11 (2018) 3366. https://doi.org/10.3390/en11123366.

[2] H.R. Ghatak, Biorefineries from the perspective of sustainability: Feedstocks, products, and processes, Renewable and Sustainable Energy Reviews. 15 (2011) 4042–4052. https://doi.org/10.1016/j.rser.2011.07.034.

[3] D. Sharma, A. Saini, Lignocellulosic Waste Valorization and Biorefineries Concept, in: D. Sharma, A. Saini (Eds.), Lignocellulosic Ethanol Production from a Biorefinery Perspective: Sustainable Valorization of Waste, Springer, Singapore, 2020: pp. 195–215. https://doi.org/10.1007/978-981-15-4573-37.

[4] K. Özdenkçi, C. De Blasio, H.R. Muddassar, K. Melin, P. Oinas, J. Koskinen, G. Sarwar, M. Järvinen, A novel biorefinery integration concept for lignocellulosic biomass, Energy Conversion and Management. 149 (2017) 974–987. https://doi.org/10.1016/j.enconman.2017.04.034.

[5] E. de Jong, G. Jungmeier, Biorefinery Concepts in Comparison to Petrochemical Refineries, in: Industrial Biorefineries & White Biotechnology, Elsevier, 2015: pp. 3–33. https://doi.org/10.1016/B978-0-444-63453-5.00001-X.

[6] F. Cherubini, The biorefinery concept: Using biomass instead of oil for producing energy and chemicals, Energy Conversion and Management. 51 (2010) 1412–1421. https://doi.org/10.1016/j.enconman.2010.01.015.

[7] S.M.A.H. Siddiki, A.S. Touchy, Challenges and future prospects in heterogeneous catalysis for biorefinery technologies, in: Advanced Functional Solid Catalysts for Biomass Valorization, Elsevier, 2020: pp. 225–250. https://doi.org/10.1016/B978-0-12-820236-4.00010-6.

[8] S. Dutta, Catalytic materials that improve selectivity of biomass conversions, RSC Adv. 2 (2012) 12575–12593. https://doi.org/10.1039/C2RA20922E.

[9] M.S. Singhvi, D.V. Gokhale, Lignocellulosic biomass: Hurdles and challenges in its valorization, Appl Microbiol Biotechnol. 103 (2019) 9305–9320. https://doi.org/10.1007/s00253-019-10212-7.

[10] J.B. Heo, Y.-S. Lee, C.-H. Chung, Raw plant-based biorefinery: A new paradigm shift towards biotechnological approach to sustainable manufacturing of HMF,

Biotechnology Advances. 37 (2019) 107422. https://doi.org/10.1016/j.biotechadv.2019.107422.

[11] A. Limayem, S.C. Ricke, Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects, Progress in Energy and Combustion Science. 38 (2012) 449–467. https://doi.org/10.1016/j.pecs.2012.03.002.

[12] Different pretreatment technologies of lignocellulosic biomass for bioethanol production: An overview - ScienceDirect, (n.d.).

[13] Structure of Lignocellulosic Biomass | SpringerLink, (n.d.).

[14] H. Chen, Lignocellulose biorefinery product engineering, in: Lignocellulose Biorefinery Engineering, Elsevier, 2015: pp. 125–165. https://doi.org/10.1016/B978-0-08-100135-6.00005-3.

[15] A. Corma, S. Iborra, A. Velty, Chemical Routes for the Transformation of Biomass into Chemicals, Chem. Rev. 107 (2007) 2411–2502. https://doi.org/10.1021/cr050989d.

[16] S. Nanda, J. A. Kozinski, A. K. Dalai, Lignocellulosic Biomass: A Review of Conversion Technologies and Fuel Products, Current Biochemical Engineering. 3 (2016) 24–36.

[17] S. Nanda, J. Mohammad, S.N. Reddy, J.A. Kozinski, A.K. Dalai, Pathways of lignocellulosic biomass conversion to renewable fuels, Biomass Conv. Bioref. 4 (2014) 157–191. https://doi.org/10.1007/s13399-013-0097-z.

[18] D. Martin Alonso, J. Q. Bond, J. A. Dumesic, Catalytic conversion of biomass to biofuels, Green Chemistry. 12 (2010) 1493–1513. https://doi.org/10.1039/C004654J.

[19] Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review - ScienceDirect, (n.d.).

[20] T. Kan, V. Strezov, T.J. Evans, Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters, Renewable and Sustainable Energy Reviews. 57 (2016) 1126–1140. https://doi.org/10.1016/j.rser.2015.12.185.

[21] X. Han, Y. Guo, X. Liu, Q. Xia, Y. Wang, Catalytic conversion of lignocellulosic biomass into hydrocarbons: A mini review, Catalysis Today. 319 (2019) 2–13. https://doi.org/10.1016/j.cattod.2018.05.013.

[22] M. Möller, U. Schröder, Hydrothermal production of furfural from xylose and xylan as model compounds for hemicelluloses, RSC Adv. 3 (2013) 22253. https://doi.org/10.1039/c3ra43108h.

[23] H. Chen, Chemical Composition and Structure of Natural Lignocellulose, in: H. Chen (Ed.), Biotechnology of Lignocellulose: Theory and Practice, Springer Netherlands, Dordrecht, 2014: pp. 25–71. https://doi.org/10.1007/978-94-007-6898-7_2.

[24] The hierarchical structure and mechanics of plant materials | Journal of The Royal Society Interface, (n.d.). https://royalsocietypublishing.org/doi/10.1098/rsif.2012.0341.

[25] O. Bobleter, Hydrothermal degradation of polymers derived from plants, Progress in Polymer Science. 19 (1994) 797–841. https://doi.org/10.1016/0079-6700(94)90033-7.

[26] Decomposition of a Lignin Model Compound under Hydrothermal Conditions - Wahyudiono - 2007 - Chemical Engineering & Technology - Wiley Online Library, (n.d.). https://onlinelibrary.wiley.com/doi/10.1002/ceat.200700066.

[27] F. Franks, P.J. Lillford, G. Robinson, Isomeric equilibria of monosaccharides in solution. Influence of solvent and temperature, J. Chem. Soc., Faraday Trans. 1. 85 (1989) 2417–2426. https://doi.org/10.1039/F19898502417.

[28] K. Kohli, R. Prajapati, B.K. Sharma, Bio-Based Chemicals from Renewable Biomass for Integrated Biorefineries, Energies. 12 (2019) 233. https://doi.org/10.3390/en12020233.

[29] J. J. Bozell, G. R. Petersen, Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited, Green Chemistry. 12 (2010) 539–554. https://doi.org/10.1039/B922014C.

[30] I.K.M. Yu, D.C.W. Tsang, Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms, Bioresource Technology. 238 (2017) 716–732. https://doi.org/10.1016/j.biortech.2017.04.026.

[31] L.T. Mika, E. Cséfalvay, Á. Németh, Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability, Chem. Rev. 118 (2018) 505–613. https://doi.org/10.1021/acs.chemrev.7b00395.

[32] I.K.M. Yu, D.C.W. Tsang, Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms, Bioresource Technology. 238 (2017) 716–732. https://doi.org/10.1016/j.biortech.2017.04.026.

[33] Reche - Bifunctional niobia and zirconia catalysts for 5-h.pdf, (n.d.). https://publications.aston.ac.uk/id/eprint/33426/1/Tapia_Reche_M._2017.pdf

[34] L. Zhu, X. Fu, Y. Hu, C. Hu, Controlling the Reaction Networks for Efficient Conversion of Glucose into 5-Hydroxymethylfurfural, ChemSusChem. 13 (2020) 4812–4832. https://doi.org/10.1002/cssc.202001341.

[35] Insights into HMF catalysis - ScienceDirect, (n.d.). https://www.sciencedirect.com/science/article/abs/pii/S1226086X18308773

transformation, Journal of Environmental Chemical Engineering. 9 (2021) 106721. https://doi.org/10.1016/j.jece.2021.106721.

[37] Recent advances in catalytic and autocatalytic production of biomass-derived 5-hydroxymethylfurfural - ScienceDirect, (n.d.). https://www.sciencedirect.com/science/article/pii/S1364032120306055?casa_token=bCtw9M4_nw8AAAAA:Gp6YNsWVws9ZmeBhqUv8bUEBjROJXLDGHWiR_pbKqvci5nIRBPPnxWJLwOmqf4O8fgo8UfDNTENR (accessed November 22, 2021).

[38] I. Agirrezabal-Telleria, I. Gandarias, P.L. Arias, Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review, Catalysis Today. 234 (2014) 42–58. https://doi.org/10.1016/j.cattod.2013.11.027.

[39] Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: A review - ScienceDirect, (n.d.).

[40] Conversion of 5-hydroxymethylfurfural to chemicals: A review of catalytic routes and product applications - ScienceDirect, (n.d.).

[41] From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis - ScienceDirect, (n.d.).

[42] C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A.M. Raspolli Galletti, New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock, Catalysts. 6 (2016) 196. https://doi.org/10.3390/catal6120196.

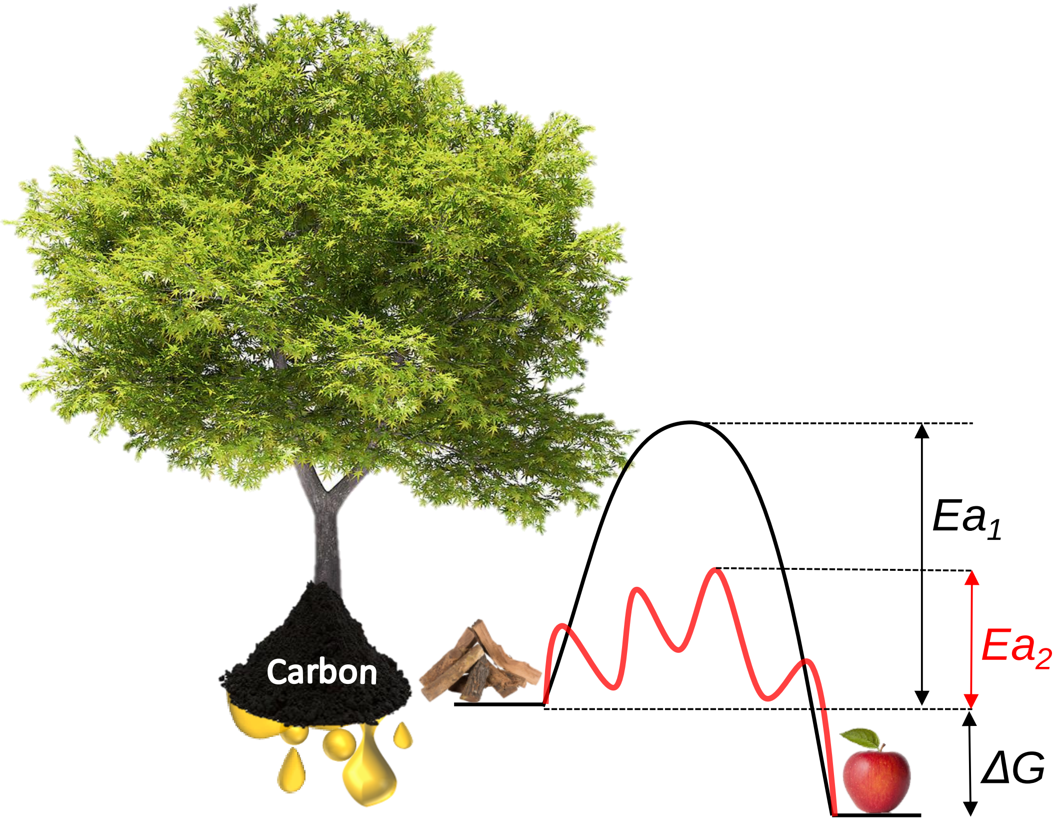
[43] A review on solid acid catalysis for sustainable production of levulinic acid and levulinate esters from biomass derivatives - ScienceDirect, (n.d.).

[44] L. Yan, Q. Zhang, W. Deng, Q. Zhang, Y. Wang, Catalytic valorization of biomass and bioplatforms to chemicals through deoxygenation, in: Advances in Catalysis, Elsevier, 2020: pp. 1–108. https://doi.org/10.1016/bs.acat.2020.09.002.

[45] Z. Lin, R. Chen, Z. Qu, J.G. Chen, Hydrodeoxygenation of biomass-derived oxygenates over metal carbides: from model surfaces to powder catalysts, Green Chem. 20 (2018) 2679–2696. https://doi.org/10.1039/C8GC00239H.

[46] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, A review of catalytic hydrodeoxygenation of lignin-derived phenols from biomass pyrolysis, Bioresource Technology. 124 (2012) 470–477. https://doi.org/10.1016/j.biortech.2012.08.089.

[47] Advances and Challenges in the Valorization of Bio-Oil: Hydrodeoxygenation Using Carbon-Supported Catalysts | Energy & Fuels, (n.d.). https://pubs.acs.org/doi/10.1021/acs.energyfuels.



Objectives

The main objective of this project is the design of catalyst series based on multi/mono functionalized carbon materials effective in the processes of lignocellulosic biomass derivatives chemical valorization in liquid phase. The reactions of isomerization and/or dehydration and hydrodeoxygenation reactions are mainly concerned as an important part of the biorefinery concept for sustainable development.

In particular, homemade series are compared to commercially available carbon-based materials. Both series encounter several and different treatments in order to elaborate suitable carbonaceous catalyst and/or supports for noble metals.

Two partial objectives can be formulated. In first approximation the design is focused on achieving acid carbon catalysts highly active and selective in the reactions of hexoses (glucose and fructose) isomerization and dehydration to produce two platform molecules, levulinic acid (LA) and 5-hydroxymethyl furfural (HMF) with important yields and via green sustainable chemistry processes. In the second part of the thesis project the levulinic acid and HMF are used as starting molecules to produce by hydrodeoxygenation (HDO) reaction green solvents/biofuel/biodiesel, i.e. gamma valerolactone (GVL) and dimehtylfurane (DMF) in particular. In this part different noble metal (Ru, Pt and Pd) are used as active sites supported on a functionalized carbon surface.

The results that describe the main goals achievement in this thesis are organized in 6 specific chapters including the present part and the final general conclusions and perspectives.

After a small **introduction** of the state-of- art and specific goals of the thesis along the **chapter II** the used experimental methodology to conduct the research is presented. This part includes a details on catalytic system synthesis and methods of characterization, feedstock preparation, catalytic reactions and data collection and analysis.

Chapter III is dedicated to fructose dehydration to HMF, where the general interest goes in development of novel acid catalysts based on active commercial carbon and carbon nanofibers modified chemically by different sulphonating agents and organic acids. The first part of the chapter proposes a study on the effect of different sulphonating agents on material's physicochemical and catalytic properties in the reaction of fructose dehydration. Different active sites are generated and applied in two different environments: solvent free and using dimethyl sulfoxide (DMSO) as reaction media. The second part of the chapter consists in covalent heterogeneization of ionic liquids and organosilicate homogeneous catalysts via grafting on carbon supports. The new hybrid materials are tested again in the fructose dehydration reaction using methylisobutylketone /H_2O biphasic system.

The **chapter IV** explores the optimization of glucose valorization to different valuable products, such as fructose, HMF, and levulinic acid. In the first part of the chapter the influence of alkaline and alkali earth halide functionalization of activated charcoal is applied in the reaction of glucose isomerization to fructose, being the isomerization the first step of the glucose conversion to HMF. The role of the cation (K^+, Ca^{2+}, Sr^{2+} and Mg^{2+}) and halide (F^-, Cl^- and Br^-) is discussed and the best reaction conditions are selected to achieve maximal fructose yield and selectivity. Lately, different bifunctional catalysts are compared studying the reaction kinetics and proposing suitable reaction paths for direct glucose conversion to 5-hydroxymethylfurufral. Catalyst recyclability and stability is also examined. The last part of this chapter presents the effectiveness of the combination between homogeneous and heterogeneous catalysts (*p*-toluenesulfonic acid **functionalized carbon catalysts** promoted by calcium chloride) to achieve one pot glucose dehydration to levulinic acid.

Chapter V and VI describe the upgrading of the obtained levulinic acid and HMF in chapters III and IV to valuable chemicals via hydrodeoxygenation reaction using different mono/bimetallic nanoparticles supported on different functionalized carbon materials.

Finally, the major findings of the project are summarized in general conclusions and some recommendations for further research in this challenging field are also provided.

Experimental techniques

Summary

In this chapter the experimental techniques and methods are summarized together with brief description of the physicochemical bases of the employed methods of characterization. The general conditions of product analysis are also presented.

II.1. Introduction

The characterisation of catalysts is a relevant part for the catalysis discipline. It is one of the fundamental aspects that aims to obtain a scientific transcendence in understanding the physicochemical properties responsible for the material' catalytic function in a given reaction.

Since the heterogeneous catalytic reaction occurs exclusively on the surface of the catalyst, the determination of the surface and textural properties, the surface chemical composition and the characteristics of the active phase is highly relevant for elucidating and establishing a direct relationship between structure and reaction behaviour. The characterization of the materials should provide a valuable information not only to understand how active or inactive the catalysts are, but also to find a way to improve its activity, selectivity and stability.

This chapter briefly describes the theoretical basis of the used characterisation techniques, together with the experimental procedures and methods used to evaluate the physico-chemical properties of solids. It also specifies all experimental and analytical conditions used for the catalytic activity measurements.

II.2. Characterization Techniques

II.2.1. Powder X-Ray Diffraction (XRD)

XRD is a rapid and non-destructive analytical technique used to determine the crystalline structure, phase composition and defects degree of the used solids.

This technique is based on the elastic scattering of the X-rays by the atoms present in the periodic lattice. The scattered waves may either deflected without energy lost, resulting in a constructive interference or can suffer a loss of their energy in a destructive way. Consequently, when X-rays interact with the atoms constituting the crystallographic planes of a crystal they provoke a combination of constructive and destructive interferences of the scattered waves causing X-ray diffraction.

The diffraction of X-rays by the crystals is described by the Bragg´s Law (Eq. 1) where the scattering angle is correlated with the distance between the planes in the crystalline structure (Figure II.1).

$$n \lambda = 2\, d_{hkl} \sin \theta \qquad \text{Eq. 1}$$

where **n** is the order of reflection, **λ** the wavelength of electromagnetic radiation, d_{hkl} the lattice spacing and **θ** the angle between the incident beam and the normal to the reflecting lattice plane.

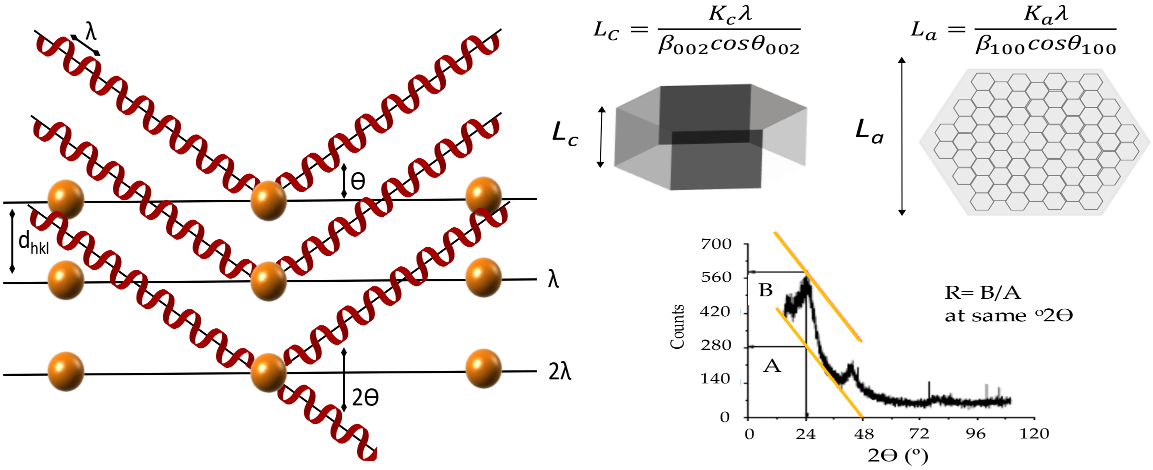


Figure II.1. *Diffraction phenomena and XRD specta parameters calculation.*

The crystalline domain of all present phases can be calculated through Debye-Scherrer equation (Eq. 2) [1].

$$t = m\, \lambda / \beta \cos \Theta \qquad \text{Eq. 2}$$

where **t** is the crystal domain size, **m** is the shape factor, which is a constant depending on particle shape and plane arrangement, **λ** is the wavelength of the incident radiation and **β** is the width at half the maximum height of the diffraction peak.

In this thesis the XRD patters of all prepared samples (supports and catalysts) were recorded on a PANalytical X´Pert Pro diffractometer using CuKα radiation (40 mA, 45 kV, λ=1.5406 Å) in a 2ϴ range between 10 and 90º, using a step size of 0.05º and step time of 300 s.

X-ray diffraction can be applied also to a partially amorphous materials such as carbonaceous materials and allows the evaluation of their graphitization degree by calculation of the average parameters of the carbon network such as, $\mathbf{L_c}$- the length of the crystalline domain in the plane (002), and $\mathbf{L_a}$-the length of the crystalline domain in the plane (100).

II.2.2. X-Ray Fluorescence (XRF)

XRF is a non-destructive analytical technique, which uses the interaction of the X-rays with the sample in order to determine its chemical composition. According to instrument configuration and set up, it is able to analyse elements from beryllium (Be) to uranium (U) in concentration ranges from 100 wt.% to sub-ppm levels.

XRF is based on the excitation of the sample with primary X-ray radiation. In the process, the electrons from the inner electron shells are knocked out, while the electrons from the outer shells fill the resultant voids. This fact causes a fluorescence emission characteristic in its energy distribution for a specific element (Figure II. 2).

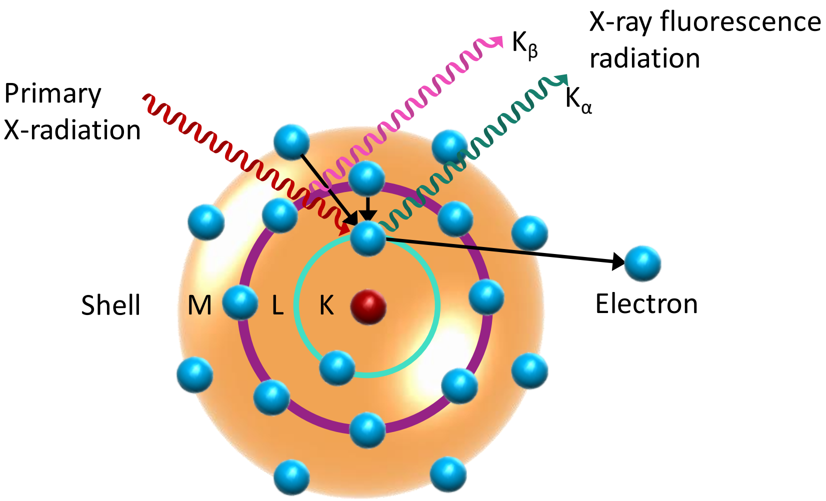


Figure II.2. X-ray fluorescence phenomena

For the fluorescence measurements the sample are dispersed in pellets of boric acid and covered by thin wax film. The analysis are made using an AXIOS PANalaytical spectrometer equipped with Rh tube for elemental analysis.

II.2.3. CHNS analysis

Total elemental analysis of the carbonaceous materials has never been easier task. The CHNS analysis has been used to compare the compositions of the samples. The principle of the CHNS analyser is based on burning the sample at high temperature where dry combustion takes place in the presence of inert gas such as helium and pulsing of oxygen. The sample is flash combusted causing instantaneous oxidization of the material into simple compounds and elements detected with tolerance limit deviation of 0,3wt.%.

The determination of carbon, hydrogen, nitrogen and sulphur percentage was carried out using an elementary analyser TRUSPEC CHNS Micro by Leco. The samples were measured according to American standard, ASTM D 5373, for carbonaceous solids, using 50-90 mg of sample in an aluminium vessel.

II.2.4. Inductively coupled plasma atomic emission spectroscopy (ICP)

Although XRF is an appropriate method to determine the chemical composition of the materials, it is not very sensitive and useful for carbon element detection. On the contrary, ICP allows the determination of this element. In this process all present elements (atoms or ions) are exited in a plasma generated at high temperatures (5000-7000K) and then allowed to return to its fundamental states emitting characteristic wavelengths. The element type is determined by the position of the emission and its concentration by the intensity of the same. The elemental composition and concentration of unknown sample is established by comparing its ICP signal to a verified ICP spectroscopy reference standards. Thus the ICP provides quantitative and qualitative information.

Horin Jobin Yvon ICP spectrometer and HF digestion was used to measure the noble metal contents for all carbon supported catalysts present in this thesis.

II.2.5. Textural Properties by N_2 Adsorption: specific surface area, pore volume and pore size.

The evaluation of the textural properties is considered as an important requirement in catalyst characterization as the reaction pathways and molecular transport are influenced by the pore structure and distribution for the porous materials.

The contact of the solid with N_2 gas at 77 K causes an attraction of the gas molecules with the surface of the solid by van der Waals forces, a process known as physisorption. It is thermodynamically reversible at isothermal conditions, and this process is differenced with the chemisorption by its low interaction energy. The number of physiosorbed molecules will depend on the relative pressure P/P_0 (the ratio of absolute gas pressure to the saturation pressure) of N_2 gas in equilibrium. The amount of gas at a specific part of the surface will depend, on the other hand, on the local surface energetic properties and geometry.

There are different methods of extracting information form the adsorption desorption isotherms. BET method is the one used to determine the total specific surface area whereas the t_{plot} and BJH equation are applied for the quantification of micropores/external surface and mesoporous surface respectively. BET method, named upon the initials of the scientists that postulate it (Brunauer, Emmett and Teller), incorporated the concept of multimolecular layer adsorption to the Langmuir´s isotherm. For BET method, the forces active in the condensation of the gases are responsible also for the binding energy in the multimolecular absorption. The form of the obtained adsorption- desorption isotherms allows us to classify the materials according to their behaviour. The isotherm obtained from the adsorption process can be classified in six types of isotherms (IUPAC classification), according to the pore size and gas sorption. The six types are: microporous (type I), nonporous or macroporous (types II, III and VI) and mesoporous (types IV and V). Porous materials are classified by IUPAC as: microporous ($Ø \leq$ 2nm), mesoporous ($2 < Ø \leq 50$ nm) and macroporous ($Ø > 50$ nm).

The textural properties of the samples were determined in a Micromeritics TRISTAR II equipment. Prior to the measurement, the samples were degassed for 12 hours at different temperatures.

Barrett-Joyner-Halenda (BJH) method was used to determine the pore size distribution. It is based on a cylindrical pore model and pores clear-out by a stepwise reduction of the relative pressure and adsorbate evacuation.

II.2.6. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTG)

TGA is an analytical method where the sample mass is monitored as a function of temperature and/or time while subjected to programmed temperature changes in controlled atmosphere. The mass of the sample changes can be produced via different processes during the heating, such as degradation, sublimation, decomposition, vaporization, adsorption, desorption, oxidation or reduction. A thermobalance, a combination of sensitive analytical balance and electronically programmed furnace, is used in to carry out the measurements. A controlled environment of the sample can include inert or reactive atmosphere (oxygen) either dynamic (flowed through) or static. Additionally, DTG technique provides a comparative analysis between the sample and a reference material under the same atmosphere conditions and temperature. This technique allows the characterization of the heat processes (exo/endo) associated with phase transitions and chemical reactions.

The measurements in this thesis were carried out in TA Instruments Q600 Simultaneous TG/DTA/DSC instrument using nitrogen atmosphere, heating ramp 10º C min^{-1} and temperature up to 1000º C. The real loss of weight and the weight and heat flow derivatives are recorded as a function of time and temperature.

II.2.7. X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a technique based on the photoelectric effect, that allows the analysis of material' surface chemistry. It is able to measure the elemental composition, empirical formula and the chemical/electronic state of the elements within the material.

When the surface of the sample is irradiated with an X-ray beam, the photons are adsorbed completely by the core electron of an atom. If the photon energy is high enough, the electron will be ejected with a kinetic energy (E_k). The binding energy of the core electrons is given by the Einstein relationship (Eq. 3):

$$\boldsymbol{E_k = h\nu - E_k - \Phi} \qquad \text{Eq. 3}$$

where $\mathbf{E_k}$ is the kinetic energy of the photoelectron, *h* is the Planck constant, *v* is the frequency of the exciting radiation, $\mathbf{E_b}$ is the binding energy of the photoelectron with respect to the Fermi level of the sample and **Φ** is the working function induced by the analyzer.

XPS measurements were carried out on a SPECS spectrometer equipped with PHOIBOS 150 MCD analyzer working with fixed pass energy of 40 eV and 0.1 eV resolution for the studied zones. Al Kα radiation (1486.6 eV) was used working on 250W and 12.5 kV voltage. The analytical chamber operates at ultra-high vacuum at around 10^{-10} mbar pressure. Prior the analysis, the samples were pressed into a thin disk. All XPS spectra were recorded at room temperature with binding energy calibration on C*1s* at 284.6 eV with an uncertainty ±0.2. The obtained data were processed using the CasaXPS software. The decomposition into components was performed by fitting using Gaussian-Lorentzian functions with the Shirley subtraction of the background.

II.2.8. Electron Microscopy

Electron microscopy is a technique, which use as lightning source a beam of electrons to obtain high resolution images. There are two types of electron microscopies: transmission (TEM) and scanning (SEM).

II.2.8.1. Transmission Electron Microscopy (TEM)

In this kind of microscopy, the electron beam passes through a thin sample, and its interaction with the components of the sample can be used to observe different features such as crystal structure, supported particles dispersion, size and morphology. The beam strikes with the sample, being a part of the radiation transmitted and focused by the objective lens into an image recorded by charge coupled device (CCD) camera.

The TEM micrographs were obtained with a FEI Talos electron microscope operated at an acceleration voltage of 200 kV, equipped with a Field Emissions filament. Micrographs were taken with a side mounted Ceta 16M camera. The samples were supported on a holey carbon-coated copper grid without using any liquid.

II.2.8.2. Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray (EDX) Spectroscopy

In this case, the electron beam scans the sample surface to create the image. The electrons interact with the sample, generating different X ray signals used to obtain information about the surface topography and composition.

The interaction sample-electron can be divided into two categories: elastic and inelastic. In the elastic interaction, the electron is deflected by the sample' atomic nuclei or by other shell electrons with an analogous energy. The energy lost of this interaction is practically zero, but a modification of the direction is produced and these electrons are known as backscattered electrons (BSE). In the inelastic interaction, on the contrary, an energy lost is observed and its amount depends on the electrons of the samples, their excitation (single or collective) and on the electron binding energy. This results in excitation of sample' electrons, generating secondary electrons (SE), which are used to image or analyse the sample.

As a complementary technique frequently Energy Dispersive X-ray Spectroscopy (EDX) is used and provides information about the chemical composition of the samples using their characteristic X-rays produced after interaction with the electron beam.

SEM micrographs and EDX elemental analysis were performed on Hitachi S4800 SEM-FEG high resolution (5 nm) scanning electron microscope provided with SE and BSE detectors and a Bruker X Flash Detector 4010 EDX analyser with a resolution of 133 eV in the Mn Kα line. Operating conditions were varied for every experiment.

II.2.9. Vibrational Spectroscopies

When a molecule absorbs a photon, three processes can take place: electron movement, vibration of the constituent atoms and molecule rotation. However, these processes occur at different scale time. Vibrational spectroscopy is the common label given to describe measurements involving both Infrared (IR) and Raman spectroscopy (RS). Although, both techniques result from a modification of the vibrational modes of the molecules, only the one that are produced changes in the dipole moment are active in IR, while the vibrations that cause changes in polarizability are Raman active.

II.2.9.1. Infrared Spectroscopy

Infrared spectroscopy is a very sensitive technique that can be used for qualitative and quantitative analysis.

When a sample is subjected to IR radiation, the molecules present in it, can absorb the radiation. The intensity of that absorption will depend of the probability of the transition between ground and excited states. As commented above only the transitions with changes in the dipolar moment will be active in IR, and the intensity of the resulted bands are proportional to the produced alteration.

❖ *In situ* transmission IR spectroscopy

In situ IR spectroscopy makes possible the analysis of the species adsorbed over the surface of the sample at a controlled temperature in the presence of reactants. In the case of IR transmission, spectra are obtained as a result of the direct transmission of an IR beam through the sample. A spectrometer records the transmission, being the intensity calculated using the Lambert-Beer law (Eq. 4).

$$\boldsymbol{T = I / I_0} \qquad \text{Eq. 4}$$

Where **T** is the transmittance, **I** is the intensity reaching the detector in the presence of the sample and **I_0** is the intensity measured by the detector in absence of the sample.

In situ IR measurements of the synthetized samples were performed in a homemade reactor-cell which consist on a stainless-steel cylinder with a toroidal sample holder in its centre, where a sample wafer of 16 mm is placed. The cell is equipped with two CaF_2 terminal windows and two KBr windows which limit the dead volume to 0.12 cm^3 and the optical path below 3 mm. A heating system is incorporated in order to reach the desired temperature, as well as an air-cooling system to protect both ends of the cell. Spectra were collected by a Thermo Nicolet iS50 FT-IR spectrometer equipped with a liquid-nitrogen cooled mercury cadmium telluride (MCT) detector at a resolution of 4 cm^{-1} and an average of 64 scans.

❖ *In situ and Operando Diffuse Reflectance Infrared Spectroscopy (DRIFTS)*

This technique is complementary to *in situ* transmission, being the radiation scattered by a powder sample. That scattering is due to diffuse and specular reflectance. The IR radiation colliding with the sample undergoes absorption, refraction and diffraction before re-emerging. Specular reflectance, which is a mirror-like reflection from the front surfaces of the analysed sample, may distort the diffuse reflectance component of the spectrum, but with a proper preparation of the sample, this problem may be avoided.

In situ and operando DRIFTS measurements were performed in a high-temperature reactor chamber supported on a Praying Mantis (Harricks) DRIFTS optical system using ZnSe windows. Spectra were collected by a Thermo Nicole iS50 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4 cm^{-1} and an average of 64 scans. 50 mg of the finely ground solids were loaded in the catalytic cell and the reaction flow was introduced using a series of AALBORG mass-flow controllers. In such case, the system was heated at 100ºC to avoid water condensation during the reaction process.

For every FTIR experiment, the outlet gas composition was analysed by mass spectrometry in a PFEIFFER mass spectrum Vacuum Prisma Plus controlled by the Quadera® software.

II.2.9.2. Raman Spectroscopy

Raman is based on the inelastic light scattering in a substance, where the incident light transfer energy to molecular vibrations. In general, a monochromatic laser beam illuminated the sample and interacts with its components, originating a scattered light in all directions. Much of this scattered radiation have a similar frequency to incident radiation, being Rayleigh scattering. Just a small fraction, has a different frequency and constitutes Raman scattering. In the case that the frequency of incident radiation is higher the Stokes lines appear in the Raman spectrum, while if that frequency is lower, anti-Stokes lines arises. Scattered radiation is usually measured at right angle to the incident radiation.

Raman spectra of the samples were taken on a dispersive Horiba Jovin Yvon LabRam HR800 Confocal Raman Microscope with a green laser ($\lambda = 532.14$ nm), working at 5 mV power and using a 600 grooves/mm grating. The microscope used a 50x objective with a confocal pinhole of 1000 μm.

II.1.10. pH slurry

Measurements of the isoelectric point provide information on the basicity and/or acidity of the external surface of the materials. The acid/base properties of the materials are of a fundamental aspect for the catalytic process in general, and acquire a greater importance when the process is carried out in liquid phase.

The acidity of the solids was evaluated by measuring the slurry by titration, using a pH electrode (Metrohm) according to the procedure described by Markus et al. 50 mg of the sample were dispersed in 50 mL of distilled water, the suspension was continuously stirred with a magnetic stirrer and the pH was followed over time. The isoelectric point of the sample corresponds to the pH measured when a constant pH value is reached.

II.1.11. Temperature programmed adsorption-desorption of ammonia (TPD-NH_3)

TPD is a useful technique for the characterization of total acidity expressed as number and strength of the acidic groups present on the surface of the sample. The surface acidic properties were measured by ammonia temperature-programmed adsorption-desorption and compared to the results obtained after pH measurements. 100 mg sample was placed in U-shaped quartz reactor and activated at 200 °C in helium flow for 2 h using heating rate of 10 °C/min. Then the sample was cooled to 120 °C in helium flow. At this temperature, 5% NH_3 in He was passed through the sample for 1 h followed by cooling to 100 °C in He flow. TPD was carried out from 100 to 500 °C at a heating rate of

10 °C/min using He as gas vector 35 mL/min. After each TPD measurement, the amount of adsorbed ammonia was determined form the calibration curve obtained varying the ammonia volumes in helium.

II.2. Pyrolysis

Pyrolysis of a residual biomass was used to produce some of the materials described in this thesis and it was carried out on laboratory scale in a horizontal IBERFLUID furnace Model FK 1000, equipped with a continuous horizontal tubular steel reactor of 7.8 cm of internal diameter. The biomass was placed in ceramic vessels of 50 mL volume in the temperature controlled zone in the centre of the reactor. The setting of the pyrolysis atmosphere was done using Bronkhorst mass flow controllers, located on a panel at the reactor inlet. Each reaction gas was controlled with a separate mass flow controller, thus being able to introduce pure atmospheres or a mixture of them, in any composition interval. To minimize clogging problems in the exhaust gas pipe two cold steel traps were placed for the condensation of the bio-oils. A diagram of the pyrolysis equipment is shown in Figure II.2.

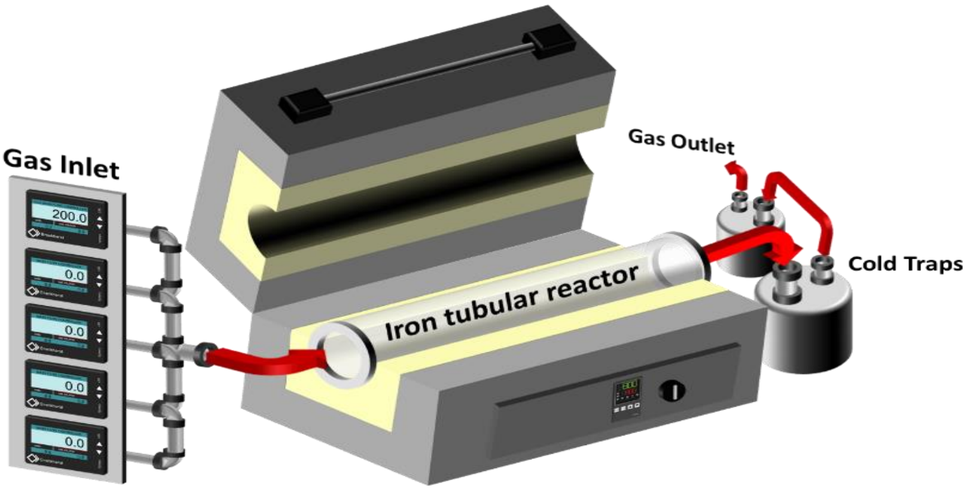


Figure II.2. *representative scheme of the pyrolysis equipment.*

II.3. Catalytic activity measurements

II.3.1. Experimental devise

The reaction studies over carbonaceous based catalysts cab be divided in two groups i) glucose/fructose dehydration and/or isomerization reaction and ii) hydrogenation reaction.

For the firsts group, the experiments were carried out in a glass batch reactor (Shlenck) of 50 mL (**Figure II.3**) at atmospheric pressure with agitation rate of 600 round per minutes (rpm). To maintain the temperature constant both the reactor and thermocouple were emerged in oil bath and heated with an IKA-MAG HS 7 heater.

Figure II.3. *Schlenck reactor used for hexoses dehydration.*

The second group of reactions, the levulinic acid and HMF hydrogenation were carried out in Parr-type pressure reactor, model 4848, coupled with stirrer, heater and pressure controller, Figure II.4. After reactive loading (levulinic acid or HMF) in 10 mL of solvent the desired amount of catalyst is loaded inside the reactor subsequently closed and purged seral times with hydrogen. After, the reactor is brought to the working temperature and once the temperature stable, the hydrogen pressure is increased to the desired value and the stirring rate is set into 400 – 800 rpm range taking this time as a zero reaction time.

Temperature and pressure remained constant in the range of 1 °C and 0.4 bar, respectively.

***Figure II.4**. Parr reactors used for the hydrogenation reaction*

Once the reaction completed, the temperature is reduced, the reactor is depressurized to evacuate hydrogen, and the catalyst is recovered by vacuum filtration, for analysis if necessary. The reaction products were sampled and analysed at the end of the reaction.

II.3.2. Analytical method for products separation and analysis

Both, Gas chromatography coupled with mass spectroscopy GC-MS and High-Performance Liquid Chromatography HPLC were used as separation and analytical techniques to obtain reactive conversion and products distribution.

II.3.2.1. Principe and distinction

HPLC (high performance liquid chromatography) and GC (gas chromatography) are scientific methods used to determine concentration the different molecules within a sample. Both, use the same principle: the sample and the mobile phase pass through a column where the molecules are separated and subsequently quantified and qualified. In general, heavier molecules elute, or flow, more slowly than the lighter ones but the polarity of the column also plays a role in elution time. Although the idea is the same, GC and HPLC have several differences.

- **HPLC vs. GC**

As the name suggests High Performance Liquid Chromatography uses a liquid as sample and mobile phase (single or a mixture of solvents) while the gas chromatography uses a single gas as a carrier. HPLC separations are mostly carried out at lower temperatures (less than 80 ºC) while Gas Chromatography separations are carried out at elevated temperatures. The latter also allows a constant (isothermal) heating or a variable temperature programming. HPLC detection is commonly based on nondestructive detection such as UV, RI (refractive index) or photodiode array detectors, conductivity and laser detection. On the other hand, Gas Chromatography detection is based largely on destructive principles such as a FID, NPD and FPD. Mass spectrometry detectors can also be coupled to both LC and GC methods. On the other hand, GC chromatography separations are mainly carried out on compounds ranging in molecular weights up to a few hundreds. Such compounds are separated based on the differences in their volatilities and must remain stable at high temperatures. However, the compounds separated on HPLC have higher molecular weights ranging from a few hundreds to several millions for large polymers and biomolecules. Such compounds tend to degrade at higher temperature which conditions the temperature of analysis. As for the columns, the GC uses long and thick columns in comparison to that used in HPLC. Gases have less viscosity so the lengthy column, increases the interaction time between the eluting compounds and stationary phase.

II.3.2.2. Mass spectrometry

Mass spectrometry is an analytical tool useful for measuring the **mass-to-charge ratio** (*m/z*) of one or more molecules present in a sample that can be liquid, gas or solid. These measurements are often used to calculate the **exact molecular weight** of the sample components. Typically, the mass spectrometers are used to identify unknown compounds via molecular weight determination, to quantify known compounds and to determine structure and chemical properties of molecules.

The principle of operation of a mass spectrometer is based on the action of an electromagnetic field on a charged particle. The mass spectrometer is used to measure the mass of the ion and to determine its abundance. When a polyatomic molecule is introduced, its ionization usually produces several types of ions of distinct masses. Every mass spectrometer consists of at least three components: Ionization Source, Mass Analyzer and Ion Detection System. The ions produced after sample ionization are separated according to their mass-to-charge ratio in the analyzer and eventually fragmented and analyzed in a second analyzer. The ions detection and abundance measurements occurs with a detector that converts the ions into electrical signals able to be registered by a computer.

II.3.2.3. Used equipment

Liquid chromatography with RID and DAD detector is one of the most used techniques to analyse carbohydrates. The main difficulties in the analysis of carbohydrates arise from their considerable number of isomeric forms and possible configurations. Sometimes the combination of both techniques is necessary to analyze the products of the reaction.

After every catalytic test, either group 1 or group 2, the product distributions where analysed by High Pressure Liquid Chromatography (HPLC) Infinity 1260 infinity, equipped with a Diode array and Refractive index detector (RID). The used columns were Hi-Plex H 300 × 7.7 mm for dehydration and hydrogenation while the Meta Carb column 300 × 7,8mm was used for the isomerization tests and high-resolution separation of hexoses. The standard HPLC configuration parameters used for the analysis of the majority of samples are summarized in Table II.1.

Table II.1. HPLC configuration parameters used in Agilent Infinity 1260.

Column type	**Hi-plex H**	**Meta carb**
Temperature	40 °C	75 °C
Eluent	MiliQ water or 0.01 M H_2SO_4	MiliQ water
Eluent flow	0,2 - 0.6mL/min	0.6 mL/min
Type of detector	RID DAD	RID

The products originated by levulinic and HMF hydrogenation analyzed also by GC-MS using a GC 5780 Agilent series GC System coupled using capillary column (HP-5, 30 m length × 0.32 mm id).

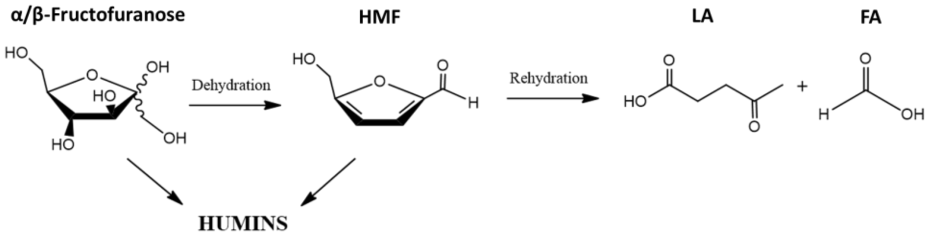
CHAPTER III.FRUCTOSE DEHYDRATION REACTION OVER ACIDIC CARBONACEOUS CATALYSTS.

Summary

This chapter is devoted to the catalytic HMF production from fructose where the quest for greener synthesis and/or suitable surface modification of the catalysts and reaction media are the main objectives. On first-hand some carbonaceous materials (commercial activated carbon AC and carbon nanofibers CNF) are functionalized with available mineral and/or organic acids and the final catalysts are screened in free solvent, monophasic dimethyl sulfoxide (DMSO) solvent or methylisobutyl ketone/water (MIBK/H_2O) biphasic system. For the both series of catalysts, functionalized AC and CNF, the influence of the textural-structural properties and reaction parameters on HMF production are discussed. Partial conclusions are included, and special attention has been paid to the possible mechanism by which the functionalized carbon solid catalysts improved fructose dehydration activity.

III.1. Introduction

Sugars derived from lignocellulose with annual production of $1*10^{11}$ tons/year [1-4], are the most important renewable source up to date to produce fuels and chemicals able to replace the fossil fuel fuels and industrial commodities. The hydrolysis and dehydration of sugars produces, among others, the polyvalent 5-hydroximethylfurfural (HMF) molecule that carries two different functionalities, aldehyde and alcoholic, which together with the furan ring allows numerous chemical transformations to products of high added value [5,6]. Although cellulose conversion to HMF highly desirable and low-cost process its insolubility in water or other solvents reduces the HMF yields pushing the technology to two-step process; hydrolysis to glucose and glucose transformation to HMF. Glucose is most available sugars monomer in nature and can be transformed to HMF by tandem of steps requiring high energy barrier and distinct active sites. One of the steps is glucose isomerization to fructose and subsequent rapid dehydration of the latter to HMF. That is why, fructose is frequently chosen as initial substrate to produce HMF by simple dehydration under acidic conditions at low temperatures. Many considerable efforts have been focused on the production of HMF from fructose with high yields. However, commercial viability of this approach faces one main challenge, minimization of the undesired products (humins, levulinic and formic acid) formation, accompanied by the high cost of products separation.



Scheme III.1. Fructose dehydration reaction.

The low reaction rate in aqueous media forces the use of organic solvents and increase the price of the processes which now requires a separation procedure high energy and time-consuming operation. The dehydration of fructose is usually catalyzed by Brønsted or Lewis's acids or even ionic liquids with acidic functions that can be used as co-catalysts and solvents [7]. The post-treatment of homogeneous catalysts, especially in case of acids, could cause important corrosion problems [8]. On the contrary, the employment of heterogeneous catalysts provides important advantages, the ease of separation and recovery, regeneration and reutilization and better scaling up opportunity [9].

Many functionalized solid catalysts have been reported for this reaction: zeolites, simple or functionalized metal oxides, polymer ion exchange resins, mesoporous silica and metals organic frameworks containing sulfur (S) and (SO_3H) groups [10–14]. However, most of them cannot maintain their acidity, especially in water, without deactivation of the functional groups. Besides, the uncontrolled strength and acidity type decreases the selectivity to HMF, either by rehydration of the produced HMF to levulinic and formic acids or to a cross polymerization condensation to humins (Scheme III.1).

That is why in this chapter, available commercial activated carbon and cabon nanofibers materials are functionalized by different agents creating different functional groups with varied acid properties. Different acidic sites like SO_3H or nitrogen containing groups are generated and tested in fructose transformation to HMF under different reaction media. Several reaction parameters are optimized such as, time, temperature, and substrate/catalyst ratio. The deactivation of the catalyst is also verified for each series.

Our interest goes **first** to the investigation of the viability of the sulfonated AC catalysts in solvent free fructose dehydration reaction. The same catalysts are later investigated and compared to the performance of other catalyst series in presence of DMSO. **Finally**, functionalized CNF catalytic systems are tested in MIBK/H_2O biphasic system media.

III.2. Effect of sulphonating agent on the catalytic behavior of activated carbons in fructose dehydration reaction in solvent free or DMSO media

Previous studies determined that sulphonated/sulfated catalysts increase notably the reaction rate for fructose dehydration [15–21]. However, some of them are expensive and corrosive. It has been demonstrated that sulphonated groups oxygen' bonded to the surface can increase the intrinsic hydrophilicity of the materials and potentiate the progressive absorption of water and long chain products leading to instability and deactivation [22]. Among all possible catalyst, carbon materials stood out due to their hydrophobic surface, high chemical stability, homogeneous porosity and presence of multiple acid sites [23,24]. What is more, carbon materials offer the possibility to change their properties by means of relatively well-controlled functionalization [25,26]. The functionalization, covalent or not, allows surface properties modification and introduction of catalytically active sites. Covalent functionalization or grafting can be achieved via C−S or C−C bonds introduction [27]. Sulphonation with benzenesulphonic acids via aryl diazonim salts reduction method presents several advantages, including the use of non-oxidizing mild conditions, low dosage of sulphonic precursor and structure/textural properties preservation of the parent carbons [28,29]. On the contrary the introduction of sulphonic groups via treatments with sulfuric and/or chlorosulphonic acid [17-18,30] influences significantly the parent activated carbons. Indeed, *in situ* sulphonated hydrothermal carbons and functionalized graphene oxide (GO) and carbon nanotubes (CNTs) showed outstanding HMF production [20,31-32]. In addition, activated carbons (ACs) and ordered mesoporous carbons (OMCs) with high surface area, narrow pore size distribution and important pore volume allow easier functionalization to obtain high functional groups density and good reactive accessibility to all active sites [33].

That is why, our particular interest goes to a novel acid catalysts design based on active commercial carbon modified chemically by different sulphonating agents. Therefore, this part of the chapter proposes a study of the effect of different sulphonating agents on materials physicochemical and catalytic properties. By different treatments a variety of active sites will be generated and screened in the fructose dehydration reaction in two different environments: solvent free and in presence of dimethyl sulphoxide (DMSO) as reaction media.

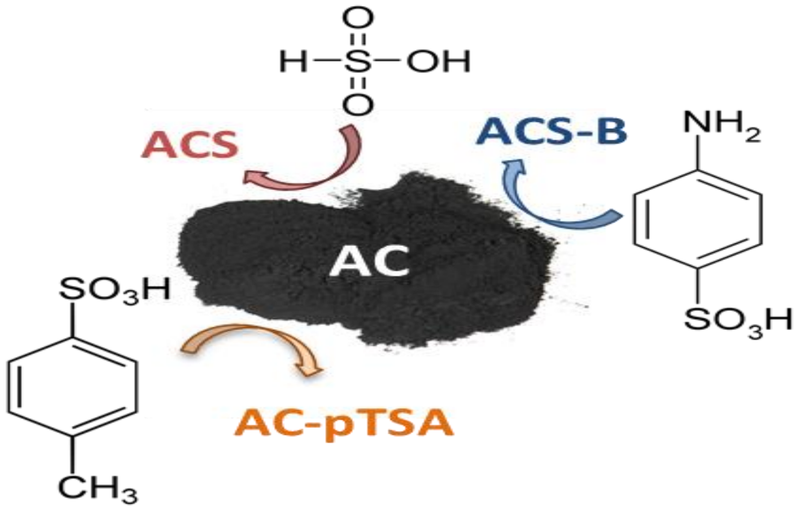
III.2.1. Experimental

Catalysts preparation

Sulfuric acid functionalized AC is obtained after treatment of a commercial activated carbon (1g) with concentrated sulfuric acid solution (20 ml) under reflux at 150 °C for 6 hours. The resulting solid, labelled ACS, is washed several times with distilled water and dried overnight at 110°C.

For the covalent functionalization with 4-benzendiazoniumsulphonate (4-BDS), sulfanilic acid (2.5 g) is firstly dispersed in 150 ml HCl solution (1M) and kept in ice bath at 0 - 4 °C. Then the diazotation is started by drop-by-drop addition of 1M $NaNO_2$ until transparency of the final solution. After 1 hour stirring, the precipitate, 4-BDS, is filtered and washed abundantly with distilled water. Finally, 4-BDS and commercial AC (1 g) are mixed in 150 ml HCl solution (0.1M) for 3 hours under continuous stirring. The resulting sulphonated carbon (ACS-B) is washed several times with distilled water and dried in vacuum at 110 °C for 24 hours.

Finally, for *p*-toluenesulphonic acid (pTSA) functionalized AC sample, the carbon powder (1g) is immersed in 15 ml pTSA solution 0.5 M for 24 hours. After this, the water is evaporated at 80 °C under reduced pressure (~150 mbar) in a rotary evaporator. The final material is dried at 110 °C for 24 hours and named AC-PTSA. All samples are represented schematically in Scheme III.2.



Scheme III.2. Different sulfonated agents incorporated in AC.

Catalytic tests

The dehydration reaction is performed with and without solvent. The solvent free process is carried out in a batch reactor purged with nitrogen. The mixture of catalyst and fructose (20 mg+180 mg) is homogenized in ultrasound for 5 min and then reacted at the desired temperature and time under agitation of 600 rpm. The products are extracted in 5 ml Milli-Q grade water, after 30 min of contact. Then, the solution is microfiltered and analyzed by HPLC using a Hi-Plex H column (300 × 7.7 mm) at 40 °C, a refractive index (RI) detector (Varian 360-LC) and 0.01M H_2SO_4 as mobile phase. The catalytic activity results are expressed in terms of fructose conversion, HMF yield and products selectivity as defined below. All insoluble (non-analyzed) products in the conditions of extraction or reaction are considered as humins, *i.e.* they correspond to the C balance loss detected by the fraction distribution calculations. The quantification of the products is made as follows:

$$\mathbf{Conversion}\ (\%) = \frac{[\mathrm{fructose}]_\mathrm{i} - [\mathrm{fructose}]_\mathrm{f}}{[\mathrm{fructose}]_\mathrm{i}} \times 100$$

$$\boldsymbol{HMF\ Selectivity}\ (\%) = \frac{[HMF]_f}{[analyzed\ products\ by\ HPLC]} \times 100$$

$$\boldsymbol{HMF\ Yield}\ (\%) = \frac{[\mathrm{HMF}]_\mathrm{f}}{[\mathrm{fructose}]_\mathrm{i}} \times 100$$

$$\boldsymbol{Humins}\ (\%) = \left[1 - \frac{\text{Final Carbon moles}}{\text{Initial Carbon moles}}\right] \times 100$$

where *i* stands for initial and *f* for final

For the reaction in DMSO media, 5 ml of solvent is added to the catalyst and reactant mixture (20 mg +180 mg) in a 50 ml Schlenk reactor equipped with a Young valve and containing a magnetic stirrer. The reaction is carried out at desired time and temperature under constant stirring rate of 600 rpm. The obtained products are analyzed following the procedure described above.

Recycling

After each reaction cycle, the catalyst is recovered by filtration, washed with ethanol and dried at 110°C overnight before the next run. The reactive/catalyst ratio is maintained constant in every run, according to the recovered catalyst mass.

III.2.2. Catalyst’s characterization

Raman spectroscopy is widely used for determining the existing defects in carbon based materials [34]. All samples display two important bands at around 1340 $\mathrm{cm^{-1}}$ and 1600 $\mathrm{cm^{-1}}$, corresponding to the well-known D and G band, respectively (Figure III.2.1). The former is associated to sp^3 hybridized carbon in amorphous structural defects and the later, the G band, is the fingerprint of the graphitic sp^2 hybridized carbon. The relation of bands intensities (I_D/I_G) can serve as an empirical estimation of the disorder in the carbonaceous materials induced by the functionalization process (Table III.2.1). A quasi-similar I_D/I_G ratio is obtained for the AC samples functionalized with sulfuric and sulfanilic acids, indicating that the functionalization with -SO_3H groups does not affect carbon ordering in the commercial sample. Nevertheless, a slight deviation of the G band for the ACS-B sample is observed and can be originated by a change in the local electronic density produced by the introduction of bulky 4-BDS functional groups in vicinity to the graphite sheets.

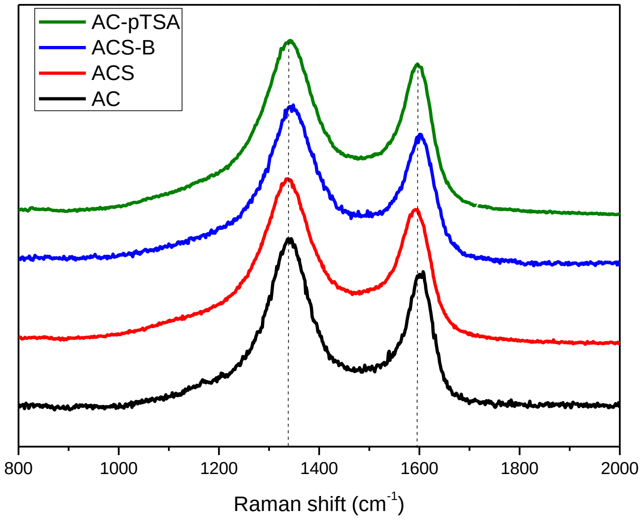


Figure III.2.1. *Raman spectra for AC and sulphonated carbon catalysts.*

On the other hand, the AC-pTSA sample present higher (I_D/I_G) ratio indicating the introduction of some disorder by *p*-toluenesulphonic acid functionalization.

Table III.2.1. FWHM value of the 002 diffraction, average crystallite size and I(D)/I(G) ratio.

Catalyst	FWHM (002) (º2θ)	Crystallite size (Å)	I(D)/I(G)
AC	6.47	14	1.20
ACS	6.10	14	1.21
ACS-B	5.78	13	1.19
AC-pTSA	9.12	9	1.30

All carbon based materials present similar X-ray diffraction patterns to the initial commercial activated carbon, indicating that the functionalization does not affect the crystalline structure (Figure III.2.2). The patterns present two clear wide diffractions in the 20-25 and 40-45 ° 2θ range associated to (100) and (002) carbon diffractions, respectively. The third typical diffraction around 80º 2θ due to carbon (110) is hardly observed but present for all samples. The (100) and (002) diffractions give us the information about the nature of carbon materials (turbostratic state) and amorphous structure associated to the random order of all carbon sheets. In the diffraction pattern some sharp diffractions can be also found and attributed to the presence of mineral SiO_2 phases, quartz and cristobalite [35].

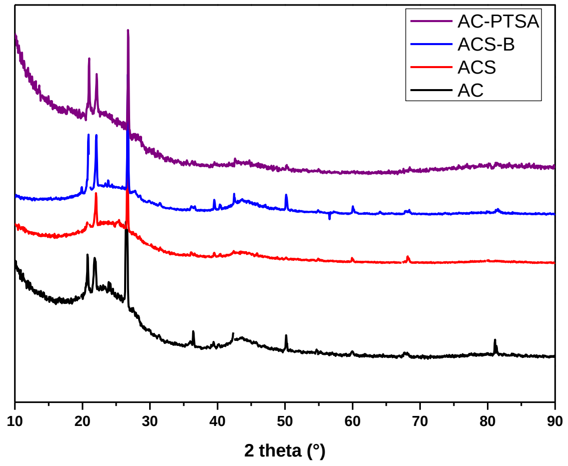


Figure III.2.2. *XRD pattern of the prepared samples.*

In general, the functionalized samples showed lower intensity diffractions suggesting collapse of the pore structure due most probably to some surface modifications upon chemical and thermal treatments [36]. The crystallite size of the commercial AC and the full width at half maximum (FWHM) value of the (002) plane are calculated as 14 and 6.47° 2θ respectively. The FWHM value change reflects the modification of the particle size and carbon sheets order behavior, higher the value lower the size and higher the disorder provoked by the presence of defects. The ACS and ACS-B samples show similar FWHM values to that of activated carbon meaning that the turbostratic state of carbon remains unchanged, as deduced also by the I(D)/I(G) ratios reported from Raman analysis. In contrast, the FWHM value raises for AC-pTSA catalyst suggesting higher amorphization of the structure after *p*-TSA functionalization along with the presence of unorganized polycyclic aromatic carbons.

N_2 adsorption/desorption isotherms of all samples are presented in Figure III.2.3. According to IUPAC classification all samples present isotherms of type IV-H4 with well-defined hysteresis loop typical for mesoporous materials. Moreover, the isotherms exhibit an inclined slope at low relative pressures indicating also the presence of micropores.

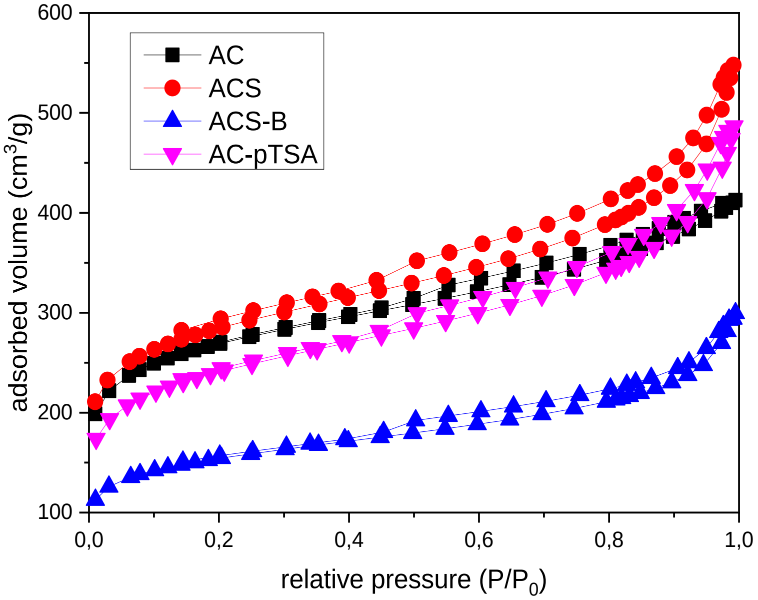


Figure III.2.3. *Nitrogen adsorption–desorption isotherms and pores distribution of AC and sulphonated carbon catalysts.*

The quantitative analysis of N_2 adsorption–desorption isotherms are summarized in Table III.2.2, evidencing several effects induced by the different sulphonation treatments. In general, the active carbon pore size increases after the functionalization treatments, being the increase not related with the variations of pore volume and overall specific surface. The treatment with sulfuric acid (ACS sample) increases the pore volume and BET surface by increasing the mesoporous surface proportion. It is logical to think that small molecules can easily penetrate and modify the pore structure of the starting AC. On the contrary, the functionalization with bulky 4-BDS (ACS-B) and *p*-TSA (AC-pTSA) provokes 40% and 10% loss of specific surface, respectively, with pore sizes near three times higher the initially available. Considering the treatment method and size of introduced functional groups one may expect that sulfanilic acid and *p*-TSA functionalization introduces voluminous groups such as $-SO_3H-C_6H_4$ and $-SO_3H-CH_3-C_6H_4$ whereas the ACS would present only small size $-SO_3H$ groups with different steric hindrance effects on the porous surface. Comparing now ACS-B and AC-pTSA samples, it is evident that the latter presents higher pore volume and external surface. This indicates that *p*-TSA occupies the internal surface, enlarges the pores and blocks partially some micropores (indicated by the drop in the value of total adsorption of nitrogen at low partial pressures, Figure III.2.3). However, the use of 4-BDS as functionalization agent reduces the external surface blocking not only the micropores (see Figure. III.2.3) but also the mesopores of lower size.

Table III.2.2. Textural properties of the studied samples

Catalyst	BET Surface Area (m^2/g)	BJH pore volume (cm^3/g)	Pore diameter (nm)	Mesoporous surface (m^2/g)	External Surface (m^2/g)
AC	928	0.368	4.6	319	414
ACS	980	0.577	6.2	370	454
ACS-B	532	0.320	6.2	222	266
AC-pTSA	834	0.548	6.2	377	451

The samples composition (N and S wt.%) are estimated by combining EDX and elemental analysis (Table III.2.3). The SEM-EDX analysis of AC sample (Figure III.2.4) evidences low oxidation degree along with low sulfur content and SiO_2 presence in good agreement with the XRD patterns.

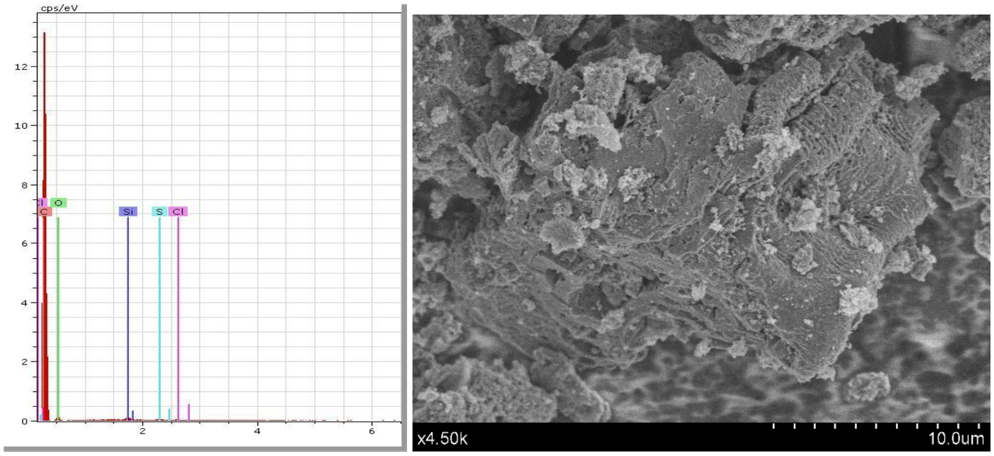


Figure III.2.4. *Representative SEM image and EDX spectrum of AC based solid catalyst.*

All carbon samples present irregular particle shapes, as shown in the representative SEM image in Figure.III.2.4. AC elemental analysis ratifies low sulfur and oxygen contents revealing at the same time high C/H ratio and low nitrogen content. The latter indicates the presence of well-formed carbon aromatic sheets with oxidized carbon ends (typical for an activated carbon) with some heteroatoms such as nitrogen and sulfur.

Table III.2.3. Elemental analysis and measured pH of the studied samples

Catalyst	O/C	C/H	S (wt.%)	N (wt.%)*	pH
AC	0.13	142.8	0.18	0.21	6.62
ACS	0.21	105.4	0.70	0.19	3.85
ACS-B	0.61	71.2	1.24	0.53	3.70
AC-pTSA	0.20	27.7	1.24	0.08	3.36

*calculated from elemental analysis.

The sulphonation of the samples aimed to introduce more oxygen and sulfur and it was successfully achieved for all functionalized samples, as demonstrated by the lower C/H ratio and higher S content. The surface XPS analysis also confirms those changes (Table III.2.4).

Table III.2.4. Atomic contents (C, O and S) of the studied catalysts.

Sample	C, %at	O, %at	S, %at
AC	93,2	5,6	1,2
ACS	82,6	13,6	3,8
ACS-B	81,9	13,4	4,7
AC-pTSA	65,7	22,9	11,4

The XPS survey spectra (Figure III.2.5) show principally the presence of C, O and S with some Si and Na impurities issued from activated carbon mineral component (observed in XRD profiles and

EDX analysis). The superficial S content increases from AC to AC-pTSA, decreasing likewise the C content on the surface. The O content appears strictly related to the sulfur content resulting logical when considering the introduction of $-SO_3R$ groups (R= H, O, aryl).

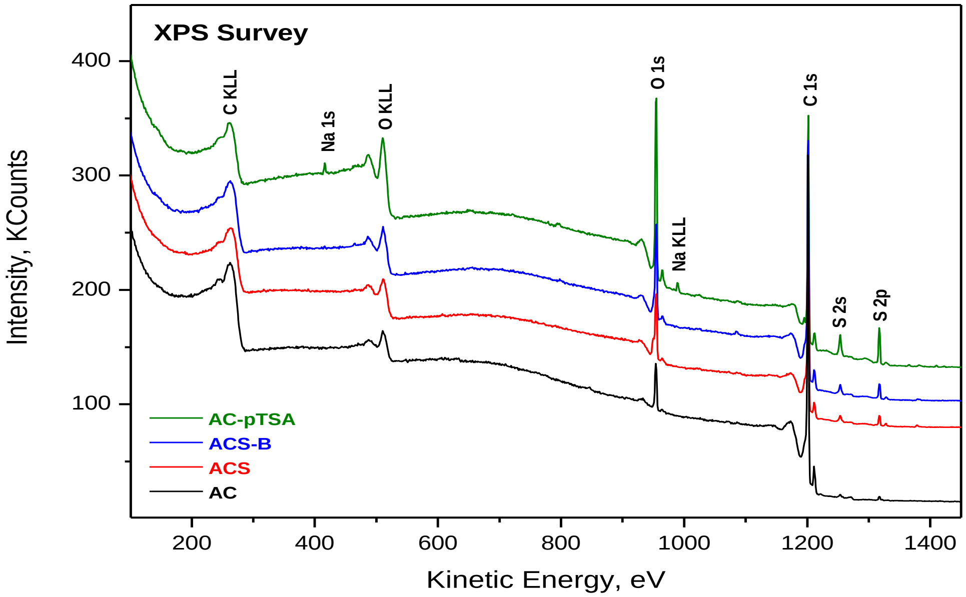


Figure III.2.5. *XPS survey spectra of studied catalysts.*

The C*1s* spectra (Figure III.2.6) can be resolved in 5 contributions corresponding to graphitic carbon-carbon bonds (284.5 eV), three C-O bonds (single bounded phenols 285.7 eV, double bonded ketone or quinone C=O 286.8 eV and C-O in ester groups at 288.5 eV) and C π–π^* transition loss peak/plasmon contribution at 291 eV [37].

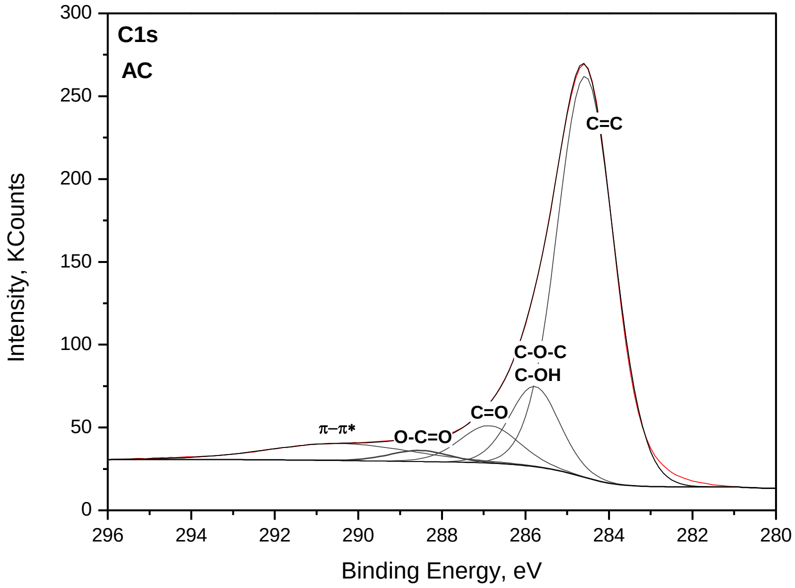


Figure III.2.6. *XPS C1s region of AC sample.*

The O2*p* contributions (Figure III.2.7) are related to that of activated carbon with two or three resolved peaks corresponding to carbonyl and carboxyl C=O (531.6 eV), oxygen in epoxy C-O and hydroxyl groups (532.4 eV) and O-H (carboxyl, 533.5 eV) respectively. The latter appears exclusively in ACS and ACS-B sample. The C-OH/C=O ratio varies within the series indicating some redistribution of oxygen content upon functionalization.

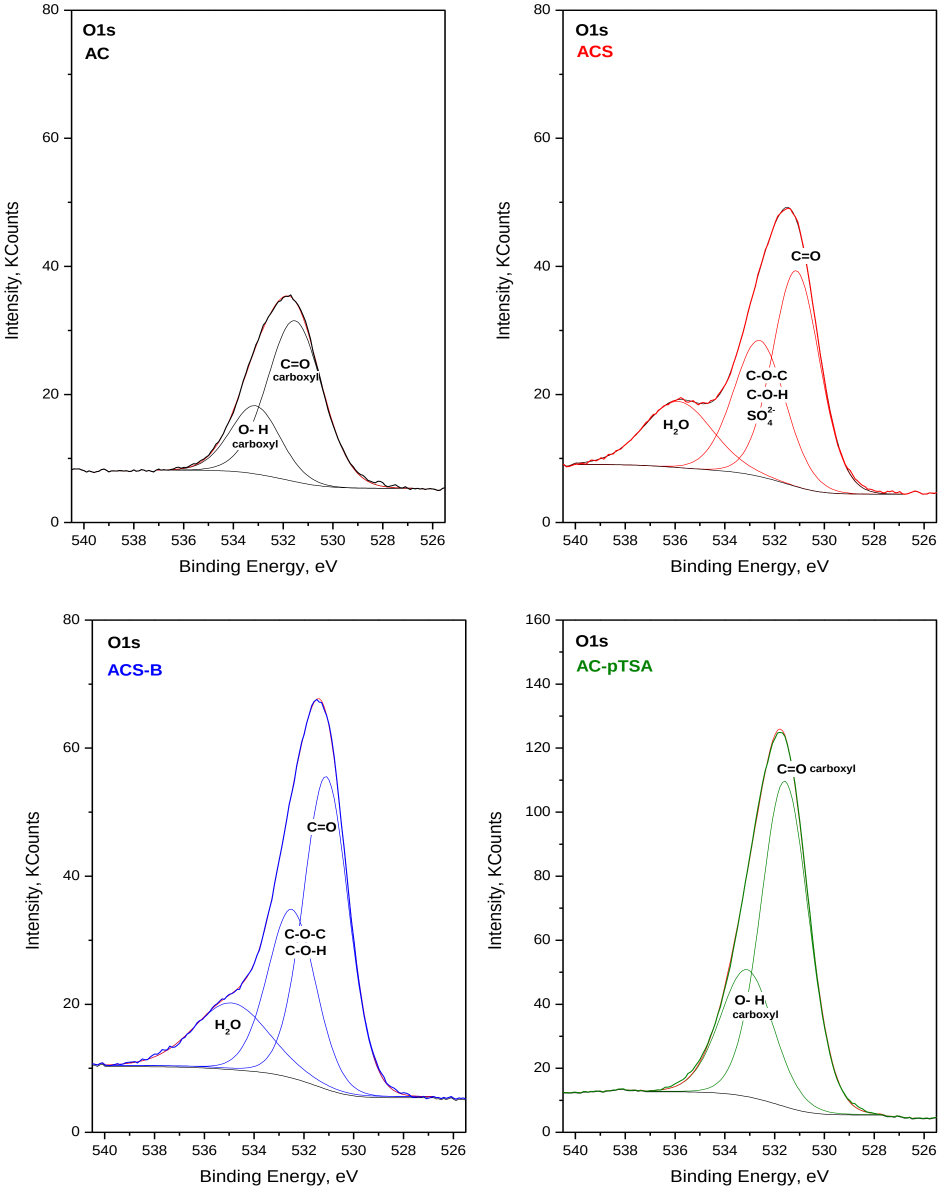


Figure III.2.7. *XPS O1s region of all studied samples.*

The sulfur component can be also separated in two different participations, one at binding energies superior to 169 eV and the other between 168-168.8 eV (Figure III.2.8). The former is attributed to the $H/R\text{-}SO_4$ and the latter to $H/R_2\text{-}SO_3$ groups [38]. An additional sulfur component is observed for the activated carbon situated at around 164 eV and corresponds to thiophen type C-S bond.

One can conclude that the total and superficial sulfur content increased in AC>ACS>ACS-B>AC-pTSA sequence being the functional groups a mixture of sulfate and sulphonate groups.

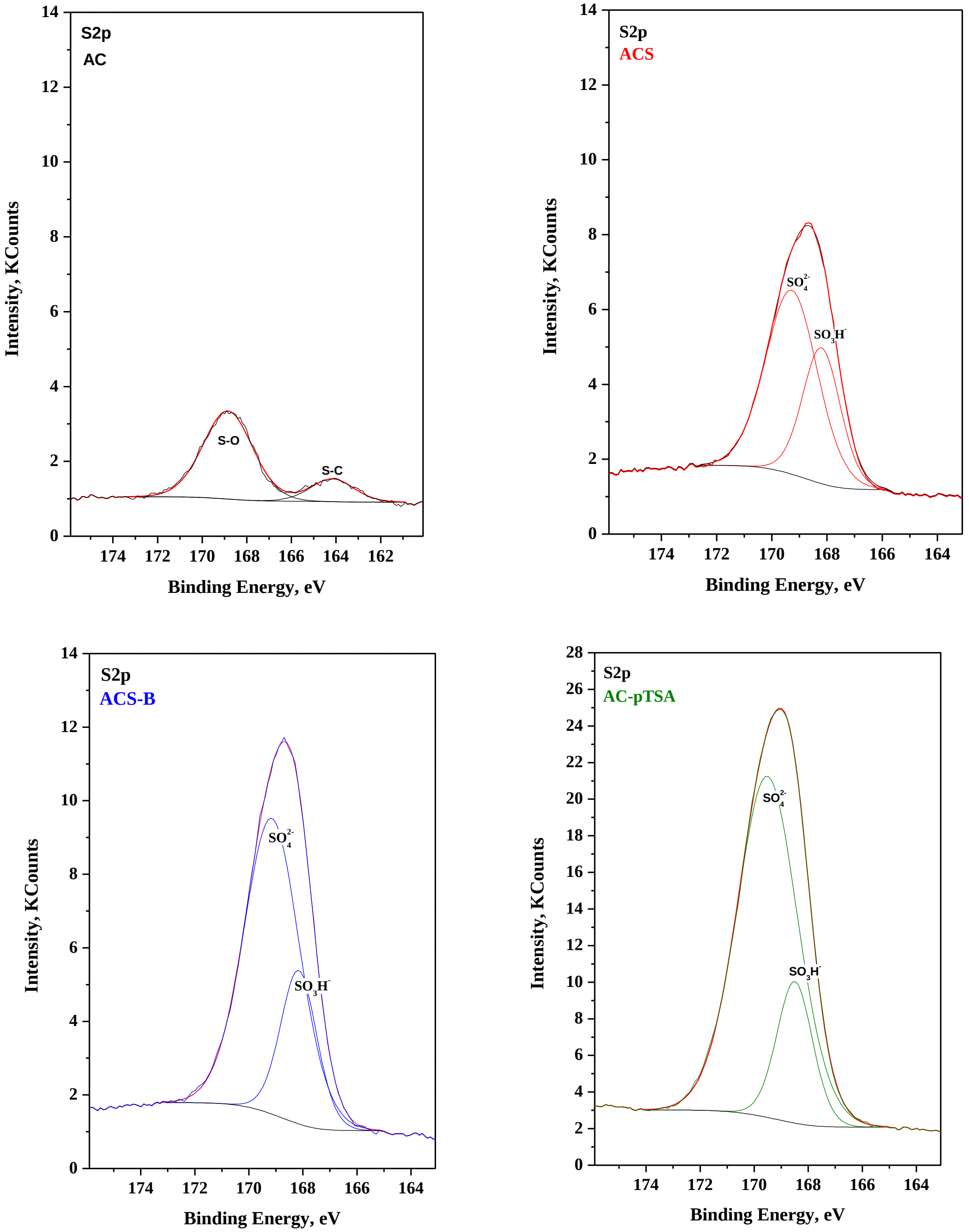


Figure III.2.8. *S2p XPS spectra of the prepared samples.*

The presence of oxygen and sulfur containing superficial groups increases the acidity of the samples, reflected in a decrease of the pH equilibrium values for all sulphonated carbon when suspended in water (Table III.2.3). The Brønsted acidity is introduced by the presence of $–SO_3H$ groups. It seems that the use of sulfuric acid result in low sulfur content since the hydrolyzed sulfuric acid show no significant interaction with the activated carbon surface saturated with hydroxyl and carboxylic groups. Nevertheless, some $-SO_3H$ functional groups covalently bonded to sp^2 hybridized polycyclic carbon network are present as confirmed by XPS. Sulphonation with p-TSA and 4-BDS are far more efficient giving higher amount of sulfur covalently bonded to the surface. ACS-B sample is the most oxidized one showing the highest O/C ratio together with higher nitrogen percentage suggesting a successful grafting of 4-BDS on carbon external surface and the presence of its diazoic function.

The thermal stability profiles of sulphonated carbon samples are investigated by using thermo-gravimetric analysis (TGA). The changes of the sample weight during the heating process are compared in Figure III.2.9. All sulphonated carbons are thermally stable in carbohydrates dehydration temperature window (120-180ºC). The sulphonated carbons are found to be more hydrophilic than the initial AC with distinct physisorbed water loss (20-130 ºC range) especially important for the ACS and ACS-B samples for which an increase of the OH contribution in the O2p XPS spectra is also observed. The sulphonated catalysts present an additional apparent weight loss in the 250–350 °C temperature range, assigned to the decomposition of carboxylic and SO_3H functional groups, also observed by Shu et al [39]. The significant weight loss for each sample at temperature above 500 °C is attributed to a gradual decomposition of the carbon component (O-H, C-O and C-C bond breaking in the activated carbon skeleton) [40]. All samples present mineral component around 10% related to the presence of SiO_2. Within the series the AC, ACS and ACS-

B samples showed the same temperature of C skeleton decomposition while the presence of *p*-TSA promotes C combustion. Also, the presence of more defect for this sample, as observed by Raman, can possibly accelerate its combustion.

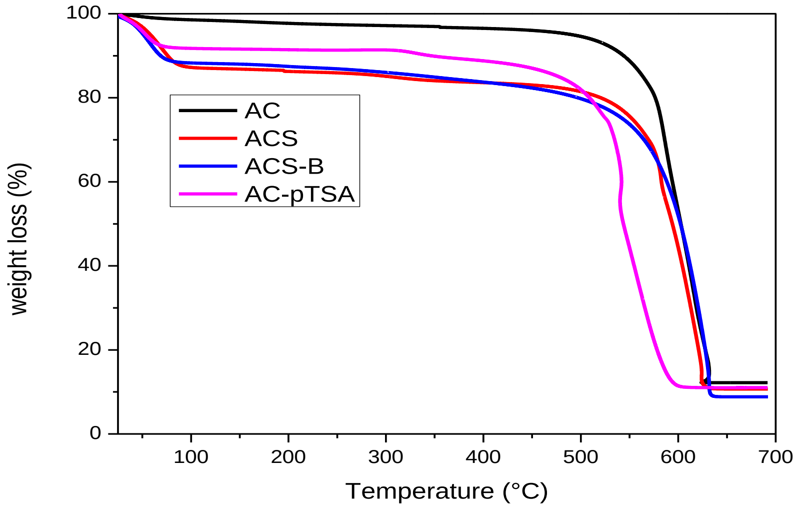


Figure III.2.9. *TGA analysis of AC and sulphonated carbon catalysts.*

III.1.4. Fructose dehydration reaction activity

III.1.4.1. Solvent free dehydration

HMF production from fructose is a simple reaction where fructose loses three molecules of water to produce HMF. Nerveless, several byproducts could be formed such as glucose (Glu, produced by isomerization of the initial fructose), levulinic and formic acid (Lev+for) produced by rehydration of the formed HMF and humins produced either by self-polymerization of hexoses tautomers or by HMF condensation. Their distribution depends on the used conditions, such as atmosphere, temperature, concentration, reaction duration and solvent nature.

Initially, the catalytic performance of all samples is evaluated in absence of solvent with the aim to produce HMF by a green chemistry process, that should avoid solvent extraction step. The reaction is carried at 120 °C for 4 hours. The liquid products selectivity, fructose conversion, HMF and humins yields are presented in the Figure III.2.10.

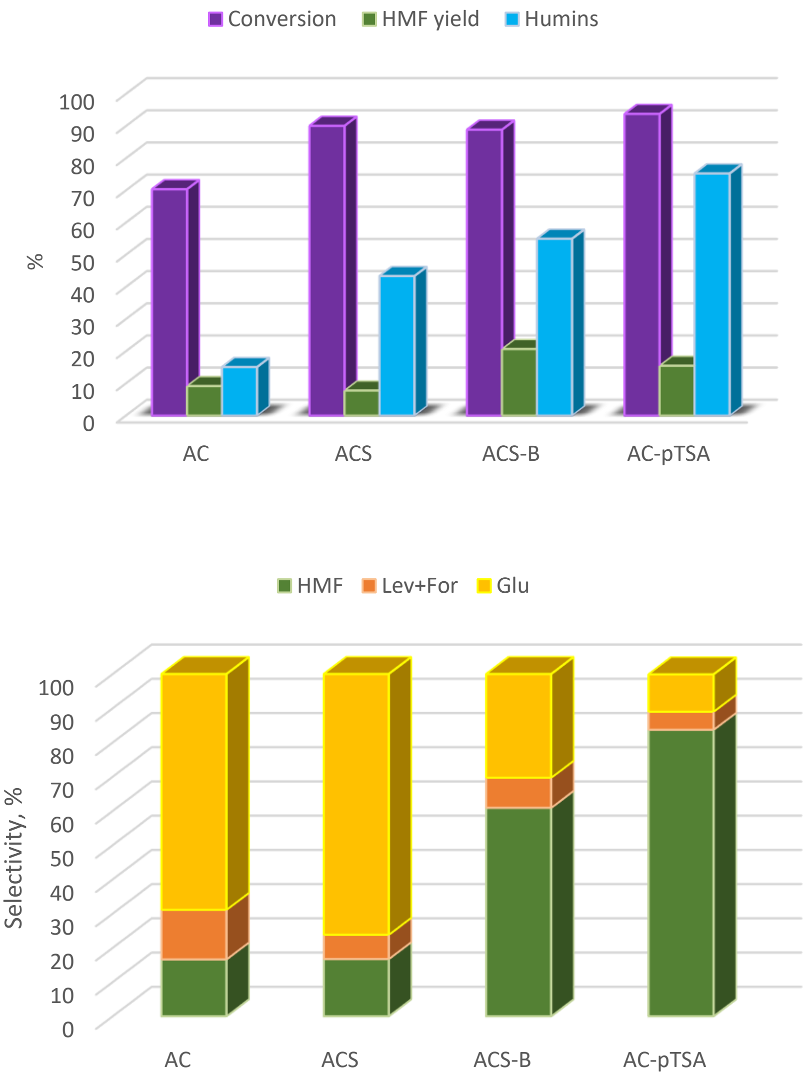


Figure III.2.10. *Solvent free fructose dehydration over sulphonated carbon catalysts ($m_{fructose}$=180 mg, m_{cata}= 20 mg, temperature= 120°C, time=4h). Glu stands for Glucose and Lev+for for levulinic and formic acids.*

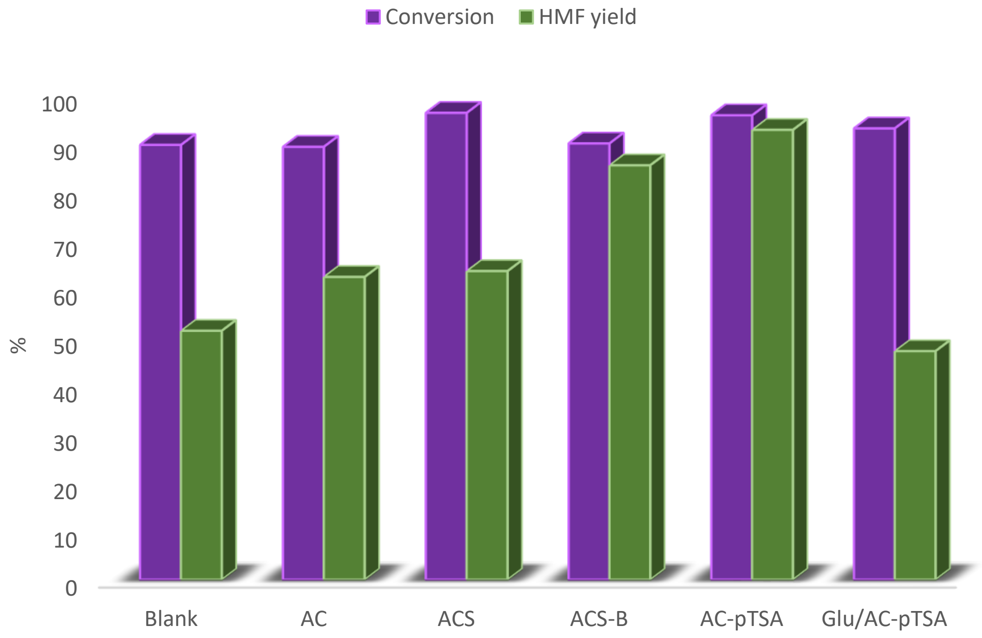
After sulphonation, fructose conversion increases from 70 to 90% but showing low HMF yield and important humins formation. The analyzed products are glucose (Glu), HMF, levulinic and formic acid (lev+for). HMF and humins production increases gradually within the series, with ACS-B catalyst giving the best HMF yield. While for AC and ACS the main product is glucose, for ACS-B and AC-pTSA the HMF takes the advantage. In general, the dehydration process in solvent free conditions prevents HMF rehydration to levulinic acid and formic acids (less than 15% of selectivity). Although difficult to occur during the reaction in absence of water the HMF rehydration could appear during the products extraction step. Fructose is converted to glucose via reversible isomerization through Lobryede Bruynevan Ekenstein (LBE) transformation encouraged by the centers generated on AC surface by the nitrogen functionalities that act potentially as Lewis active sites. The humins production, is related clearly to the presence of aldehyde functions and their participation in self or cross polymerization reactions. Indeed, the formation of humins from glucose is much more faster than from fructose [41]. The presence of Brønsted acid sites increases, in general, the total number of sites and facilitates fructose dehydration but also raises the possibility to form humins. Humins formation can be originated on strong Brønsted acid sites helped by the fructose tautomer adsorption capacity and affinity to mesoporous carbonaceous materials. What is more, the humins production seems to depend not only on the type of active sites but also on the available surface. Higher the surface and pore volume, higher the humins production. It might be concluded that higher pores volume and mesoporous surface enable hexoses and/or HMF oligomerization. Furthermore, the high selectivity to HMF followed by high humins formation in functionalized AC catalysts suggests that the humins are generated via HMF condensation and not via fructose polymerization. On the other hand, the humins appearance at short time and low temperature in solvent free conditions (where the solid-solid interactions are important with increased reactive collision probability) contributes significantly to the observed carbon loss. So, the reaction must be controlled by a presence of solvent capable to extract 5-HMF in the moment of its production, in order to promote HMF stability and to suppress HMF/hexoses condensation/polymerization.

III.1.3.2. Catalytic dehydration in DMSO

Dimethyl sulphoxide (DMSO) is an aprotic organic solvent that attends multiple role during fructose conversion process. It is presence prevents formic and levulinic acid formation and suppress humins formation, directing the reaction to higher HMF yield. DMSO by itself, can catalyze the fructose transformation with relatively high conversion (90%) and moderate 5-HMF yields (57%) (Figure III.2.11, blank test). DMSO is able to stabilize the carbocation intermediate resulting after first water molecule removal from β-D-fructofuranose to form a [carbocation-DMSO] complex. This complex is immediately converted to other intermediates where the second and third water molecules are removed to produce 5-HMF [42]. Theoretical studies proposed as catalytically active sites [$DMSOH^+$] homogeneous species [43].

Similar to the solvent-free dehydration the observed high fructose conversion for all materials seems to be a consequence of materials textural properties (mesoporosity in particular), while the differences in 5-HMF selectivity and yield can be related to the different distribution of active sites type and force (Figure III.2.11). The introduction of sulphonic groups increases both, pores size and specific area and reflects in high fructose conversion for all functionalized catalysts (in comparison to AC). Nevertheless, the minor effect on the 5-HMF selectivity and yield observed for ACS (similar to that of AC) in comparison to all samples, suggests that those activity parameters are controlled by the acid sites abundance and strength. The introduction of $–C_4H_5$-

SO_3H groups in the ACS-B sample alters insignificantly fructose conversion but improves meaningfully the HMF production due to the higher sulfur content and acidity of that catalyst. And this effect is even more significant for AC-pTSA sample where a maximum yield of 92.8 % is achieved versus 62% for the AC. The increase of HMF selectivity for the last two samples diminishes the secondary reactions being glucose, humins, levulinic and formic acids merely present (Figure III.2.11). The appearance of small fraction of gluconic acid is also detected due to the presence of oxygen during the reaction and possible glucose oxidation, formed upon fructose isomerization.



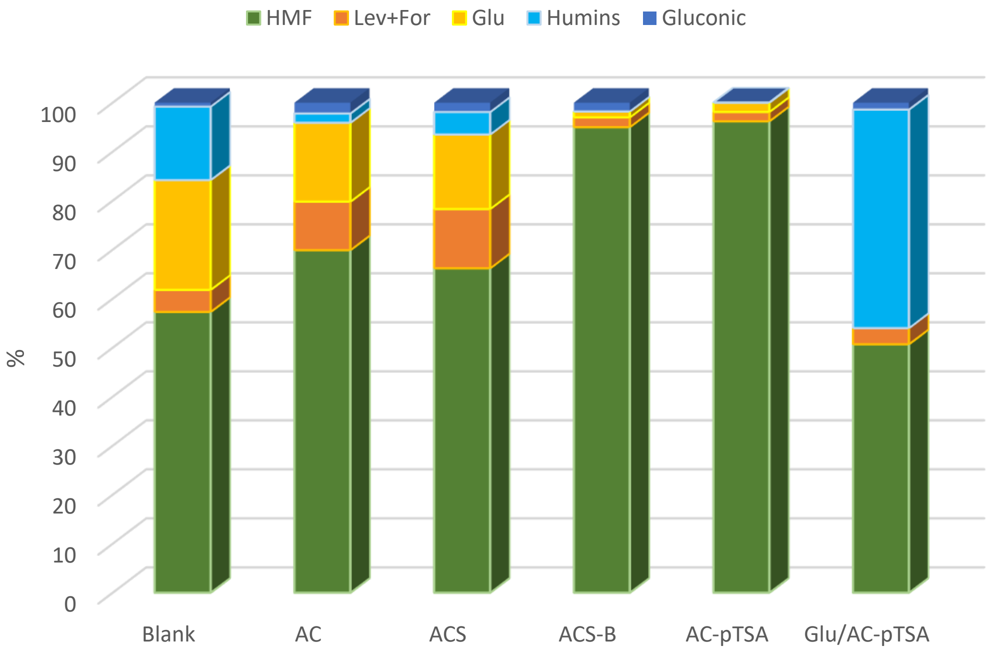


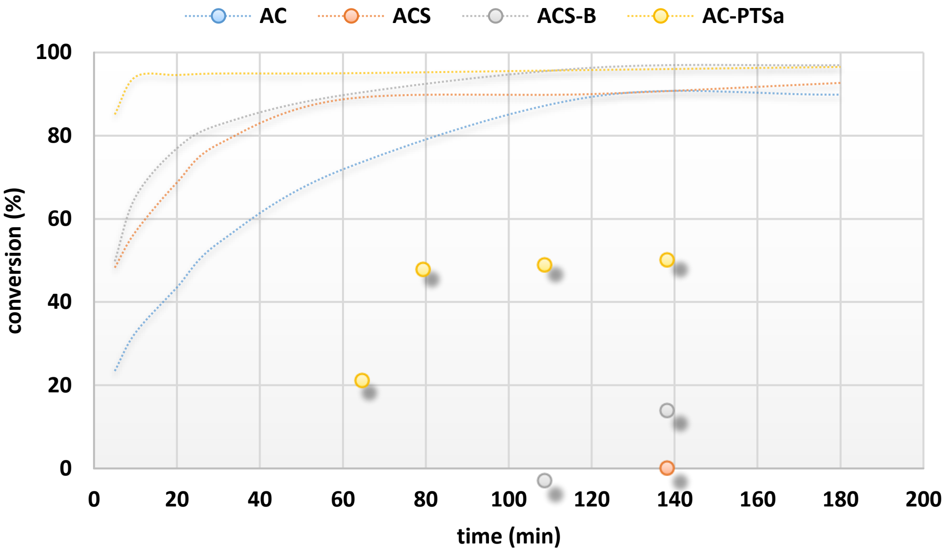
Figure III.2.11. *Catalyst screening in fructose dehydration to 5-HMF in DMSO ($m_{fructose}$=180 mg, m_{cata}= 20 mg, Temperature= 120 °C, time=120 min); for Glu/AC-pTSA sample the starting substrate is glucose* **(***$m_{glucose}$=180 mg, m_{cata}= 20 mg, temperature= 160 °C, time= 5 hours)*

The best catalyst was used for an additional test where the substrate was changed, glucose instead of fructose (Figure III.2.11 label Glu/AC-pTSA). Glucose molecule is selected for being directly available from lignocellulosic biomass (main monomer of cellulose), contrary to fructose which is generally produced from glucose by isomerization. The use of glucose in this reaction would make virtually the process time and cost saving but operates at different conditions (higher temperature) and usually lacks selectivity to HMF. The glucose dehydration reaction over AC-pTSA is carried out at higher temperature and time (160ºC and 5h) being the principal products humins and 5-HMF, the latter in much lower yield than the one obtained directly from fructose (47.2 vs. 92.8 %). It is generally proposed that HMF produced from glucose goes either through fructose (isomerization-dehydration reaction promoted over Lewis acid sites) or via direct dehydration over strong Brønsted acid sites. The poor performance of our catalyst and the absence of fructose in products distribution suggest that AC-pTSA is not able to catalyze glucose isomerization reaction. In addition, the HMF yield decreases significantly due to its oligomerization and/or cross polymerization with glucose forming humins. The increased humins yield is also facilitated at higher temperatures and longer reaction times.

Time effect on fructose dehydration

The results obtained at different reaction times at constant temperature of 120 °C are shown in figure III.2.12. Fructose conversion and HMF yields gradually increase for all samples with the highest differences within the series observed at lower reaction times. AC sample shows lower fructose conversion and almost no HMF production at the first 30 min whereas the sulphonated samples demonstrate much better activity (yields and conversion superior to 80 and 50%, respectively). After 30 min, the rate of fructose transformation and HMF production decrease suggesting either active sites saturation or loss of functional sites by some side products adsorption.

Maximum HMF is achieved after 120 min and decreased afterwards indicating the point of HMF conversion to humins by condensation. The exception is made by the ACS catalyst where the HMF yield still increases after 120 min. The latter suggests that either the humins formation rate depends on active sites' nature or that the maximum of HMF production remains unachieved in this time period.



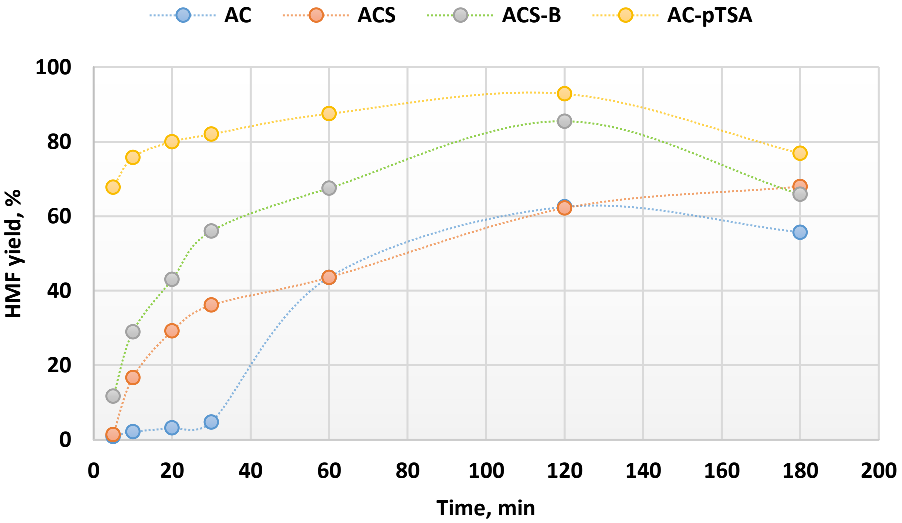


Figure III.2.12. *Time effect on fructose dehydration to 5-HMF in DMSO over all sulphonated carbon catalysts (m* $m_{fructose}$*=180mg,* m_{cata}*= 20 mg, Temperature= 120 °C).*

Temperature effect

The temperature effect is studied over AC-pTSA catalyst (Figure III.2.13). As expected, fructose conversion increases with the temperature reaching a constant value at 120 ºC. Similarly, HMF yield increases to a maximum reached at the same temperature as the maximal conversion (120ºC). An optimal temperature of 120 ºC can be selected.

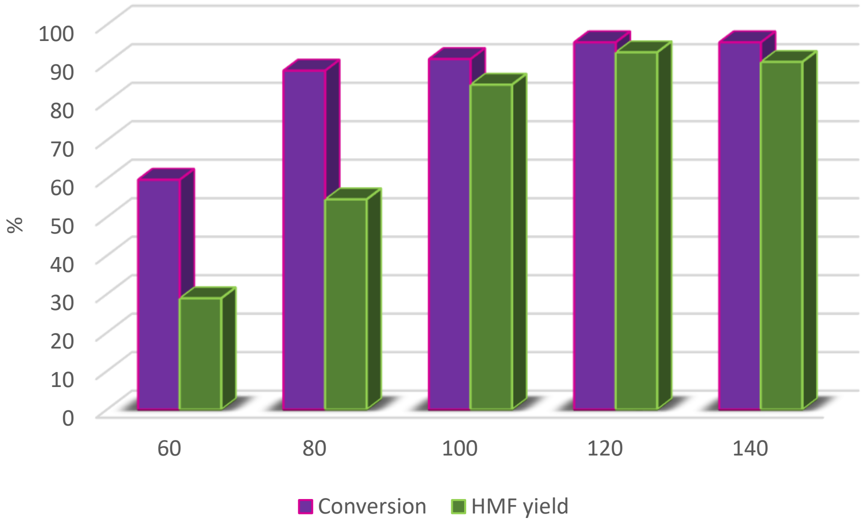


Figure III.2.13. *Temperature effect on fructose dehydration to 5-HMF in DMSO over AC-pTSA catalyst ($m_{fructose}$=180mg, m_{cata}= 20mg, time=120min).*

Substrate/catalyst ratio effect

Fructose dehydration was carried out at different substrate (fructose)/catalyst ratios. As can be seen in Figure III.2.14. fructose conversion is not affected since the major conversion is achieved by DMSO solvation effect. On the contrary, HMF yield decreases with the increase of fructose concentration due more probably to the generation of more humins, a process visually evidenced by the change in the color of the product solution from yellow orange solution to dark brown color (Figure III.2.14, inset image). The substrate/catalyst ratio of 9 has been selected as the best compromise between conversion and HMF yield.

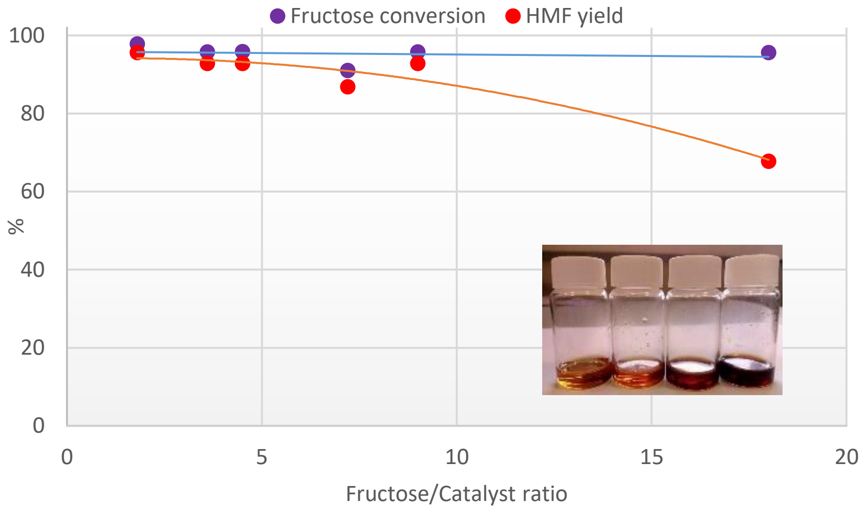


Figure III.2.14. *Substrate/catalyst ratio effect on fructose dehydration to 5-HMF in DMSO over AC-pTSA catalyst (Temperature = 120°C, time = 120 min).*

The comparison of our best catalyst AC-pTSA to already published catalytic systems shows very similar and clearly superior performance (Table III.2.6). The use of reduced catalyst charge, around 10%, and the important HMF yield converts our catalyst in very promising system for large scale HMF production.

Table III.2.6. Comparison with literature data.

Catalyst	Temperature (°C)	Time (min)	Catalyst (w/w %)	Fructose (w/v%)	HMF Yield (%)	Ref.
Ordered pores carbon, sulphonated	130	20	50	3	93.4	[44]
Spherical carbon, sulphonated	160	90	20	5	90	[45]
Mesoporous carbon, sulphonic acid	120	30	33	2	89.4	[46]
LDMC-SO_3H	140	120	10	10	98	[47]
MLC-SO_3H	130	40	50	8	82.2	[48]
D-cyclodextrin-SO_3H	140	120	100	1	96	[49]
Glu-TsOH	130	90	80	8.3	91.2	[50]
Graphene oxide, sulphonated	120	60	10	5	85	[28]
ACS-B	120	120	9	3.6	85.5	This work
AC-pTSA	120	120	18	1.8	95.6	This work
AC-pTSA	120	120	9	3.6	92.8	This work
AC-pTSA	120	120	4.5	7.2	87	This work

III.1.3.3. Adsorption tests

The substrate product adsorption on carbon surface is very important as its pore structure and hydrophilicity/hydrophobicity can be easily adjusted to allow the control of the secondary reactions rate. Fructose dehydration must occur on at least partially hydrophilic surfaces as 3 molecules of water are removed to form a hydrophobic furan ring [18]. In addition, fast HMF desorption must occur to inhibit its continuous transformation into humins. The carbon surface must be more hydrophilic than hydrophobic and should allow the fast access to the active sites via open porous system. The tests of molecule adsorption on our AC and sulphonated carbons show that fructose molecule is much better adsorbed than HMF. As a consequence, the fructose adsorption and dehydration are faster and the produced HMF is poorly adsorbed and rapidly evacuated in the continuous phase (Table III.2.6). In that case, the secondary reactions are suppressed and the humins production goes down. This effect is much more pronounced on functionalized carbons where the change of the surface and especially the pores aperture increase the quantity of adsorbed fructose and lowers to zero that of HMF.

Table III.2.7. Adsorption tests of fructose and HMF over AC and AC-pTSA catalysts in DMSO (initial fructose and HMF concentration 36 and 25.2 mg/ml, respectively).

Sample	**Adsorbed fructose, %**	**Adsorbed HMF, %**
AC	11.8	0.3
AC-Ptsa	22.4	0

($n_{\text{fructose/ HMF}}$=1mmol, m_{cata}= 20 mg, time= 6 hours, V_{solvent}= 5 ml, Temperature = 22°C).

III.1.3.3. Catalyst recycling

AC-pTSA catalyst is selected for five successive runs of fructose dehydration to 5-HMF in DMSO (Figure III.2.15). Fructose conversion remains stable but the HMF yield slightly decreases from 92.8% to 81% in the last run pointing out to partial deactivation of the catalyst. The latter might be ascribed to a possible leaching of some active sites like SO_3H groups, as suggested by the increase of slurry pH from 3.36 for the fresh catalyst to 4.31 after the last run.

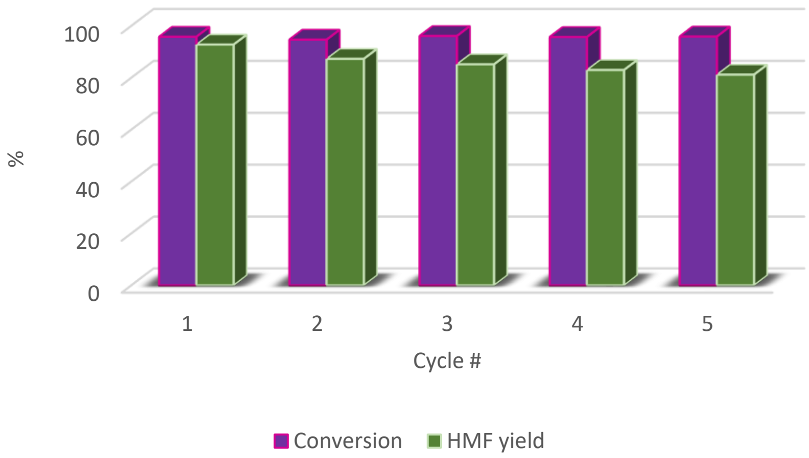


Figure III.2.15. *Catalyst recycling in fructose dehydration to 5-HMF in DMSO over AC-pTSA catalyst ($m_{fructose}$=180 mg, m_{cata}= 20 mg, Temperature= 120 °C, time=120 min)*

Partial conclusions

Fructose dehydration over sulphonated catalysts is affected clearly by the sulfur content, porosity, specific surface area and solvent. The different sulphonation methods convert successfully the commercial activated carbon in a Brønsted acid catalyst with moderate strength functional groups, active in carbohydrates dehydration to HMF.

Although attractive from green chemical point of view, the solvent free reaction leads to low HMF yields and favors the secondary reactions like HMF rehydration and oligo/polymerization. The switch to a reaction in DMSO media increases significantly fructose conversion which remains unaltered for temperatures superior to 80 ºC whatever the changes of reaction conditions (time or substrate/catalyst ratio). The conversion is ruled out mainly by the presence of DMSO (active in

References

[1] P.K. Rout, A.D. Nannaware, O. Prakash, A. Kalra, R. Rajasekharan, Synthesis of hydroxymethylfurfural from cellulose using green processes: A promising biochemical and biofuel feedstock, Chem. Eng. Sci. 142 (2016) 318–346. https://doi.org/10.1016/j.ces.2015.12.002.

[2] B. Kamm, P. Schönicke, Ch. Hille, Green biorefinery – Industrial implementation, Food Chem. 197 (2016) 1341–1345. https://doi.org/10.1016/j.foodchem.2015.11.088.

[3] A.R.C. Morais, A.M. da Costa Lopes, R. Bogel-Łukasik, Carbon Dioxide in Biomass Processing: Contributions to the Green Biorefinery Concept, Chem. Rev. 115 (2015) 3–27. https://doi.org/10.1021/cr500330z.

[4] A. Sarwono, Z. Man, N. Muhammad, A.S. Khan, W.S.W. Hamzah, A.H.A. Rahim, Z. Ullah, C.D. Wilfred, A new approach of probe sonication assisted ionic liquid conversion of glucose, cellulose and biomass into 5-hydroxymethylfurfural, Ultrason. Sonochem. 37 (2017) 310–319. https://doi.org/10.1016/j.ultsonch.2017.01.028.

[5] X. Tong, Y. Ma, Y. Li, Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes, Appl. Catal. Gen. 385 (2010) 1–13. https://doi.org/10.1016/j.apcata.2010.06.049.

[6] O. O. James, S. Maity, L. Ajao Usman, K. O. Ajanaku, O. O. Ajani, T. O. Siyanbola, S. Sahu, R. Chaubey, Towards the conversion of carbohydrate biomass feedstocks to biofuels via hydroxylmethylfurfural, Energy Environ. Sci. 3 (2010) 1833–1850. https://doi.org/10.1039/B925869H.

[7] B. Saha, M.M. Abu-Omar, Advances in 5-hydroxymethylfurfural production from biomass in biphasic solvents, Green Chem. 16 (2014) 24–38. https://doi.org/10.1039/C3GC41324A.

[8] G. Portillo Perez, A. Mukherjee, M.-J. Dumont, Insights into HMF catalysis, J. Ind. Eng. Chem. 70 (2019) 1–34. https://doi.org/10.1016/j.jiec.2018.10.002.

[9] P. Bhanja, A. Bhaumik, Porous nanomaterials as green catalyst for the conversion of biomass to bioenergy, Fuel. 185 (2016) 432–441. https://doi.org/10.1016/j.fuel.2016.08.004.

[10] L. Wang, H. Guo, Q. Xie, J. Wang, B. Hou, L. Jia, J. Cui, D. Li, Conversion of fructose into furfural or 5-hydroxymethylfurfural over HY zeolites selectively in γ-butyrolactone, Appl. Catal. Gen. 572 (2019) 51–60. https://doi.org/10.1016/j.apcata.2018.12.023.

[11] A.A. Marianou, C.M. Michailof, A. Pineda, E.F. Iliopoulou, K.S. Triantafyllidis, A.A. Lappas, Effect of Lewis and Brønsted acidity on glucose conversion to 5-HMF and lactic acid in aqueous and organic media, Appl. Catal. Gen. 555 (2018) 75–87. https://doi.org/10.1016/j.apcata.2018.01.029.

[12] J. Li, Y. Wang, B. Lu, Y. Wang, T. Deng, X. Hou, Protonic acid catalysis of sulfonated carbon material: Tunable and selective conversion of fructose in low-boiling point solvent, Appl. Catal. Gen. 566 (2018) 140–145. https://doi.org/10.1016/j.apcata.2018.08.027.

[13] Y. Xiao, Y.-F. Song, Efficient catalytic conversion of the fructose into 5-hydroxymethylfurfural by heteropolyacids in the ionic liquid of 1-butyl-3-methyl imidazolium chloride, Appl. Catal. Gen. 484 (2014) 74–78. https://doi.org/10.1016/j.apcata.2014.07.014.

[14] Md.I. Alam, S. De, B. Singh, B. Saha, M.M. Abu-Omar, Titanium hydrogenphosphate: An efficient dual acidic catalyst for 5-hydroxymethylfurfural (HMF) production, Appl. Catal. Gen. 486 (2014) 42–48. https://doi.org/10.1016/j.apcata.2014.08.019.

[15] Y. Nishimura, M. Suda, M. Kuroha, H. Kobayashi, K. Nakajima, A. Fukuoka, Synthesis of 5-hydroxymethylfurfural from highly concentrated aqueous fructose solutions using activated carbon, Carbohydr. Res. 486 (2019) 107826. https://doi.org/10.1016/j.carres.2019.107826.

[16] X. Xiong, I.K.M. Yu, S.S. Chen, D.C.W. Tsang, L. Cao, H. Song, E.E. Kwon, Y.S. Ok, S. Zhang, C.S. Poon, Sulfonated biochar as acid catalyst for sugar hydrolysis and dehydration, Catal. Today. 314 (2018) 52–61. https://doi.org/10.1016/j.cattod.2018.02.034.

[17] G. Portillo Perez, M.-J. Dumont, Production of HMF in high yield using a low cost and recyclable carbonaceous catalyst, Chem. Eng. J. 382 (2020) 122766. https://doi.org/10.1016/j.cej.2019.122766.

[18] J. Zhang, K. Dong, W. Luo, H. Guan, Catalytic upgrading of carbohydrates into 5-ethoxymethylfurfural using SO3H functionalized hyper-cross-linked polymer based carbonaceous materials, Fuel. 234 (2018) 664–673. https://doi.org/10.1016/j.fuel.2018.07.060.

[19] A. Villa, M. Schiavoni, P.F. Fulvio, S.M. Mahurin, S. Dai, R.T. Mayes, G.M. Veith, L. Prati, Phosphorylated mesoporous carbon as effective catalyst for the selective fructose dehydration to HMF, J. Energy Chem. 22 (2013) 305–311. https://doi.org/10.1016/S2095-4956(13)60037-6.

[20] J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid, Green Chem. 13 (2011) 2678–2681. https://doi.org/10.1039/C1GC15306D.

[21] B. Agarwal, K. Kailasam, R.S. Sangwan, S. Elumalai, Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: A review, Renew. Sustain. Energy Rev. 82 (2018) 2408–2425. https://doi.org/10.1016/j.rser.2017.08.088.

[22] R. Xing, Y. Liu, Y. Wang, L. Chen, H. Wu, Y. Jiang, M. He, P. Wu, Active solid acid catalysts prepared by sulfonation of carbonization-controlled mesoporous carbon materials, Microporous Mesoporous Mater. 105 (2007) 41–48. https://doi.org/10.1016/j.micromeso.2007.06.043.

[23] B. Karimi, H.M. Mirzaei, H. Behzadnia, H. Vali, Novel Ordered Mesoporous Carbon Based Sulfonic Acid as an Efficient Catalyst in the Selective Dehydration of Fructose into 5-HMF: the Role of Solvent and Surface Chemistry, ACS Appl. Mater. Interfaces. 7 (2015) 19050–19059. https://doi.org/10.1021/acsami.5b03985.

[24] B. Karimi, H.M. Mirzaei, The influence of hydrophobic/hydrophilic balance of the mesoporous solid acid catalysts in the selective dehydration of fructose into HMF, RSC Adv. 3 (2013) 20655–20661. https://doi.org/10.1039/C3RA44214D.

[25] J. Wang, S. Wang, Preparation, modification and environmental application of biochar: A review, J. Clean. Prod. 227 (2019) 1002–1022. https://doi.org/10.1016/j.jclepro.2019.04.282.

[26] R. Zhong, B.F. Sels, Sulfonated mesoporous carbon and silica-carbon nanocomposites for biomass conversion, Appl. Catal. B Environ. 236 (2018) 518–545. https://doi.org/10.1016/j.apcatb.2018.05.012.

[27] L.J. Konwar, P.M.¨ ki-Arvela, J. Mikkola, SO3H-Containing Functional Carbon Materials: Synthesis, Structure, and Acid Catalysis | Chemical Reviews, 119, 22 (2019) 11576–11630. https://pubs.acs.org/doi/10.1021/acs.chemrev.9b00199.

[28] F. Huang, W. Li, Q. Liu, T. Zhang, S. An, D. Li, X. Zhu, Sulfonated tobacco stem carbon as efficient catalyst for dehydration of C6 carbohydrate to 5-hydroxymethylfurfural in γ-valerolactone/water, Fuel Process. Technol. 181 (2018) 294–303. https://doi.org/10.1016/j.fuproc.2018.09.026.

[29] T. Zhang, W. Li, Y. Jin, W. Ou, Synthesis of sulfonated chitosan-derived carbon-based catalysts and their applications in the production of 5-hydroxymethylfurfural, Int. J. Biol. Macromol. 157 (2020) 368–376. https://doi.org/10.1016/j.ijbiomac.2020.04.148.

[30] M. Li, Q. Zhang, B. Luo, C. Chen, S. Wang, D. Min, Lignin-based carbon solid acid catalyst prepared for selectively converting fructose to 5-hydroxymethylfurfural, Ind. Crops Prod. 145 (2020) 111920. https://doi.org/10.1016/j.indcrop.2019.111920.

[31] Q. Hou, W. Li, M. Ju, L. Liu, Y. Chen, Q. Yang, One-pot Synthesis of Sulfonated Graphene Oxide for Efficient Conversion of Fructose into HMF, RSC Adv. 6 (2016). https://doi.org/10.1039/C6RA23420H.

[32] R. Liu, J. Chen, X. Huang, L. Chen, L. Ma, X. Li, Conversion of fructose into 5-hydroxymethylfurfural and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials, Green Chem. 15 (2013) 2895–2903. https://doi.org/10.1039/C3GC41139G.

[33] X. Wang, R. Liu, M.M. Waje, Z. Chen, Y. Yan, K.N. Bozhilov, P Feng, Sulfonated Ordered Mesoporous Carbon as a Stable and Highly Active Protonic Acid Catalyst, Chemistry of Materials, 19, 10 (2007) 2395–2397 https://pubs.acs.org/doi/10.1021/cm070278r.

[34] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B. 61 (2000) 14095–14107. https://doi.org/10.1103/PhysRevB.61.14095.

[35] J.L. Santos, M. Alda-Onggar, V. Fedorov, M. Peurla, K. Eränen, P. Mäki-Arvela, M.Á. Centeno, D.Yu. Murzin, Hydrodeoxygenation of vanillin over carbon supported metal catalysts, Appl. Catal. Gen. 561 (2018) 137–149. https://doi.org/10.1016/j.apcata.2018.05.010.

[36] N. Rodríguez, Y.Y. Agámez-Pertuz, E. Romero, J. de J. Díaz-Velásquez, J.A. Odriozola, M.Á. Centeno, Effect of starch as binder in carbon aerogel and carbon xerogel preparation, J. Non-Cryst. Solids. 522 (2019) 119554. https://doi.org/10.1016/j.jnoncrysol.2019.119554.

[37] S. Obata, H. Tanaka, K. Saiki, Electrical and spectroscopic investigations on the reduction mechanism of graphene oxide, Carbon. 55 (2013) 126–132. https://doi.org/10.1016/j.carbon.2012.12.018.

[38] S.S. Kim, L. Britcher, S. Kumar, H.J. Griesser, XPS Study of Sulfur and Phosphorus Compounds with Different Oxidation States, Sains Malays. 47 (2018) 1913–1922. https://doi.org/10.17576/jsm-2018-4708-33.

[39] Q. Shu, Q. Zhang, G. Xu, Z. Nawaz, D. Wang, J. Wang, Synthesis of biodiesel from cottonseed oil and methanol using a carbon-based solid acid catalyst, Fuel Process. Technol. 90 (2009) 1002–1008. https://doi.org/10.1016/j.fuproc.2009.03.007.

[40] M.S.A. Farabi, M.L. Ibrahim, U. Rashid, Y.H. Taufiq-Yap, Esterification of palm fatty acid distillate using sulfonated carbon-based catalyst derived from palm kernel shell and bamboo, Energy Convers. Manag. 181 (2019) 562–570. https://doi.org/10.1016/j.enconman.2018.12.033.

[41] G. Delgado Martin, C.E. Bounoukta, F. Ammari, M.I. Domínguez, A. Monzón, S. Ivanova, M.Á. Centeno, Fructose dehydration reaction over functionalized nanographitic catalysts in MIBK/H2O biphasic system, Catal. Today. (2020) S0920586120301334. https://doi.org/10.1016/j.cattod.2020.03.016.

[42] T.C. Tudino, R.S. Nunes, D. Mandelli, W.A. Carvalho, Influence of Dimethylsulfoxide and Dioxygen in the Fructose Conversion to 5-Hydroxymethylfurfural Mediated by Glycerol’s Acidic Carbon, Front. Chem. 8 (2020) 263. https://doi.org/10.3389/fchem.2020.00263.

[43] L.-K. Ren, L.-F. Zhu, T. Qi, J.-Q. Tang, H.-Q. Yang, C.-W. Hu, Performance of Dimethyl Sulfoxide and Brønsted Acid Catalysts in Fructose Conversion to 5-Hydroxymethylfurfural, ACS Catal. 7 (2017) 2199–2212. https://doi.org/10.1021/acscatal.6b01802.

[44] J. Wang, Y. Zhang, Y. Wang, L. Zhu, H. Cui, W. Yi, Catalytic fructose dehydration to 5-hydroxymethylfurfural over sulfonated carbons with hierarchically ordered pores, J. Fuel Chem. Technol. 44 (2016) 1341–1348. https://doi.org/10.1016/S1872-5813(16)30058-5.

[45] J. Zhao, C. Zhou, C. He, Y. Dai, X. Jia, Y. Yang, Efficient dehydration of fructose to 5-hydroxymethylfurfural over sulfonated carbon sphere solid acid catalysts, Catal. Today. 264 (2016) 123–130. https://doi.org/10.1016/j.cattod.2015.07.005.

[46] J. Wang, Z. Zhang, S. Jin, X. Shen, Efficient conversion of carbohydrates into 5-hydroxylmethylfurfan and 5-ethoxymethylfurfural over sufonic acid-functionalized mesoporous carbon catalyst, Fuel. 192 (2017) 102–107. https://doi.org/10.1016/j.fuel.2016.12.027.

[47] L. Gan, L. Lyu, T. Shen, S. Wang, Sulfonated lignin-derived ordered mesoporous carbon with highly selective and recyclable catalysis for the conversion of fructose into 5-hydroxymethylfurfural, Appl. Catal. Gen. 574 (2019) 132–143. https://doi.org/10.1016/j.apcata.2019.02.008.

[48] L. Hu, X. Tang, Z. Wu, L. Lin, J. Xu, N. Xu, B. Dai, Magnetic lignin-derived carbonaceous catalyst for the dehydration of fructose into 5-hydroxymethylfurfural in dimethylsulfoxide, Chem. Eng. J. 263 (2015) 299–308. https://doi.org/10.1016/j.cej.2014.11.044.

[49] R.S. Thombal, V.H. Jadhav, Biomass derived β-cyclodextrin-SO 3 H carbonaceous solid acid catalyst for catalytic conversion of carbohydrates to 5-hydroxymethylfurfural, Appl. Catal. Gen. 499 (2015) 213–216.https://doi.org/10.1016/j.apcata.2015.04.021.

[50] J. Wang, W. Xu, J. Ren, X. Liu, G. Lu, Y. Wang, Efficient catalytic conversion of fructose into hydroxymethylfurfural by a novel carbon-based solid acid, Green Chem. 13 (2011) 2678–2681. https://doi.org/10.1039/C1GC15306D.

[51] X. Qi, M. Watanabe, T.M. Aida, J. Richard Lee Smith, Catalytic dehydration of fructose into 5-hydroxymethylfurfural by ion-exchange resin in mixed-aqueous system by microwave heating, Green Chem. 10 (2008) 799–805. https://doi.org/10.1039/B801641K.

[52] J. Liu, M. Yang, C. Gong, S. Zhang, K. Sheng, X. Zhang, Insights into the glucose isomerization mechanism of Al-hydrochar catalyst probed by Al-oxide species transformation, Journal of Environmental Chemical Engineering. 9 (2021) 106721. https://doi.org/10.1016/j.jece.2021.106721.

[53] G.-W. Jang, J.-J. Wong, Y.-T. Huang, C.-L. Li, CHAPTER 7:Synthesis of HMF in Ionic Liquids: Biomass-Derived Products, in: Ionic Liquids in the Biorefinery Concept, 2015: pp. 202–226. https://doi.org/10.1039/9781782622598-00202.

CHAPTER IV. GLUCOSE DEHYDRATION TO VALUABLE PRODUCTS.

Summary

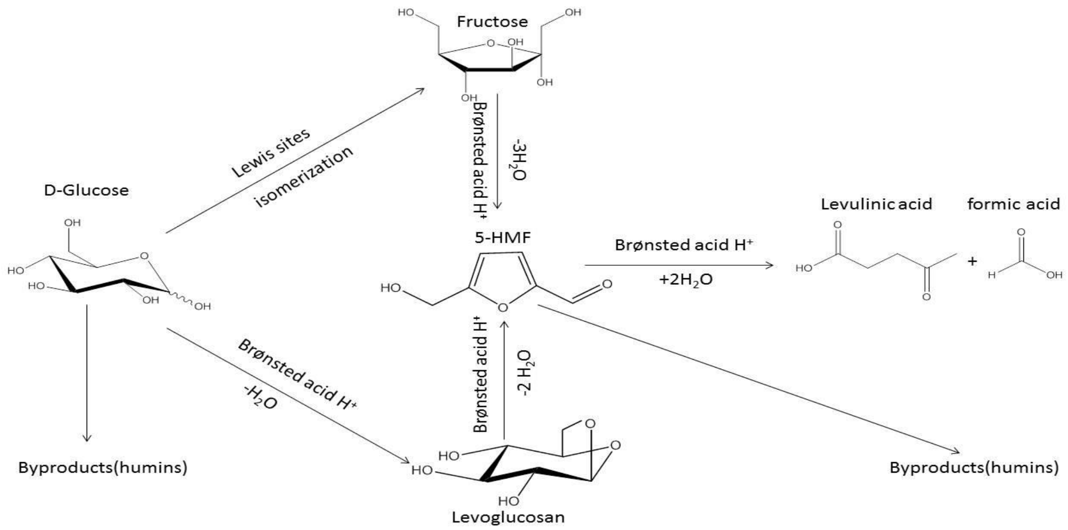
Exploring available catalytic systems to understand their behavior is a must to properly design efficient catalysts aiming to definitively drive biomass from laboratory to industrial scale. Glucose dehydration reaction involves cascade reactions with specific requirements, different active sites in each case and secondary reactions hard to avoid which are extremely linked to catalyst’s nature and reaction conditions. In the present chapter, mono and/or bifuncionalized carbonaceous catalysts with homogeneous, heterogeneous and heterogeneous/homogeneous mode are considered with the unique goal to decrease the energy barriers of each reaction step improving the yield towards biomass-derived valuable products, fructose, HMF and LA, while understanding the catalytic behavior of cost-effective catalysts. The choice of catalytic systems and the effect of main reactions parameters over activity and selectivity is studied and discussed in each part of the chapter.

IV.1. Introduction

Among all, lignocellulosic wastes have been considered as a promising carbon source for sustainable economy development [1–5]. In particular, glucose a multifunctional six-carbon molecule, is one of the most valuable and low-cost carbon monosaccharides that can be used for biorefinery purposes [4]. Its natural abundancy along with its facile production from lignocellulosic biomass containing materials convert this molecule in an excellent starting renewable feedstock either to produce fuels or high valued chemical commodities such as furfural, hydroxymethylfurfural (HMF), formic acid (FA), lactic acid and levulinic acid (LA), each of them considered platform chemicals [5].

The direct conversion of cellulose, as most abundant glucose polymer to HMF and LA is a highly targeted reaction, but the crystalline structure rigidity makes difficult its solubilization and causes low HMF yields. That is why the carbohydrate monomers, such as glucose and fructose are preferred as main molecules to transform in high-value chemicals. It is demonstrated in the past chapter that fructose dehydration is a simple reaction processed at low temperature and results in an excellent selectivity to HMF and low humins formation. However, fructose is not naturally spread and must be previously produced.

Glucose is rapidly considered as the best choice to substitute fructose due to its lower cost, high availability (cellulose monomer), and greater solubility. Nevertheless, this molecule present different steps of reaction, greater participation in secondary reactions and needs higher temperature to convert to HMF thus decreasing the main product selectivity. Glucose transformation to valuable products as LA via HMF includes, in general, three processes. Isomerization to fructose, direct/indirect dehydration to HMF and rehydration to LA (Scheme IV.1).



Scheme IV.1. *Glucose dehydration to valuable products.*

Therefore, the selective production of each part valuable chemicals derived from glucose and using heterogeneous catalyst is a subject of interest receiving recently much attention for optimizing the energy barriers to platform molecule production and minimizing the process costs of biorefinery application.

In this chapter, our interest goes **first** to the aqueous glucose isomerization over different metal halide monofunctionalized catalysts based on activated carbon.

Further, a mono/bi functionalized catalysts are elaborated for the glucose dehydration to HMF in MIBK/H_2O biphasic system.

And finally the performance of homogeneous and heterogeneous systems containing carbon catalysts is contrasted in one-pot transformation of glucose to LA.

In all parts different Bronsted acidic sites based on sulfonated carbon and Lewis acidic sites based on metal alkali earth/alkaline halide are used as homogeneous catalysts or functionalization agents for the preparation of mono/bi functionalized activated carbons. Glucose transformation to valuable products is carried out optimizing the reaction parameter such as, time, temperature, solvent media. The recycling and deactivation behavior of the catalyst is also tested during the chapter.

For this reaction, carbons [41,42], zeolites [43], mesoporous silicas [44], metal oxides [45], heteropolyacids [46,47], sulfonated resins [48] and metal-organic frameworks [49] are reported as heterogeneous catalysts. The group of activated carbons, generated from low-cost precursors, appears as the most versatile materials as catalysts. They exhibit high specific surface area, adaptable pore structures, tailored functional surface chemistry and good thermal stability at high temperatures [50]. Several studies have focused on glucose isomerization and dehydration reactions over functionalized carbon catalysts where the highest HMF yields are obtained using dimethyl sulfoxide (DMSO) [39, 40] as a solvent. Nevertheless, the high boiling point of this solvent makes difficult HMF separation. Iris K. M. Yu *et al.* [53] studied the catalytic activity of Al/biochars in microwave-assisted glucose to fructose isomerization obtaining fructose yields comparable to those reported over inorganic catalysts. Li *et al.* [54] used niobia/carbon composites in glucose to 5-hydroxymethylfurfural reaction at 160°C obtaining 97.6% conversion, with 59.3% HMF and 35.4% humins yields. Activated carbon (AC) by itself demonstrated important activity, showing around 51% HMF yield with 78% selectivity in NaCl saturated reaction media [55].

The simple chemical structure and ease of functionalization converts the activated carbons in very useful materials for active sites modification and study. That is why they are chosen as raw material for the preparation of bifunctional Brønsted/Lewis tandem site solid catalysts with a final objective to study their efficiency in the conversion of glucose to HMF in biphasic water - methyl isobutyl ketone (MIBK) systems. The functionality of the catalyst will be modified to achieve an optimal HMF yields for low humins formation.

IV.3.1 Experimental

Catalysts preparation

The bifunctionality of the catalysts is assured by the introduction of Brønsted and/or Lewis acid sites over activated carbon in two steps. Firstly, the Lewis site, i.e. metal chloride, ($CaCl_2$ or $ZnCl_2$) is impregnated over 1 g of AC using 20 mL solution containing 20 wt.% of metal chloride.

After 3 hours of aging, the excess of solvent is removed in rotary evaporator under reduced pressure and after drying at 110 °C the resulting solid is activated 2h at 400°C (10°C/min ramp) under nitrogen flow (100 ml/min). After activation the solid is washed abundantly with distilled water and dried at 110°C. Two samples are originated after this, Ca/AC and Zn/AC, respectively.

The second step introduces Brønsted acidity by sulfonation of the as prepared Ca/AC and Zn/AC (and bare AC for comparison) samples with *p*-toluenesulfonic acid (*p*-TSA). The solids (1g of catalysts or AC, respectively) are treated with 0.5M *p*-TSA solution during 24 h followed by solvent evaporation at 80°C under reduced pressure in rotary evaporator. The solids are dried at 80°C for 12 h, washed abundantly with water and dried again at 110°C. The obtained samples receive the labels *p*TSA-AC, *p*TSA-Zn/AC and *p*TSA-Ca/AC, respectively.

Catalytic tests

Glucose dehydration is carried out in 50 mL glass reactor equipped with a Young valve and stirrer flea. Glucose (1mmol) and catalyst (40 mg) are mixed in MIBK/H_2O (6/1 v/v ratio) biphasic system containing 1.5 mL of water. The reactor is sealed and introduced in preheated paraffin oil bath at the temperature of reaction for a desired time under stirring at approximately 600 rpm. After each experiment, the reactor is cooled down in ice bath and the mixture is microfiltered with 0.45 μL syringe nylon filter. The obtained products are analyzed by High-Performance Liquid Chromatography (HPLC).

Glucose conversion and HMF selectivity/yield are calculated according to the equations described below. All insoluble (undetected) products, in both, water and MIBK, are considered humins.

$$Conversion\,(\%) = 100 \cdot \left(1 - \frac{n_{final}\,(Glucose)}{n_{initial}\,(Glucose)}\right)$$

$$Selectivity_i\,(\%) = 100 \cdot \left(\frac{n_{final}\,(Product_i)}{\sum_i n_{final}\,(Products)}\right)$$

$$Yield_i\,(\%) = 100 \cdot \left(\frac{n_{final}\,(Product_i)}{n_{initial}\,(Glucose)}\right)$$

where n_i and n_f are the initial and final moles of analyzed compound.

IV.3.2. Catalyst characterization

The thermal stability of all prepared samples, analyzed by TGA, is presented in Figure IV.3.1. For all samples, mass loss within the 25-110 °C temperature range is observed and ascribed to physically adsorbed water release. A difference in this water content is obvious within the series, with all sulfonated samples presenting higher water content in comparison to bare AC (less hydrophilic) and metallic halides treated samples. This observation allows us to conclude that the sulfonation treatment increases significantly surface hydrophilicity by introducing the corresponding sulfonic groups. For the metal halide doped carbons, higher water release is observed for Ca/AC which may be attained to the presence of structural water in the used calcium precursor. The combination of Lewis/Brønsted sites increases even more the hydrophilicity of the samples. With the temperature, all samples show a slow but continuous weight loss, more noticeable for the sulfonated catalysts due to the decomposition of sulfonic groups bonded to the carbon layers around 340 °C [41]. Without exception, the oxidation temperature of functionalized samples is lower to that of commercial AC suggesting more oxidized surface for the functionalized samples and/or increased hydrophilicity leading to faster degradation. The highest rate of oxidation of Zn-containing samples can be attributed to the transformation of chloride to oxide at temperatures inferior to 500 ºC and its participation in carbon reduction reaction [56].

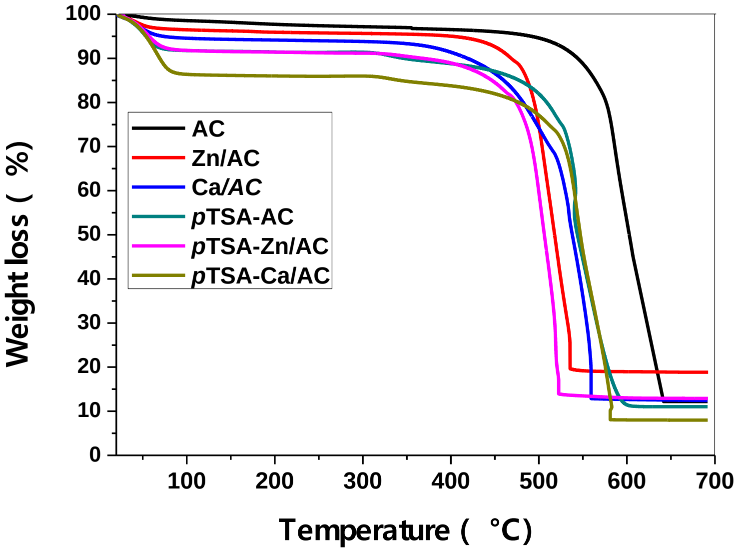


Figure IV.3.1. *Thermogravimetric analysis of prepared samples.*

Nitrogen physisorption isotherms are presented in Figure IV.3.2. The similarity between all hysteresis curves suggests analogous textural properties for all samples and commercial carbon.

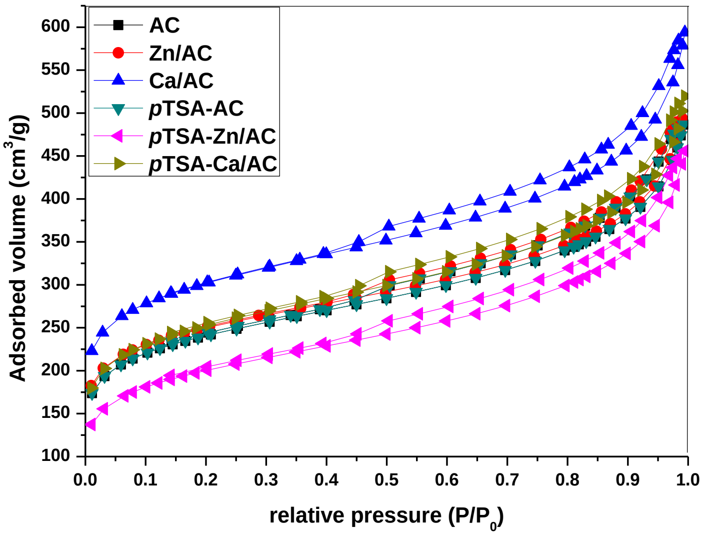


Figure IV.3.2. *N_2 physisorption isotherms of prepared catalysts.*

According to IUPAC classification, the isotherms are of type IV, defined by the typical hysteresis loop of all mesoporous materials. The measured isotherms show also a high-adsorbed volume at relatively low pressures suggesting the presence of micropores.

The textural properties of prepared catalysts are summarized in Table IV.3.1. Some alterations related to carbons' functionalization are also observed. The impregnation with metal chlorides gives rise to pore size/volume and mesopores/micropores ratio increase. The samples are activated at 400°C during 2 h in nitrogen and such a treatment could provoke partial gasification induced by the presence of metal and could alter solid's textural properties. Comparing with activated carbon the specific surface area increases in the case of calcium and decreases for zinc chloride. Higher Zn content is then expected on the external surface blocking the AC micropores and on the contrary, calcium seems to diffuse to the internal surface of the support. On the other hand, *p*TSA incorporation leads to a decrease in both S_{BET} and microspores surface which may be related to the *p*TSA' bigger cross-sectional area and possible burying of some micropores. The microporosity decreases for all samples, being the *p*TSA presence the most significant factor influencing the porosity. A significant microporosity percentage loss suggests higher fraction of blocked micropores. All these results also manifest that the functionalization with *p*TSA is successfully achieved and suggests the presence of SO_3H groups on catalyst surface.

Table IV.3.1. Textural properties of carbon based catalysts

Samples	**BET Surface area[a] (m^2/g)**	**Average pore size[b] (nm)**	**Pore volume[b] (cm^3/g)**	**Surface micro[c] (m^2/g)**	**Surface meso (m^2/g)**	**External Surface (m^2/g)**	**Micro %**
AC	928	4.62	0.368	513	318	414	55.0
Zn/AC	861	6.44	0.545	428	371	434	49.7
Ca/AC	1042	6.3	0.638	525	443	521	50.4
***p*TSA/AC**	835	6.18	0.548	383	377	451	45.9
***p*TSA-Zn/AC**	700	6.27	0.557	272	365	427	38.8
***p*TSA-Ca/AC**	877	6.24	0.594	398	405	472	45.4

[a] calculated by BET equation, [b] calculated by BJH desorption [c] calculated by t_{plot} equation method

The semiquantitative chemical composition (SEM-EDS) of all carbon based materials is presented in Table IV.3.2. Silicon is present (originated from activated carbon mineral component-SiO_2) in the commercial AC and persists in all samples in random percentages. In addition, Cl^- appears after Zn/Ca impregnation, but the observed Cl/M ratio (being M = Zn or Ca) is inferior to 2, indicating that some chlorine was either removed or hydrolyzed during the activation treatment. The latter suggests that the metals are not present on the surface only as MCl_2, but also as reacting species on carbon surface. Taking into account the presence of oxygenated groups on activated carbon surface and the observation in the first part of this chapter it is logical to imagine an interaction with carbon's functional groups to form anhydrides and MO/CO$_x$M species [57,58].

Zn/AC sample shows higher metal content than Ca/AC sample for the same chlorine content. The latter might indicate lower interaction degree for $CaCl_2$. The lower interaction can be explained by the existing difference in melting temperature of $ZnCl_2$ and $CaCl_2$ (290 ºC vs. 772 °C) and as a consequence different state of the metal during the activation procedure and its interaction with carbon' surface functionalities.

Table IV.3.2. Chemical composition (at %), determined by EDS and Raman analysis for the prepared carbon based materials

Sample	**Chemical composition (at%)**						**Raman analysis**
	C	**O**	**Si**	**Ca or Zn**	**Cl**	**S**	**I(D)/I(G)**
AC	87.73	11.65	0.38	-	0.07	0.17	1.20
Zn/AC	80.76	13.37	0.81	3.95	1.1	0.004	1.12
Ca/AC	84.99	11.64	1.10	1.14	0.98	0.15	1.19
pTSA-AC	81.22	16.33	1.21	-	0.01	1.24	1.3
pTSA-Zn/AC	72.73	22.33	1.62	1.72	0.28	1.32	1.26
pTSA-Ca/AC	82.27	15.17	0.97	0.25	0.21	1.13	1.29

Finally, higher sulfur content is observed after functionalization with *p*-toluenesulfonic acid, accompanied by an increase in oxygen ratio. That means that the sulfonic groups are introduced successfully, although a decrease in the metal content is also observed due more probably to the formation of p-TSA salts and their removal from the surface after washing [59]. The S and M content can allow indirectly the estimation of Lewis/Brønsted sites and their proportion in the tandem sites, although the possible hydrolysis and interaction with carbon surface of zinc could convert some Lewis sites ($ZnCl_2$) into Zn_xOC species with more Brønsted acid character. Actually, S and Cl contents would be more accurate to estimate the real Lewis/Brønsted ratio. Based on this we can order the samples in decreasing Lewis and increasing Brønsted acidity as follows:

Zn/AC>Ca/AC>AC>pTSA-Zn/AC> pTSA-Ca/AC>pTSA-AC

Raman spectroscopy is widely used to determine the defect existence in carbonaceous materials. All samples exhibit two bands around 1340 cm^{-1} and 1600 cm^{-1}, corresponding to the D band (sp^3 hybridization, number of structural defects related to amorphous carbon) and G band (sp^2, fingerprint of graphitic carbon crystallites), respectively (Figure IV.3.3) [44]. The intensity ratio (I_D/I_G) can serve as an empirical estimation of the disorder induced by the functionalization process. I_D/I_G ratios superior to 1 indicate that there is a higher disorder degree and defects population.

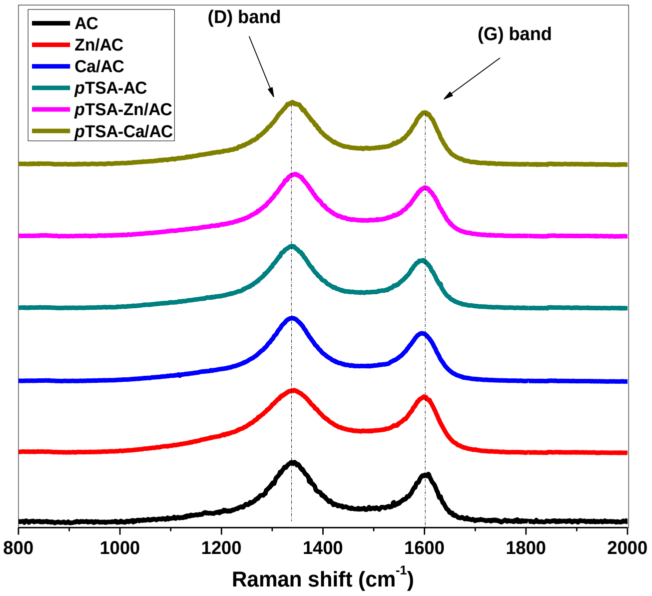


Figure IV.3.3. *Raman spectra of mono/bi functionalized AC catalysts.*

The AC treatment with $ZnCl_2$ decreases the I_D/I_G ratio of the original AC (Table IV.3.2), indicating that Zn impregnation affects the structural ranging during the post-activation most probably. The activation, on the other hand, reduces carbon species on the surface and increases the structure order. On the contrary, approximately the same I_D/I_G ratio after Ca impregnation is observed (Ca/AC vs. AC), suggesting that $CaCl_2$ incorporation does not affect the disorder degree of the commercial AC, probably also related to lower metal loading found for this sample. Nevertheless, upon sulfonation with pTSA, a general increase in the intensity ratio is observed, revealing the presence of higher disorder caused by the introduction of SO_3H groups over and between activated carbon sheets.

The XRD patterns of studied catalysts are illustrated in Figure IV.3.4. In all cases, characteristic diffractions related to the carbon structure are observed; $2\theta \approx 25°$, 44° and 80°, corresponding to (002), (100) and (110) family planes, respectively. Two different silicone oxides, crystobalite and quartz [60], as mineral component of the activated carbon are also detected [61].

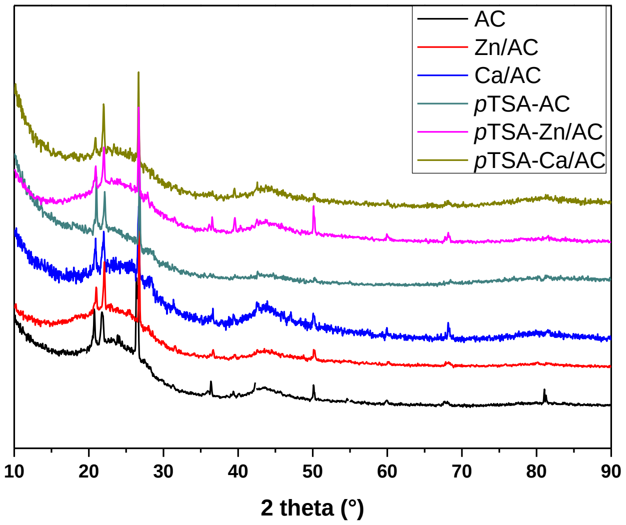


Figure IV.3.4. *X-ray diffractions of mono/bi functionalized AC catalysts.*

The doping phases (halides or *p*TSA) were not detected due more probably to their low content, low crystallinity and/or produced changes of the initial phases during the period of activation.

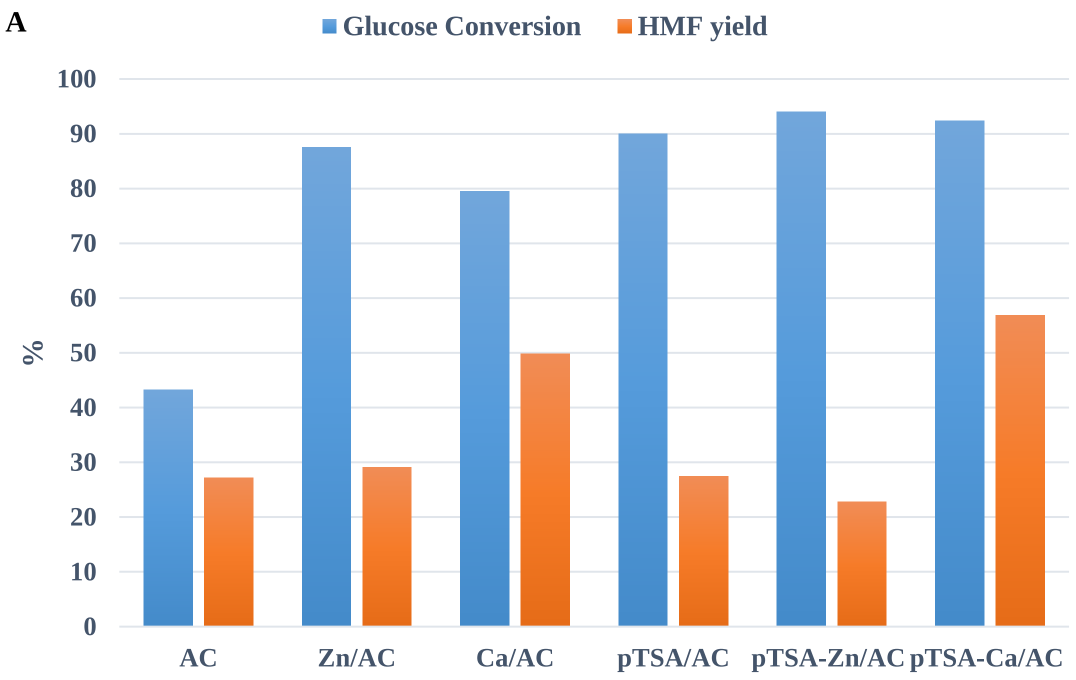
So, the introduction of bifunctionality is successfully achieved. All modification leads to changes in the active carbon textural properties with the main modifications being pore size increase and micropores blocking. The introduction of Lewis sites, $ZnCl_2$ in particular, results in more important changes mainly due to the highest metal content detected. The presence of Zn also influences essentially the thermal stability of the material, increasing on first place carbon hydrophilicity and decreasing the temperature of carbon decomposition. The absence of $ZnCl_2$ phase suggests important interaction with the activated carbon surface through ZnO_xC/$ZnCl_xC$ species. The presence of sulfonic groups is confirmed by the S content increase and specific surface decrease (due essentially to micropores blocking by pTSA) indicating the introduction of some Brønsted acidity.

IV.3.3 Catalytic activity of catalysts in glucose dehydration

IV.3.3.1. Catalysts screening

Glucose can be converted into 5-hydroxymethyl furfural (HMF) via two pathways in presence of Lewis and/or Brønsted acid sites. The main pathway includes glucose (Glu) isomerization into fructose (Fru) preferably over Lewis sites and fructose dehydration to HMF preferably over Brønsted acid sites. The second pathway goes through direct dehydration of glucose via levoglucosan (LGA) intermediate preferably over Brønsted sites also responsible to irreversible rehydration of HMF to formic and levulinic acid (Lev+for). Both routes are resumed in Scheme IV.4.

Glucose conversion, HMF yields and products selectivity distribution over AC mono and bifunctional catalysts at 180 °C and reaction time of 24 h are presented in Figure IV.3.5.



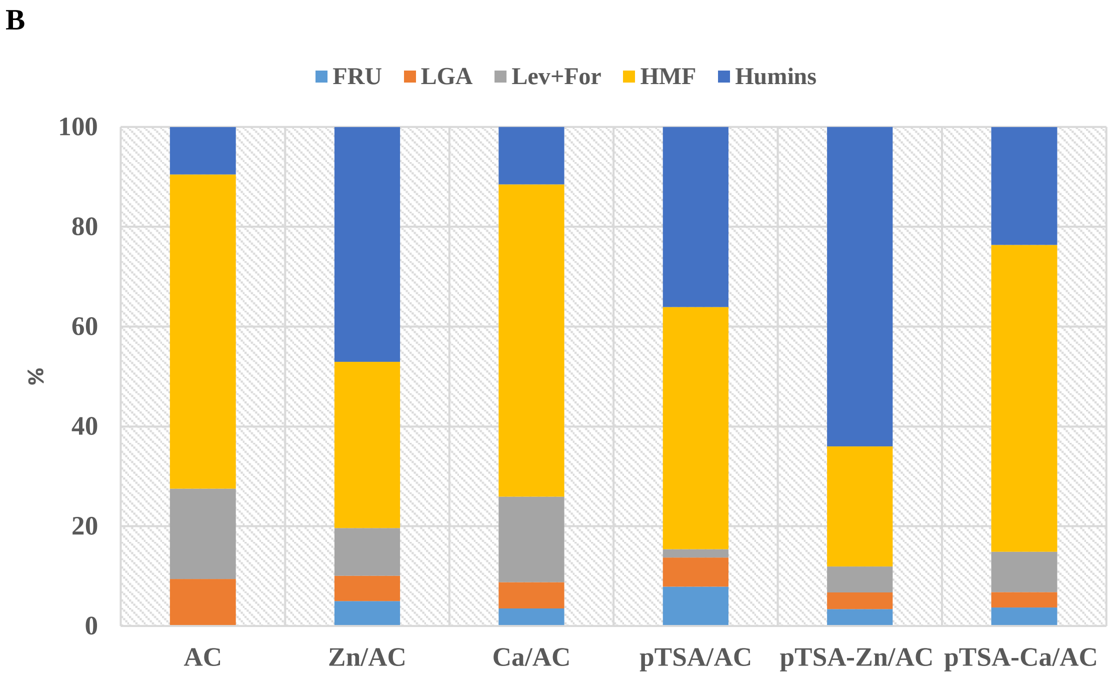


Figure IV.3.5. *Catalysts screening ($m_{glucose}$=180 mg, m_{cat}= 40 mg, T=180 °C, time=24 h, V_{total}=10.5 mL, MIBK/H_2O, 6/1 v/v) A) Glucose conversion, HMF yield B) Product selectivity.*

The functionalization of AC increases glucose conversion almost twice no matter the nature of the introduced sites (Lewis, Brønsted or both), Figure IV.3.5A. The low conversion of AC sample can be attributed to the presence of insufficient Brønsted acid sites such as carboxylic (-COOH) and hydroxyl groups (OH) on carbon surface and on its small average pores size and volume. Upon functionalization, glucose dehydration activity improves significantly, especially for the samples containing Ca. The bifunctional *p*TSA-Ca/AC catalyst reaches almost full glucose conversion and an important HMF yield (57 %). Nevertheless, the yield of HMF by itself is less informative and it is better to take into consideration the product selectivity (Figure 5B). In addition to the already cited products, fructose (Fru), HMF and its rehydration products-levulinic and formic acids (Lev+for)) it is worth to introduce humins selectivity, indirectly evaluated as a measure of the incomplete C-balance during the reaction. All matter not converted in analyzable products is considered as humins, products of aldehyde and alcohol condensation reactions. *What is the function of the acid sites in this reaction?* Both types of sites (Lewis and Brønsted) catalyze furfurals condensation to humins, but only Lewis sites catalyze the crossed condensation between monosaccharide's and furfurals to the same macromolecule [62]. The case of Zn/AC sample is very interesting and very different from the results obtained for Ca/AC catalyst. Although prepared as Lewis site catalyst, it is behaving as Brønsted acid catalyst, i.e. its product distribution and selectivity are much more similar to *p*TSA/AC catalyst than to Ca/AC sample. We can tentatively explain this with the amphoteric character of Zn^{2+} in aqueous solution and its hydration to oxo-hydroxo compounds that will behave rather as Brønsted than Lewis acid. For this catalyst a decrease of the HMF selectivity is observed and related to higher humins selectivity at high glucose conversion. If we suppose that Zn/AC catalyst presents more Brønsted sites in comparison to Ca/AC sample and that Ca^{2+} Lewis sites present less harder-acid character than Zn^{2+} sites (higher charge/atomic radii ratio for the latter) the Ca-containing samples will present less centers in number and/or in hardness which should result in minor degree of HMF/glucose polymerization, lower humins concentration and higher HMF selectivity [63].

For the bifunctional catalysts, the HMF selectivity is a function of the Brønsted/Lewis sites ratio. The higher the ratio the higher the selectivity towards HMF. We can assume that *p*TSA-Ca/AC catalyst present a fine site balance and results in high HMF and low humins selectivity. The higher Brønsted to Lewis ratio for this sample is confirmed also by the higher Lev+For selectivity, being the HMF hydration reaction catalyzed only by Brønsted sites. All catalysts present low fructose and levoglucosane (LGA) selectivity indicating that HMF production includes both pathways in a parallel manner and that their transformation is faster than their formation.

In summary, Ca containing samples give the best activity/HMF selectivity ratio and the time effect and kinetic modelling was made over *p*TSA-Ca/AC sample compared with *p*TSA-AC and Ca/AC.

IV.3.3.2. Reaction condition optimization

Temperature effect

Generally, there is a reciprocal relationship between temperature and time of reaction in catalysis, higher the temperature shorter the reaction time. Although beneficial for the overall conversion the change of the temperature could affect very negatively the selectivity especially when simultaneous reactions occurred. Indeed, the reaction temperature affects significantly the conversion and HMF selectivity over PTSa-Ca/AC catalyst (Figure IV.3.6).

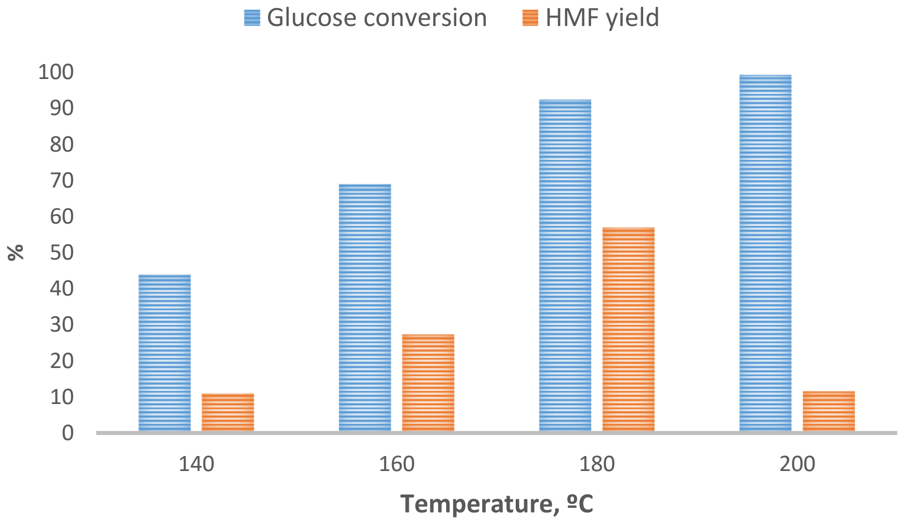


Figure IV.3.6. *Temperature effect over pTSA-Ca/AC catalyst, (m* $_{glucose}$*=180 mg, time=24h,* V_{total}*=10,5 ml, MIBK/*H_2O*, 6/1, V/V).*

Glucose conversion increases linearly with the temperature with complete conversion achieved at 200 ºC. As for the HMF yield, it improves from 140 °C to 180 °C, and reaches a maximum of 57%. At higher temperature the by-products formation becomes important, lowering the yield of HMF and converting 180 °C as the most appropriate reaction temperature.

Glucose concentration effect:

For industrial purposes, the reaction mixtures must be as concentrated as possible, in order to assure higher productivity at minimum cost. Nevertheless, the higher substrate-to-catalyst ratio presents an important disadvantage; low selectivity. The effect of glucose concentration on glucose conversion and HMF yield presented in Figure IV.3.7.

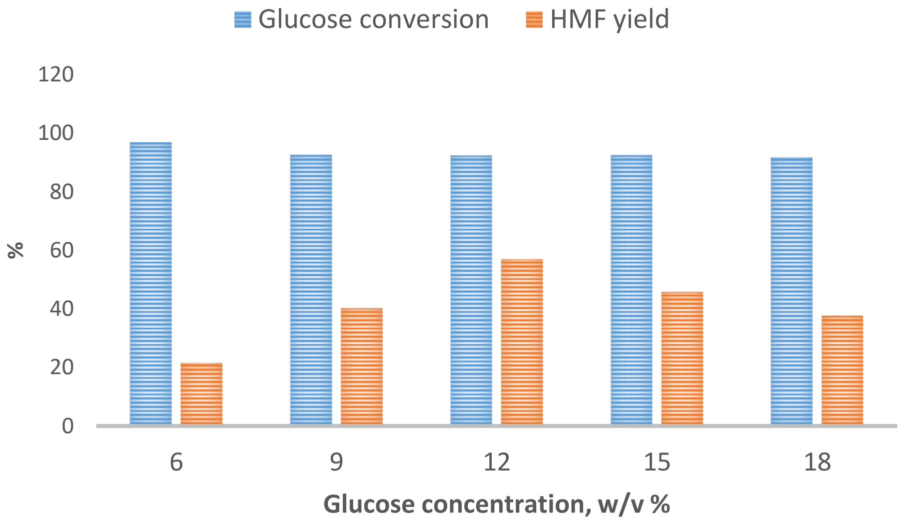


Figure IV.3.7. *Glucose concentration effect over pTSA-Ca/AC catalyst, (m* $_{glucose}$*=180 mg, time=24 h, V*$_{total}$*=10,5 ml, MIBK/*H_2O*, 6/1, V/V)*

The initial glucose conversion of 97% for the initial 6 w/v% concentration drops to 92% for the 9w/v% solution and remains constant afterwards. A maximum HMF yield is achieved for 12 w/v% solution (92% and 56 %) afterwhich the yield decreases due to the formation of humins. However, the moles of produced HMF remain constant after 12 w/v% or 1 mmol (Figure IV.3.8) indicating that the humins are a function of glucose. Glucose solutions with concentration of 12 w/v % are used for all other optimizations.

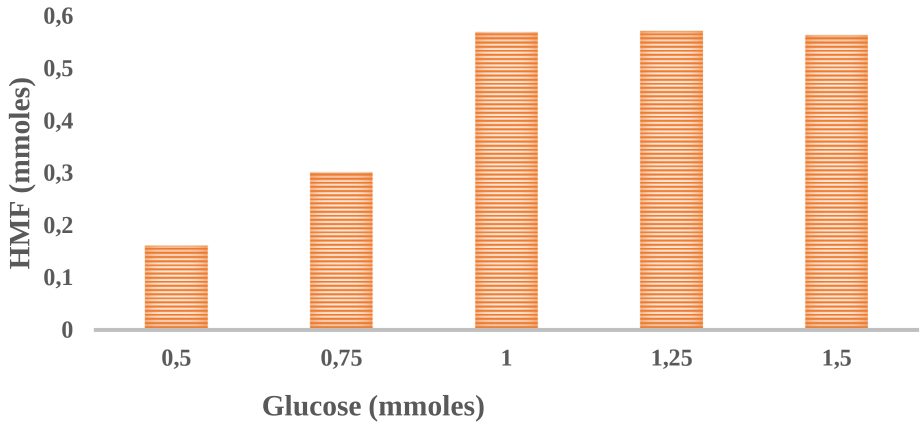


Figure IV.3.8. *Effect of glucose charge over formed HMF.*

MIBK/H_2O ratio

The dehydration of glucose is usually performed in biphasic systems with the aim to inhibit byproducts formation and to allow easier extraction of HMF [64]. Methyl isobutyl ketone (MIBK) is one of the most appropriate solvents for the effective conversion of hexoses in a biphasic system. It prevents the secondary reactions and presents high partition HMF coefficient and lower boiling point. The reactivity of glucose at four different MIBK/water ratios (2:1, 4:1, 6:1 and 8:1) over pTSA-Ca/AC catalyst is presented in Figure IV.3.9.

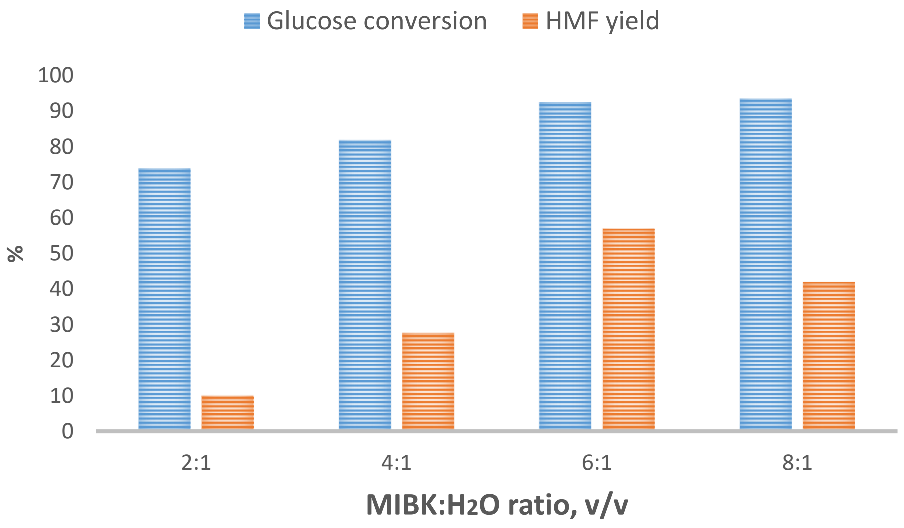
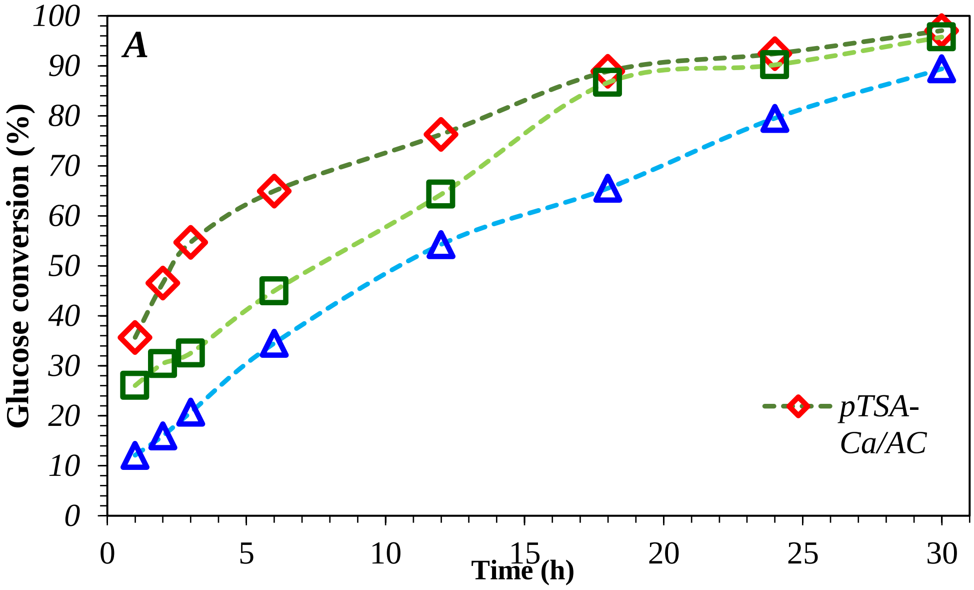


Figure IV.3.9. *Effect of MIBK/H_2O ratio over pTSa-Ca/AC catalyst, (m$_{glucose}$=180 mg, m$_{catalyst}$=40mg, T=180°C, time=24h, v$_{H20}$=1,5ml).*

The glucose conversion and HMF selectivity are low at low MIBK/H_2O ratio and increased gradually with MIBK concentration. Meanwhile the conversion remains constant at the highest ratio the HMF yield drops with around 10 %. According to the results, MIBK/water ratio of 6:1 is chosen as the optimal for the reaction.

Time effect

The kinetics of the reaction for *p*TSA/AC, Ca/AC and *p*TSA-Ca/AC are presented in Figure IV.3.10.



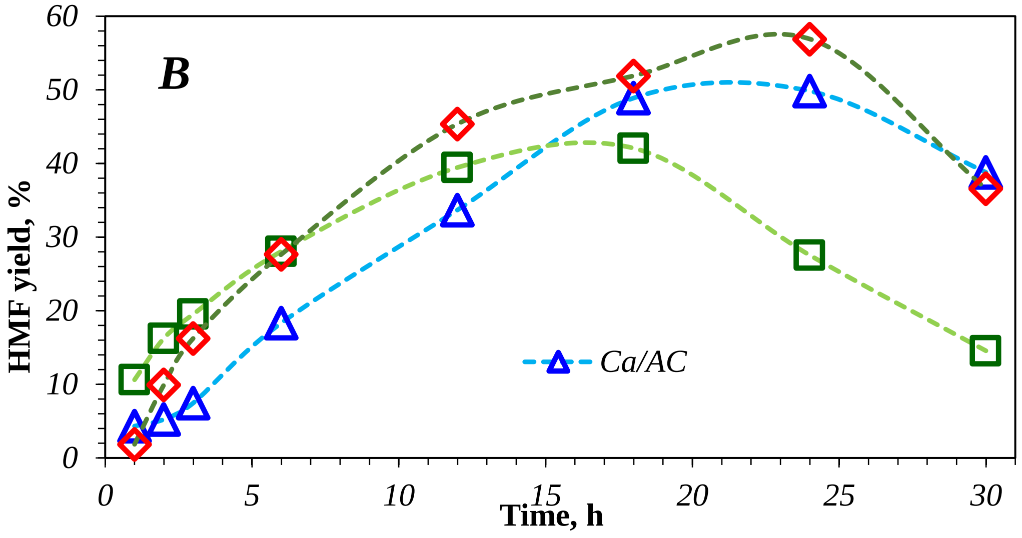
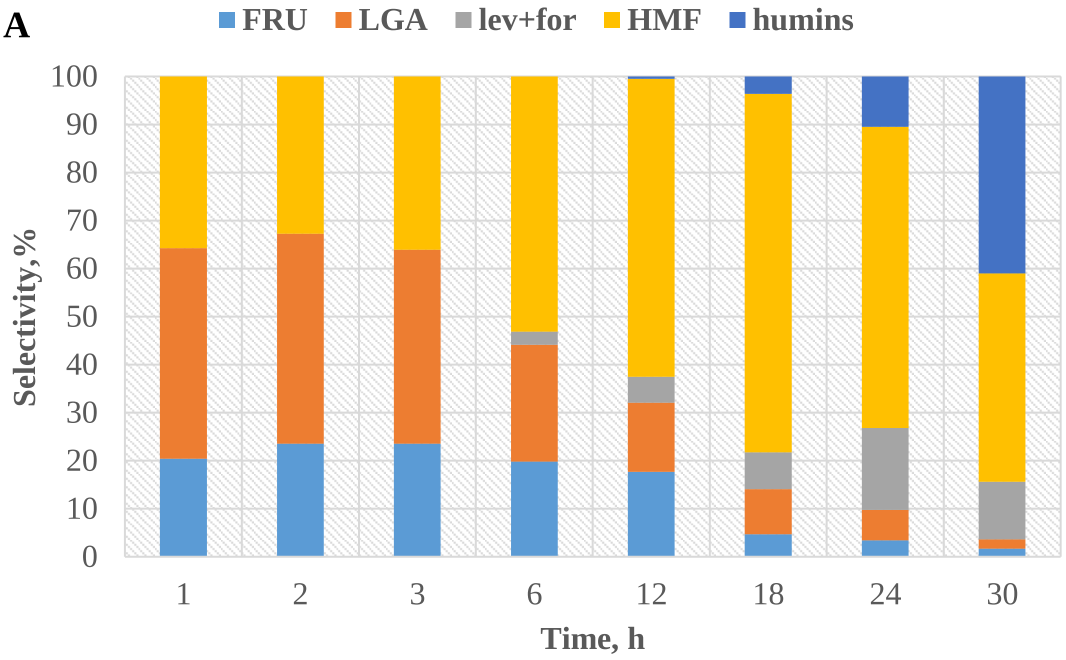
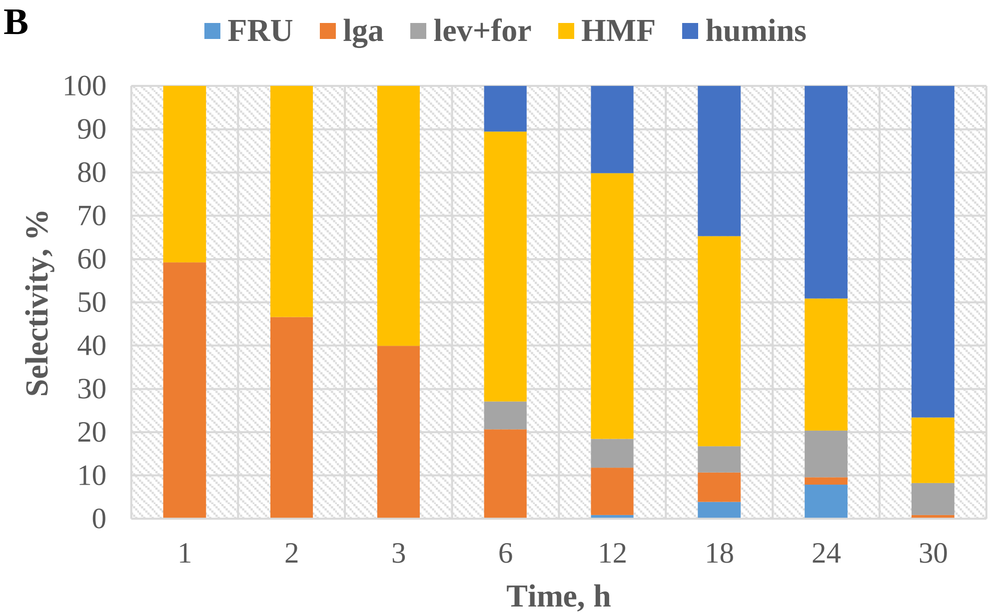


Figure IV.3.10. Evolution along time of A) Glucose conversion; and B) HMF selectivity over pTSa-Ca/AC, Ca/AC and pTSA/AC (m $_{glucose}$= 180 mg, time= 24 h, v$_{H2O}$=1,5mL MIBK/H_2O, 6/1 v/v)

Glucose conversion increases gradually with reaction time no matter the nature of the active sites. The HMF yield presents, however, an optimal value reached earlier for *p*TSA/AC catalysts and later for the Ca containing systems. After that value, the HMF yield decreases due to the participation of furfural in rehydration and condensation reactions. An interesting observation arises after considering all reaction products (Figure IV.3.11). When the Brønsted sites prevail (*p*TSA/AC, Figure IV.3.11 B) the LGA intermediate is the one present in the first 12 h of reaction, suggesting that the HMF formation over this catalyst goes via LGA pathway (Scheme IV.4.). For the catalysts containing Lewis sites (Ca/AC, Figure IV.3.11 A) or tandem Brønsted/Lewis sites (*p*TSA-Ca/AC, Figure IV.3.11 C) the HMF formation proceeds simultaneously via both, LGA and fructose pathways.


A
FRU
LGA
lev+for
HMF
humins
Selectivity, %
0
10
20
30
40
50
60
70
80
90
100
1
2
3
6
12
18
24
30
Time, h


B
FRU
lga
lev+for
HMF
humins
Selectivity, %
0
10
20
30
40
50
60
70
80
90
100
1
2
3
6
12
18
24
30
Time, h

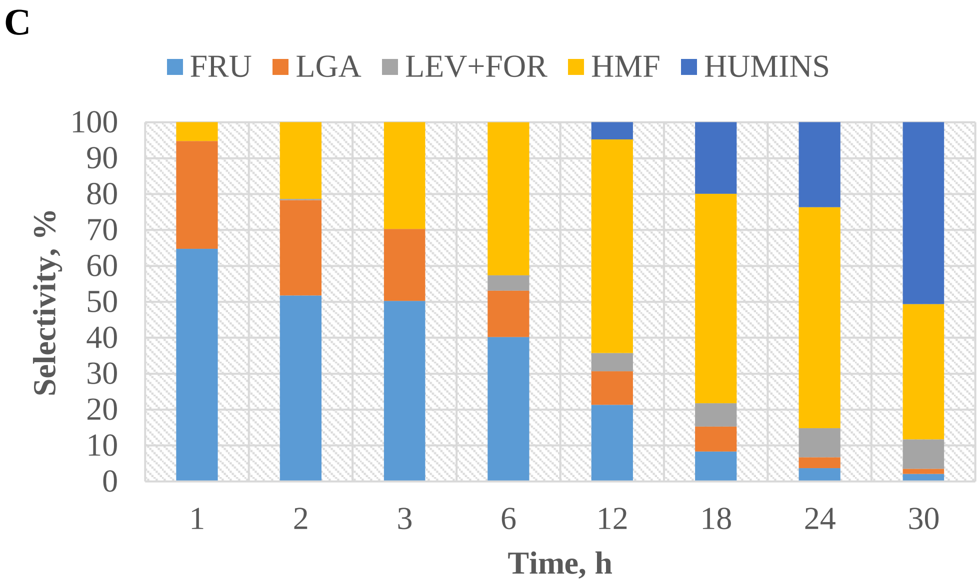


Figure IV.3.11. *Product selectivity distribution over A) Ca/AC, B) pTSA/AC, and C) pTSa-Ca/AC catalyst, (m* $_{glucose}$*= 180 mg, time= 24 h,* v_{H20}*= 1,5 mL, MIBK/*H_2O*, 6/1v/v).*

Another important observation is the appearance of humins in the early stage of reaction proceeding via LGA pathway (*p*TSA/AC, Figure IV.3.11 B). Humins presence suggests an important rate of glucose-glucose and HMF-HMF self- polymerization and even some HMF-glucose cross-polymerization. On the contrary, the fructose mediated route (Figure IV.3.11 C) includes formation of di-fructose-di-anhydrides with groups blocked for condensation [65].

In general, the mechanism of reaction seems to be a function of Brønsted/Lewis sites ratio. It is initiated by the protonation of glucose' C_2-OH over AC and -SO_3H Brønsted sites. On first step an enol intermediate is generated and it transforms subsequently either in fructose via hydride transfer from C_2 to C_1 facilitated by Lewis sites or directly in 5-HMF via successive dehydration and cyclization steps, catalyzed by Brønsted sites [66].

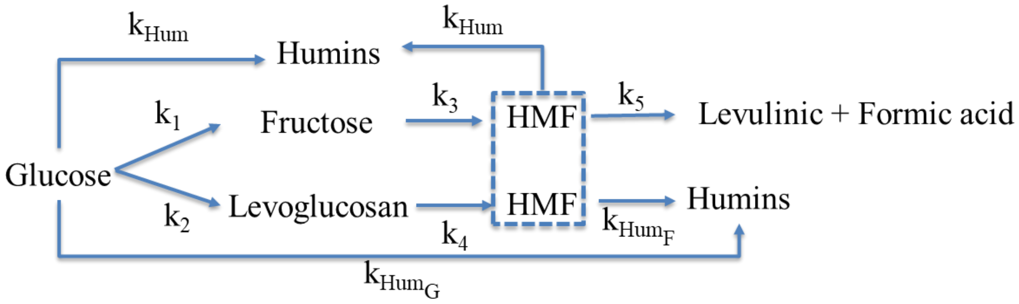
In the same time, the protonation of glucose intermediates is greatly influenced by the solvent system. In particular, it is plausible to suggest that MIBK as an aprotic solvent, like dimethylsulfoxide or THF, enhances the rate of C_2-O bond breaking, leading to an improvement of the rate of HMF formation [67]. Thus, the aprotic solvent addition influences the conformation of glucose, which can be responsible for the change in reaction pathway. In previous study Yun Yu *et al.* [40]. reported that the presence of aprotic solvent provokes a change in glucose tautomer's balance (β-D-glucopyranose as major tautomer) and leads to a direct HMF formation instead of usually preferred isomerization to fructose or production of β-D-anhydroglucopyranose (LGA). This means that in presence of aprotic solvent and strong Brønsted sites the isomerization steps is suppressed and the HMF is formed either via LGA or by a direct HMF formation (*p*TSA-AC case).

However, in presence of Lewis site (Ca-containing catalyst) glucose dehydration pathway swiches to fructose production by lowering the energy of C_2-C_1 hydride transfer. The appearence of this route decreases the rate of humins formation, thus improving the selectivity of the process. *But what is the effect of* Cl^-*?* It has been reported [68], that Cl^- participates as proton aceptor during the H bonding reactions and facilitates the transformation of β-D-glucopyranose in α-D-glucopyranose being the later more easily transformable in enol form (first reaction step) and lowering the energy of the rate-determining step in HMF formation (glucose and/or fructose enolization). Nevertheless, more detailed study is necessary to elucidate the effect of the Cl^-.

If we focus on the catalysts containing Ca, the added Brønsted acidity of the SO_3H group in *p*TSA-Ca/AC facilitates C_2-O bond breaking giving higher fructose yields and faster successive dehydration and rehydration reactions. In contast, poor Brønsted acidity like in the case of Ca/AC sample, makes the reaction pathways energetically challenging between the oficial routes and direct HMF formation in the presence of aprotic solvents with metal halides accelerating the rate-determining step. As a result HMF with moderate to high yields is formed with minimum humins formation. This clearly demonstrates that Ca/AC catalysts is as suitable catalyst as the bifunctional catalyst *p*TSA-Ca/AC in terms of HMF production with low carbon lost.

IV.3.3.3. Kinetic modelling

Based on the literature we have assumed a multi-step pathway model (Scheme IV.5) to analyze the experimental results. Two models are proposed including coincident main steps and different pathways for humins generation. The model 1 considers humins generation from both, glucose and HMF, in separate reactions (k_{HumF} and k_{HumG}); while the model 2 considers the participation of both components in a cross polymerization reaction (k_{Hum}).



Scheme IV.5. Main reactions involved on kinetic models 1 and 2.

The initial glucose can isomerize to fructose or dehydrate to levoglucosan and both products dehydrate to HMF. HMF can further rehydrate or participate in polymerization reaction, either alone or cross polymerizing with glucose. As discussed above dehydration is better catalyzed by Brønsted sites while the isomerization goes improved in presence of Lewis sites.

As a first approach, we have assumed a simple power-law kinetics of first order for all the reactions considered in the above scheme, i.e. $n_i=1$. Therefore, the net rates of each component are given by the following expressions:

Kinetic model 1:

$$r_{Glucose} = \frac{d[Glucose]}{dt} = -k_1 \cdot [Glucose]^{n_1} - k_2 \cdot [Glucose]^{n_2} - k_{Hum_G} \cdot [Glucose]^{n_{HumG}}$$

$$r_{Fructose} = \frac{d[Fructose]}{dt} = k_1 \cdot [Glucose]^{n_1} - k_3 \cdot [Fructose]^{n_3}$$

$$r_{HMF} = \frac{d[HMF]}{dt} = k_3 \cdot [Fructose]^{n_3} + k_4 \cdot [Levoglucosan]^{n_4} - \\ - k_5 \cdot [HMF]^{n_5} - k_{Hum_F} \cdot [HMF]^{n_{HumF}}$$

$$r_{Levoglucosan} = \frac{d[Levoglucosan]}{dt} = k_2 \cdot [Glucose]^{n_2} - k_4 \cdot [Levoglucosan]^{n_4}$$

$$r_{Levulinic} = \frac{d[Levulinic]}{dt} = k_5 \cdot [HMF]^{n_5}$$

$$r_{Humins} = \frac{d[Humins]}{dt} = k_{Hum_G} \cdot [Glucose]^{n_{HumG}} + k_{Hum_F} \cdot [HMF]^{n_{HumF}}$$

(eq.12)

Kinetic model 2:

According to the previous consideration for the humins formation, the net rates of reaction for Glucose, HMF and humins are now given by the following expressions:

$$r_{Glucose} = \frac{d[Glucose]}{dt} = -k_1 \cdot [Glucose]^{n_1} - k_2 \cdot [Glucose]^{n_2} - k_{Hum} \cdot [Glucose] \cdot [HMF]$$

$$r_{HMF} = \frac{d[HMF]}{dt} = k_3 \cdot [Fructose]^{n_3} + k_4 \cdot [Levoglucosan]^{n_4} - \\ - k_5 \cdot [HMF]^{n_5} - k_{Hum} \cdot [Glucose] \cdot [HMF]$$

$$r_{Humins} = \frac{d[Humins]}{dt} = k_{Hum} \cdot [Glucose] \cdot [HMF]$$

The rest of equations remain unchanged. The kinetic parameters were calculated by non-linear least squared multivariable regression, minimizing the total weighted sum of squared residuals for each component:

$$WSSR = \sum_{i} \left(\frac{y_{i,j,\mathrm{exp}} - y_{i,j,\mathrm{calc}}}{\overline{y_{i,\mathrm{calc}}}} \right)^2 \quad ; \quad \overline{y_{i,\mathrm{calc}}} = \frac{1}{n} \cdot \sum_{j} y_{i,j,\mathrm{exp}}$$

The *i* index stands of each one of the products detected in the reaction and n is the number of experimental point of each curve of Figure IV.3.12. The weighting factor taken is the average value of the yield of each component.

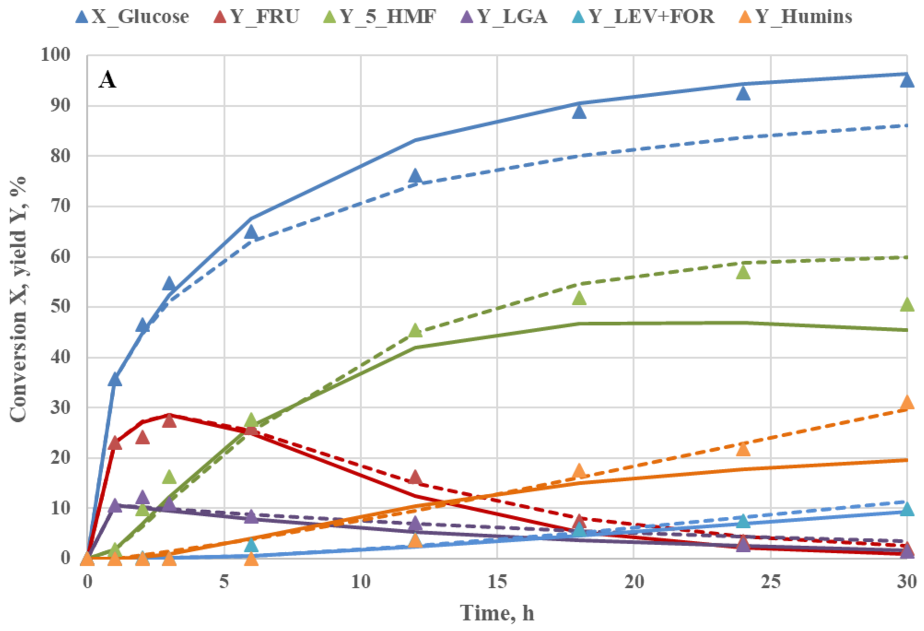
The first approximation of the model (not shown) with fixed first-order for all considered reactions shows very poor concordance with the experimental data for the *p*TSA containing systems (especially for the *p*TSA/AC). So, it was decided to include the n_1 order corresponding to glucose to fructose reaction as a variable parameter.

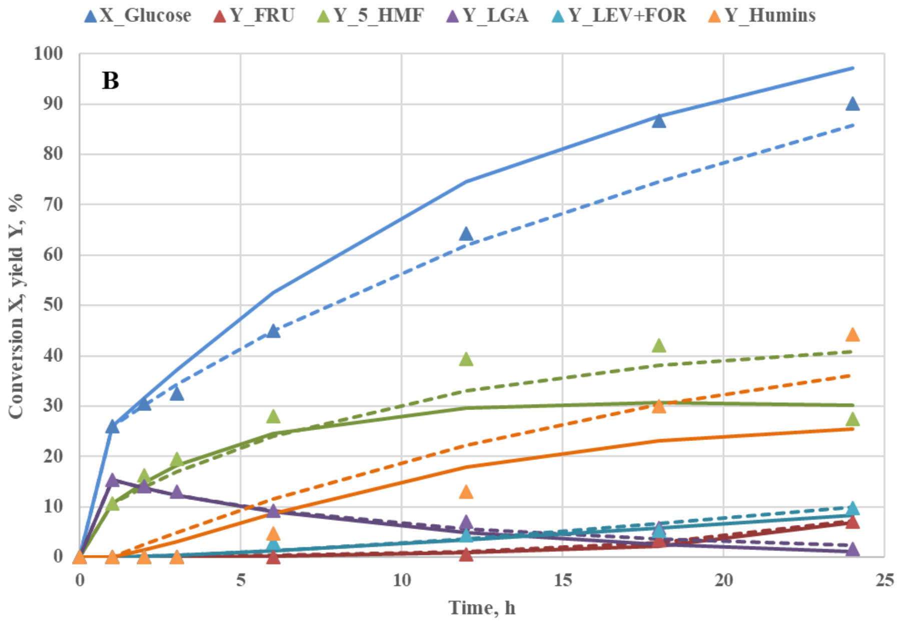
Table IV.3.3. Values of the parameters of kinetic models.

	Model 1		
Parameters	***pTSA-Ca/AC***	***pTSA/AC***	***Ca/AC***
k_1	*2.17E-04*	*2.06E+02*	*8.13E-02*
k_2	*2.47E-10*	*2.41E-02*	*3.66E-11*
k_3	*1.63E-01*	*1.00E-09*	*4.22E-01*
k_4	*3.94E-02*	*2.35E-01*	*6.09E-09*
k_5	*8.82E-03*	*1.40E-02*	*1.64E-02*
k_{HumF}	*1.60E-02*	*7.43E-03*	*8.46E-03*
k_{HumG}	*1.19E-02*	*3.40E-02*	*7.06E-10*
n_1	*2.58*	*-1.92*	*0.88*
Total WSSR	*19.60*	*33.76*	*20.45*
	Model 2		
Parameters	***pTSA-Ca/AC***	***pTSA/AC***	***Ca/AC***
k_1	*3.02E-03*	*8.09E+00*	*6.73E-03*
k_2	*6.76E-04*	*5.79E-02*	*3.33E-02*
k_3	*1.93E-01*	*1.00E-09*	*1.98E-01*
k_4	*6.57E-02*	*4.05E-01*	*2.29E-01*
k_5	*8.33E-03*	*1.32E-02*	*1.60E-02*
k_{Hum}	*1.33E-03*	*1.57E-03*	*2.00E-04*
n_1	*1.96*	*-1.24*	*1.33*
Total WSSR	*37.44*	*53.32*	*17.43*

The as calculated parameters are summarized in Table IV.3.3 and compared to the experimental values in Figure IV.3.12 (experimental values represented by points, proposed model 1 by dashed lines and proposed model 2 by solid lines).

The calculated orders vary from positive to negative and fits fairly well the experimental data. No matter the model, Ca/AC shows n_1 order close to 1 and it could be modeled under pseudo-first order kinetics for all reactions. Nevertheless, the *p*TSA/AC sample shows a negative order close to *-2* indicating that the transformation glucose to fructose in strongly inhibited and the isomerization reaction occurs in very low extension in comparison with the Ca promoted catalysts. Although a high value for the k_1 constant obtained for *p*TSA/AC sample, its input in the overall kinetics is in fact negligible due to the calculated negative order. For the bifunctional catalyst (pTSA-Ca/AC) the kinetic order n_1 is positive and fructose is formed with a lower rate (k_1 constant) in comparison to pure Lewis site catalyst (Ca/AC). In general, the presence of metal halide (samples with Ca) increases the rates of glucose isomerization (k_1) while the presence of *p*TSA increases its dehydration (k_2)


X_Glucose
Y_FRU
Y_5_HMF
Y_LGA
Y_LEV+FOR
Y_Humins
A
Conversion X, yield Y, %
Time, h
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25
30


X_Glucose
Y_FRU
Y_5_HMF
Y_LGA
Y_LEV+FOR
Y_Humins
B
Conversion X, yield Y, %
Time, h
0
10
20
30
40
50
60
70
80
90
100
0
5
10
15
20
25

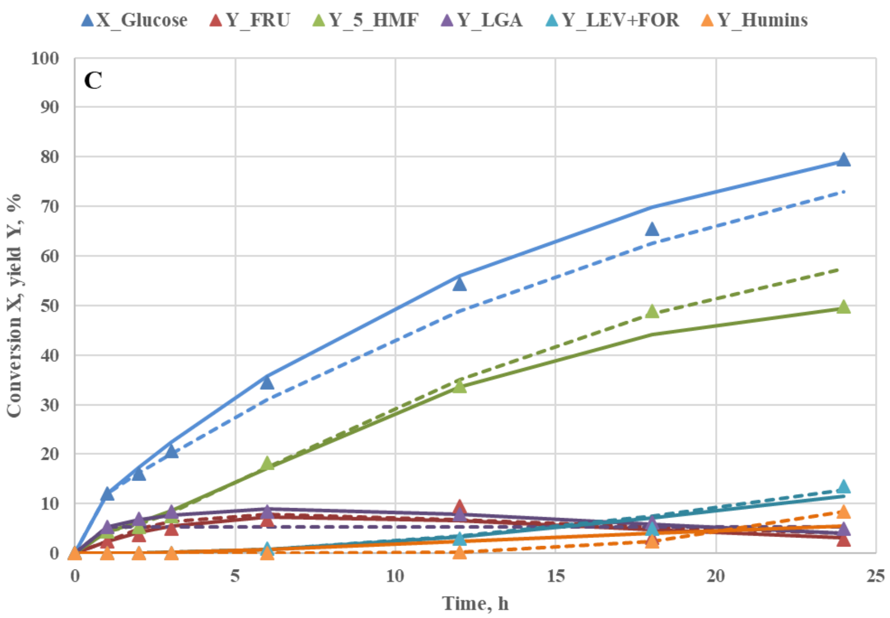


Figure IV.3.12. *Experimental (points) versus calculated model 1 (dashed lines) and model 2 (full lines) conversion and yields for A) pTSA-Ca/AC, B) pTSA /AC and C) Ca/AC catalysts.*

The humins seem to be formed in presence of HMF and, for Ca/AC sample, glucose participates in humins formation *i.e.* humins are formed by cross polymerization of glucose and HMF. We can conclude that the *p*TSA presence enhances the direct glucose transformation to humins. For both catalysts, k_1 and k_3 are higher than k_2 and k_4 suggesting that the fructose mediated route is in general faster than levoglucosan route when Lewis or tandem Brønsted/Lewis acid sites are present.

Both models indicate that for the Ca-containing catalysts the fastest reaction is fructose dehydration (k_3 constant), whereas for the *p*TSA/AC the fastest reaction is levoglucosan dehydration to HMF (k_4 constant). The kinetic models show that for all catalysts the rate of hydration of HMF to levulinic and formic acids is comparable. Similar trends are reported in the literature for different Lewis/Bronsted acid catalysts [69–71].

The main difference between the results obtained with both models can be found in the k_2 constant, corresponding to glucose transformation to levoglucosan. The bifunctional *p*TSA-Ca/AC sample accelerates the levoglucosan transformation reaction, maintaining the fructose mediated route and resulting in an equilibrate option in energetic terms, but losing some selectivity by accelerating the HMF self-polymerization reaction.

In general, the results obtained with Ca containing catalyst are best fitted with model 2, whereas the results of *p*TSA catalyst/AC are better explained by model 1 (Table IV.3.3). The presence of Lewis sites potentiates the reaction of cross polymerization while the presence of Brønsted sites produces preferably humins via HMF self-polymerization.

IV.3.3.4. Catalyst reuse

Five cuycles of reaction have been caried out with the bifunctional *p*TSa-Ca/AC catalyst, giving satisfactory results in terms of conversion and HMF yield (Figure IV.3.13). Small drop in glucose conversion (from 91 to 83%) and stable HMF yield are observed after the first cycle. In our previous study [56] we have found some leaching of the SO_3H groups of the *p*TSA. The leaching can be in principle responsible for the conversion drop but it must also influence the yields and it is not the case.

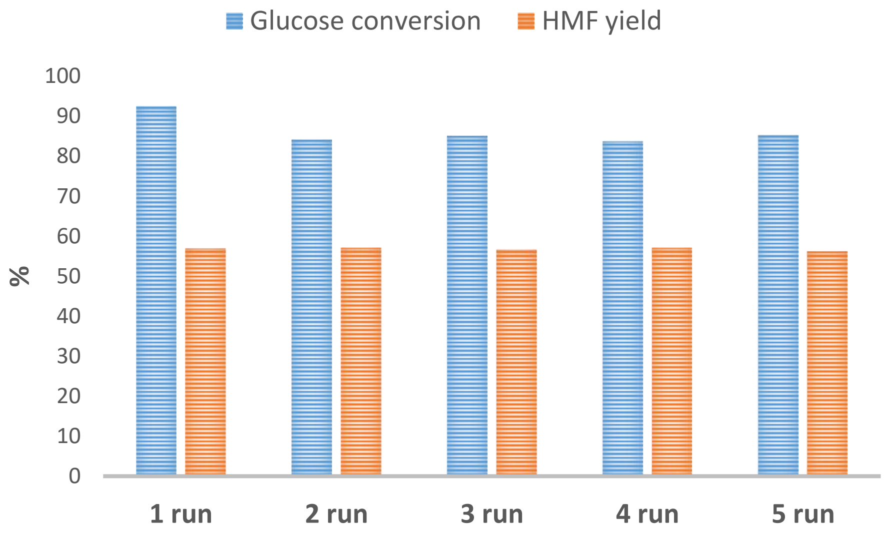


Figure VI.3.13. *Recycling study over pTSA-Ca/AC catalyst* **(***constant glucose/catalyst ratio, time=24h,* v_{H_2O}*=1,5ml MIBK/*H_2O*, 6/1, V/V)*

On the other hand, if we compare the rate constants for humins formation in the proposed models the constants in the first one are greater and suggest higher humins formation from HMF and glucose, separately. The HMF production seems then independent on glucose polymerization as after the first run the yields of HMF are kept intact while the glucose is converted less. This suggests that our loss of activity can be tentativelly atributed to some pores blocking by the formed humins, a non-acumulative process as after the first cycle catalyst seem to maintain its operation without further changes.

Partial conclusion

A series of mono/bifunctional catalysts for glucose dehydration are designed and their functionality was chosen on the base of Lewis and/or Brønsted acid sites addition. The former are introduced by impregnation and activation of metal halides (Zn and Ca chlorides) and the later by impregmation of *p*-toluenesulfonic acid (CH_3-Ph-SO_3H). The activation provokes changes in the hydrophilic/hydrophobic behavior of the solids and on their textural properties. An increase of the mean pore size is observed for all samples no matter the functionalization. Nevertheless, the overall surface area decreases with the introdution of the bulkier *p*-toluenesulfonic acid. The first catalytic screening reveals a superior activity of Ca-containing samples and their detailed study showed that the glucose to HMF reaction patway depends on catalyst composition. The presence of Ca orients the pathway trough fructose intermediate while the presence of *p*TSA directs it to a LGA intermediate. However if we combine the sites, the C_2-O bond breaking reaction is improved leading to higher fructose yields and faster dehydration and rehydration reactions. Both pathways, operates cooperativelly and HMF is produced more rapidly. Nevertheless, tandem Lewis/Bronsted sites accelerates the reaction of humin formation (bare aldehyde polymerization or cross-polimerization) and a catalyst with poor Brønsted acidity is as preferable to achieve moderate HMF yield without humins formation. The bifunctional catalysts reveals as stable efficient system maintaining HMF yield during 5 cycles of catalyst reuse.

IV.4. One pot transformation of glucose to LA over sulfonated AC promoted by calcium chloride

LA synthesis usually involves the dehydration/rehydration reactions of hexoses, such as glucose or fructose [72], the former producing HMF that is subsequently re-hydrated to equimolar LA and FA fraction. This process is usually catalyzed by acids, like sulfuric, formic or hydrochloric acids at relatively high temperatures [73–76]. The levulinic acid yield is proportional to the temperature and acid amount but its increase is conditioned by some corrosion problems and by-products (humins) formation [77]. Humins are usually originated in highly acid conditions where the condensation of HMF intermediate and/or initial hexose causes severe drop in product selectivity and final LA yield [78].

The increase of the reaction rate can be also achieved using organic solvent in monophasic or water/organics biphasic systems. In that case the formation of secondary products is reduced improving the final LA yield. Frequently, aprotic solvents such as dimethyl sulfoxide (DMSO), methyl isobutyl ketone (MIBK) or tetrahydrofuran (THF) are used [77,79,80]. Among them, the MIBK appears an excellent candidate due to its positive solvent effect over glucose transformation reactions and to the easiness of separation with the aqueous phase. But still, the main challenge of this reaction is to find very selective catalyst, unable to produce undesired products while maintaining LA selectivity high enough to allow acid separation and use.

In recent years, the research orients towards homogeneous/homogeneous, homogeneous/heterogeneous or heterogeneous/heterogeneous catalytic systems aiming to achieve a great beneficial effect on biomass transformation rate and LA productivity. A great variation of systems can be found, starting from zeolites/mineral acids [81], sulfonated carbons/chromium halide [82] p-Toluenesulfonic Acid (PTSA)/Chlorides [83] or Amberlyst 15/$Al_2(SO_4)_3$ systems [84]. The necessity of having Brønsted/Lewis acid sites has led to the use of co-catalytic systems, required to achieve a satisfactory activity and selectivity towards desired products.

In this context the main goal of this part is to examine the catalytic behavior of monofunctional homogeneous or heterogeneous systems and their combined action in multifunctional co-catalysts. In particular, heterogeneous/homogeneous co-catalyst based on sulfonated activated carbon as heterogeneous component and dissolved metal chloride as homogeneous component will be used. On first-hand the effect of the sulfonating agent and metal chloride nature will be studied and over the best performing system the effect of some main reaction parameters like biphasic media composition, homogeneous co-catalyst proportion, temperature and time of reaction.

IV.4.1. Experimental

Catalysts preparation

The catalyst preparation is described in detail in chapter III. The used carbon samples are sulfuric acid treated activated carbon (ACS), *p*-toluensulfonic acid treated AC (AC-PTSA), 4-benzendiazoniumsulphonate treated AC (ACS-B) and $CaCl_2$/AC. The functionalization is chosen with the aim to increase the number of Brønsted acid sites by the introduction of sulfonic (SO_3H) groups grafted on activated carbon surface.

Catalytic test

Glucose conversion to levulinic acid is carried out in 50 mL Schlenck reactor equipped with Young valve and magnetic stirrer. In a typical experiment, 180 mg (1 mmol) of glucose and 40 mg of catalyst are mixed in the reactor, containing 5 mL (1.5 mL of deionized water and 3.5 mL of methyl isobutyl ketone MIBK) with or without metal chloride (5 mmol) previously dissolved in the aqueous phase. The reaction mixture is introduced to a preheated oil bath at the desired temperature for a certain time. All experiments are carried out in the 155 – 195 °C temperature range as a function of time (from 0 to 180 min) in MIBK/H_2O biphasic system. After the end of the reaction the products are quenched by submerging the reactor in an ace bath and the liquid phases separated, filtered and analyzed by high performance liquid chromatography (HPLC). The catalytic results are presented in terms of glucose conversion, selectivity and product yields according to the following equations:

$$Glucose\ conversion\ (\%) = \frac{initial\ glucose\ moles - reacted\ glucose\ moles}{initial\ glucose\ moles} x100$$

$$i^{th} product\ selectivity\ (\%) = \frac{moles\ of\ the\ i^{th} product}{reacted\ glucose\ moles} x100$$

$$i^{th}\ \text{product yield}\ (\%) = \frac{\text{produced}\ i^{th}\ product\ \text{moles}}{\text{initial glucose moles}} \text{x}100$$

Catalyst Recycling

For the recycling tests, after the first run, the sample is separated from the solution, washed with ethanol and centrifuged several times before drying. The recovered amount of catalyst is recycled in a 2nd run where the reaction parameters were re-adjusted to have the same substrate/catalyst/$CaCl_2$ ratio as in the 1st run. This procedure is repeated before each cycle.

IV.4.2. Catalysts characterization

Full catalyst characterizations have been described in chapter III and here only a small summary is provided. In general, the catalyst structure is not influenced by the functionalizations, showing a diffraction patterns very similar to that of commercial activated carbon with two principal phases, low crystalline carbon and SiO_2 impurities. The adsorption/desorption isotherms (type IV-H2) are, however, influenced by the functionalization. While sulfuric acid and *p*- toluene sulfonic acid increased the mesoporous component of the samples the covalent functionalization by 4-benzendiazoniumsulfonate decreases it. And what is more, the latter blocks almost completely the micropores and also some mesopores. No matter the functionalization agent the pore size increase for all treated samples. The elemental analysis of the sample showed a total sulfur content increasing in the order AC<ACS< ACS-B ~ AC-PTSA. Three types of sulfur are detected by XPS attributed to sulfate H/R-SO_4, sulfonate H/R_2-SO_3 groups and C-S tiophen type bond present in parent activated carbon. The surface sulfur composition increase in the same order as the total content does. An increase of the acidity of the samples is observed by measuring the pH of the catalyst slurry which decreases significantly from AC to AC-PTSA (6.6 *vs.* 3.4).

Figure IV.4.1 shows ammonia desorption profiles obtained after the TPD-NH_3 of all sulfonated AC compared to the non-functionalized carbon. The temperature of ammonia desorption is indicative for the retention capacity of the acid centers and, therefore, it informs us of their relative strength, the higher the desorption temperature the greater the acidic force of the centers.

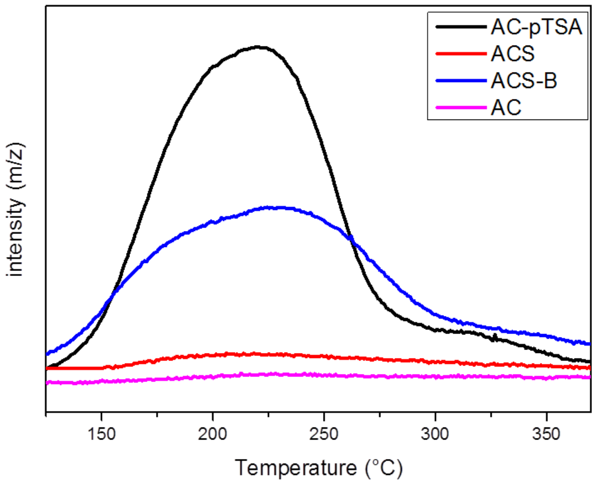


Figure IV.4.1. *NH_3-TPD profile of the studied samples*

The temperature of desorption was restricted to 400ºC due to the possibility of sulfate/sulfonate decomposition to SO_x around 480 ºC. Such decomposition could reduce the thermal stability of the carbons and could falsify the NH_3 desorption signal above 480 ºC [85].

In all cases, a broad peak in the 150–275 °C range is observed and corresponds to weak acid sites attributed to the presence of functional groups on activated carbon surface, such as -OH, -COOH, lactone or superficial sulfonic groups (-SO_3H). These groups interact with NH_3 molecules resulting in the formation of weak Lewis acid sites and ammonia desorption at low temperatures. On the other hand, the small broad peak centered at 310–370 °C for AC-pTSA and ACS-B catalysts suggests the presence of stronger Brønsted acid sites for these two samples in important interaction with the carbon structure.

The integration of the area under the desorption curve is proportional to the amount of desorbed ammonia and allow the semi-quantification of all adsorbing acid centers. The treatment with sulfuric acid of the initial activated carbon produces insignificant increase of the ammonia adsorption capacity expressed in relative area units (0.7 vs. 0.65) while the other two treatments provoke a significant growth of the acid sites (4.35 and 6.3 for the ACS-B and AC-PTSA samples respectively). It seems that the covalent functionalization of the pristine carbon with 4-benzendiazoniumsulfonate increases the fraction of the stronger acid sites while those produced after *p*-toluenesulphonic acid treatment results in abundant concentration of sites with lower acidity. The general trend in total acidity measured by NH_3-TPD is in agreement with the increasing sulfur content measured by XPS and elemental analysis and the pH of the slurry reflects the total acidity per measured area in a way that, higher the surface lower the slurry pH [86].

IV.4.3. Catalysts behavior

As commented above, glucose conversion to levulinic acid passes through various cascade reactions: i) pyranose to furanose transformation, ii) furanose dehydration to HMF and iii) rehydration to the final levulinic and formic acid mixture. The first step (glucose to fructose isomerization) is the one that needs usually more energy and results promoted in presence of Lewis acid sites as metal chlorides [87,88]. On the contrary, the second dehydration step is improved by the presence of Brønsted sites and solvents like MIBK which participates in the reaction influencing the HMF stability and suppressing its condensation rate by a continuous exchange between aqueous and organic phases [89–91]. Recently, Maellmer et al. [33], using DFT revealed that the presence of polar aprotic solvent containing chloride anion could interrupt the hydrogen-bonding networks leading to hydrophilic domains formation. They also predicted that the chloride ions will locate near the hexoses acting as stabilizers of their protonated transition state facilitating de/rehydration reaction. Although that MIBK doesn’t enter that group of solvents its combination with catalyst containing Cl^- should result in a similar effect on catalyst activity. And finally, the last step of HMF re-hydration is only possible in presence of water.

Considering all requirements to ensure/promote an efficient glucose transformation to levulinic acid, the use of biphasic system is clearly justified. The partial isolation of HMF in MIBK along with the water presence provides the perfect scenario for the different cascade reactions to take place. Water dosage should be high enough to facilitate the formation of levulinic acid, poorly produced at low water contents [34]. The biphasic media is also helpful to maintain metal chlorides active, as they could become fully coordinated in aqueous media and could not react as hexose stabilizers and promoters of the isomerization step.

In summary, the main products and/or intermediates of glucose transformation in biphasic system must be fructose (FRU) produced after glucose (GLU) isomerization, HMF as a product of pyranose/furanose dehydration and levulinic (LA) and formic (FOR) acids as products of the rehydration reaction. Additionally, HMF and glucose could participate in secondary reactions to form soluble/insoluble oligo/polymers called humins extremely difficult to quantify. That is why, their formation will be analyzed in terms of carbon balance decrease, assuming that all the compounds of the main pathways are identified and all carbon loss, if any, is a product of humins formation.

IV.3.1. Homogeneous vs. heterogeneous catalysis

The conversion of glucose in homogeneous media was carried out in presence of $CaCl_2$ and PTSA separately or in combination. 5 mmol of dissolved $CaCl_2$ are used as Lewis acid site while 0.5 M (7.5 mmol) PTSA solution was used as Brønsted acid site. Glucose conversion, LA and HMF yields and total products selectivity are presented in Figure IV.4.2.

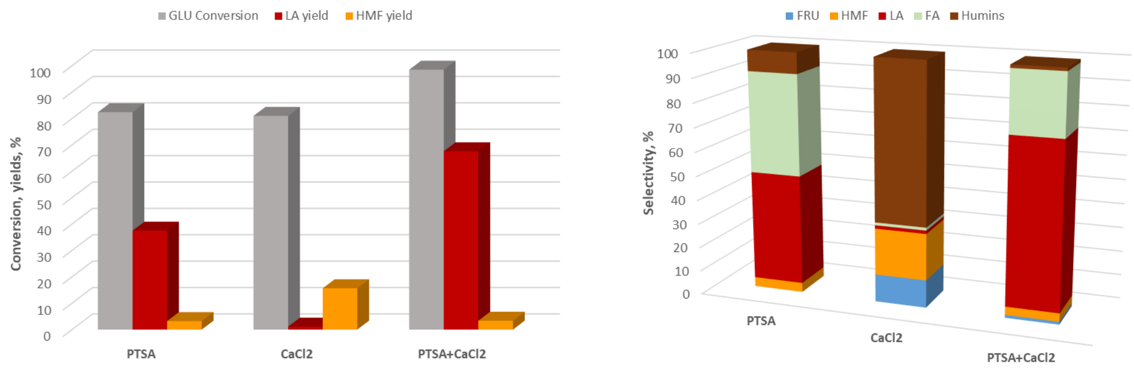


Figure IV.4.2. *Glucose dehydration over single and combined homogeneous catalysts. (time =120 min, T=175 °C MIBK/H_2O 3.5mL/1.5mL v/V, n_{CaCl2} = 5mmol, n_{PTSA}= 7,5 mmol, $n_{glucose}$ =1 mmol (12%; W/V) , $m_{catalyst}$= 40 mg)*

In terms of glucose transformation, combining both types of catalysts (PTSA+$CaCl_2$) results in higher conversion than using them separately. This beneficial effect is also observed for the levulinic acid yields. The presence of Brønsted acids, like PTSA in particular, promote LA production and suppress the secondary reactions; the humins formation decreases significantly when the catalyst is *p*-toluene sulfonic acid. The products distribution is also influenced by the type of catalyst. $CaCl_2$ is by far the less selective catalyst due to its inability to participate in dehydration/rehydration steps. Nevertheless, the presence of HMF indicates that $CaCl_2$ catalyzes its production, more probably by a partial hydrolysis in aqueous phase and the generation of protons that are the actual catalysts [35]. An important formation of humins is also observed for this catalyst due to the acceleration of its condensation rate in presence of Lewis sites.

On the other hand, PTSA catalyst had a significant impact on the LA yield. The absence of fructose in the product distribution for this sample suggests HMF production via levoglucosan route [94]. Yang et al. [95] reported a computational study on the possible direct glucose transformation to LA using Brønsted acids. The route proceeds through water molecule removal from glucose to produce an intramolecular H transfer between O2–3 and O3–4 that directly leads to the removal of formic acid and formation of stable carbonaceous species convertible in LA. Consequently, the presence of both acids accelerate the overall reaction and limits the side reaction of HMF polymerization and/or condensation resulting in higher LA yield and less carbon loss. Indeed, for the PTSA catalyst the LA and FA are obtained practically in one to one composition.

The LA selectivity and yield are significantly improved with the mixture of both active sites (Lewis and Brønsted), the two different pathways increase the LA production. The generation of humins is completely inhibited due to the fastest HMF production and conversion to LA. HMF is produced via fructose helped by the Lewis sites while the Brønsted sites converts it as soon as obtained in LA. The production of formic acid is not consistent with 1 to 1 theoretical production due more probably to a possible formic acid decomposition to CO_2, H_2, CO and H_2O at the temperature of reaction, catalyzed apparently by Lewis acid sites [87].

The same catalysts, $CaCl_2$ and PTSA, were supported on activated carbon to produce the corresponding mono/bi functional heterogeneous systems, labelled with an additional * mark using the same nomenclature (detailed information about this series can be found in chapter III).

Glucose conversion, HMF and LA yield and products distribution are presented in the Figure IV.4.3.

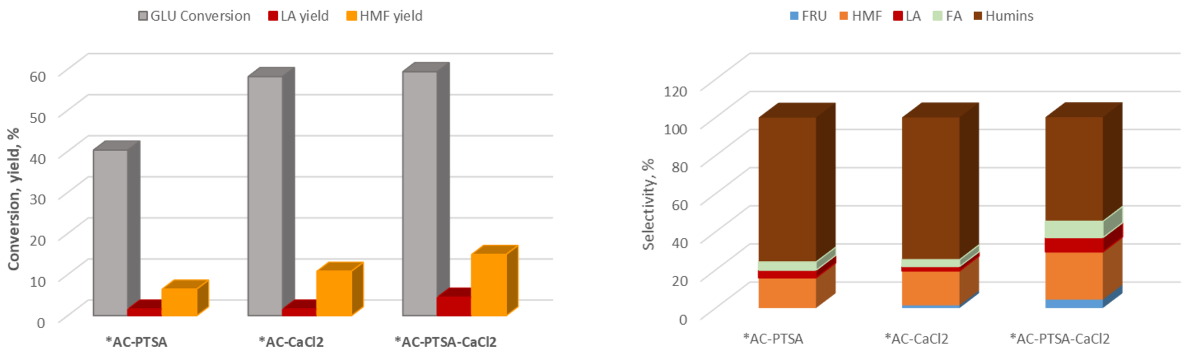


Figure IV.4.3. *Glucose dehydration over single and combined heterogeneous catalysts.*

(time =120 min, T=175 °C MIBK/H_2O *3.5mL/1.5mL v/V,* $m_{catalyst}$*= 40 mg)*

An important decrease in conversion is observed for the heterogeneous system (20-60 % loss) attributed to the different quantity of active sites. For both, supported PTSA and $CaCl_2$ the active sites loading is lower due to the different methodology for catalysts preparation [28] and loss of active sites during washing and activation procedures. In general, this loss of activity can be corrected by the use of higher charge of heterogeneous catalyst. Nevertheless, the most important effect is the change of selectivity for the heterogeneous systems. They appear much selective to humins than to LA (yield less than 5 %). The main product in liquid phase is HMF (15 % for the combined sample). Similarly, to the homogeneous system the combination of supported $CaCl_2$ and PTSA increases the conversion and selectivity to liquid phase products. It appears that the heterogeneous system participates actively in glucose dehydration resulting in higher HMF yields but inhibits the re-hydration and favoring the condensation reaction. The later suggest that a combination of heterogeneous and homogeneous co-catalyst should result beneficial by increasing i) the isomerization and rehydration rate due to the homogeneous component (dissolved chloride) and accelerating the ii) dehydration rate due to the heterogeneous component (AC-PTSA).

IV.4.3.2. Heterogeneous/homogeneous co-catalysts

Two are the general ways to influence the co-catalyst system, either by functionalizing the activated carbon or by changing the nature of the used homogeneous component (dissolved chlorides). The series of sulfonated activated carbons was tested in presence of 5 mmol of calcium chloride as homogeneous component and the results are presented in Figure IV.4.4.

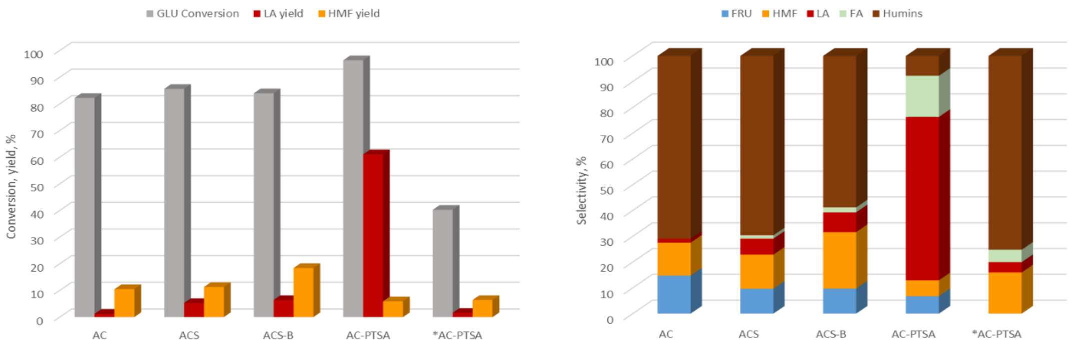


Figure IV.4.4*. Activity of the sulfonated AC/calcium chloride series. (time =120 min, T=175 °C MIBK/*H_2O *3.5mL/1.5mL v/V,* n_{CaCl2} *= 5mmol,* $n_{glucose}$ *= 1mmol, (12%; W/V) ,* $m_{catalyst}$*= 40 mg)*

The use of bare AC-pTSA catalyst in absence of $CaCl_2$ (labelled *AC-pTSA in the figure) does not present a satisfactory result in terms of LA. On the contrary, its combination with metal halide shows very similar results to homogeneously mixed catalysts. That difference in behavior is justified by the lack of Lewis sites for isomerization of bare AC-PTSA catalyst. The difficulty in producing fructose decreases the rate of HMF production and subsequent conversion and causes an increase of humins fraction. However, the same sample mixed with calcium chloride (dissolved in the aqueous phase) presents the best reaction media for LA production. Most probably glucose isomerization is promoted by the presence of calcium chloride while the dehydration/hydration steps are monitored by the heterogeneous AC-PTSA surface to finally achieve almost full glucose conversion for

61% of LA yield and negligible humins production. The positive effect can be also attributed to the facility of the alkaline-earth metal cations to interact with glucose' oxygen atoms, forming bidentate complexes. García-Sancho et al. [96] revealed that Ca^{2+} ions favor the α-D-glucopyranose tautomer by shifting the α/β conformer equilibria towards α form , the conformation preferred for direct transformation of glucose in HMF. In addition, calcium chloride presence increases the partitions coefficient of HMF [97], where it's possible that the hydrophobic AC-pTSA Brønsted acidic catalyst produce levulinic acid by hydration not only in aqueous phase but also in the organic phase (close to the interphase).

As for the other catalysts, the sulfonation of AC by sulfuric and sulfanilic acids increases levulinic acid and HMF yields, but the values are unsatisfactory compared to those of AC-PTSA catalyst. It is clear that an increase of the Brønsted sites ($-SO_3H$) increases the LA yield but it seems also to depend on the changes that are produced over the catalyst after sulfonation. The lower pore volumes measured for the AC-B catalyst can explain the lower catalytic activity in comparison to the AC-pTSA catalyst with almost the same density of acid sites observed. If we suppose that dehydration occurs on carbon, the lower surface could slow down the glucose dehydration reaction increasing the possibility of HMF polymerization to humins. Indeed an increase of that fraction is observed. The contrary occurs for the AC-pTSA sample, the great density of sites combined with higher surface and pore volume results in a finely balanced catalyst for high LA yield and low humins formation. Based on this, the heterogeneous component of the catalytic system, AC-PTSA, was selected to study the effect of metallic chloride nature.

The effect of three alkaline-earth chlorides is compared to that produced by NaCl and $ZnCl_2$ as presented in Figure IV.4.5.

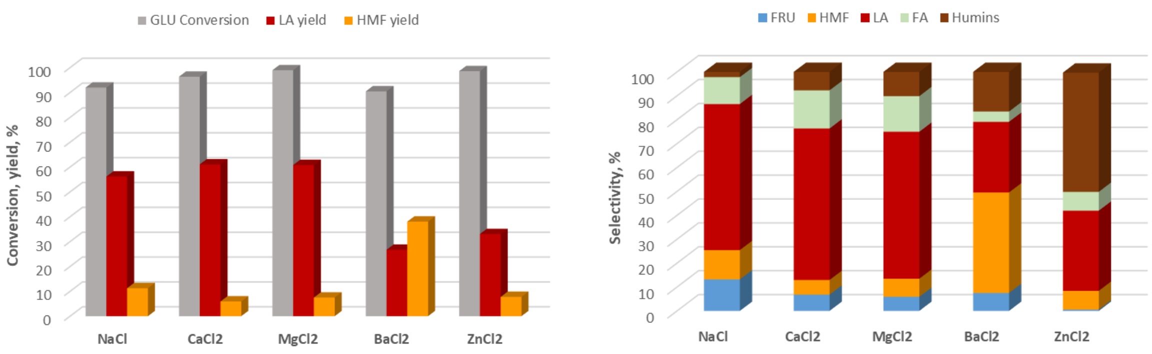


Figure IV.4.5. *Effect of chloride type. Reaction conditions: (time =120 min, T=175 °C MIBK/*H_2O *3.5mL/1.5mL v/V,* n_{MClx} *= 5mmol,* $n_{glucose}$ *= 1mmol, (12%; W/V) ,* $m_{catalyst}$*= 40 mg)*

All catalyst present glucose conversion ≥ 90 %. The use of $ZnCl_2$ results in higher humins production for moderate LA yields. Zinc possess an amphoteric character and in aqueous media can form $Zn(OH)_2$ which might increase the Brønsted acidity of the system and affect the HMF/LA production increasing the rates of polymerizations/condensations to humins. The presence of alkaline/alkali earth metals, however, lowers the rate of glucose mutarotation, alters the α/β tautomers ratio and controls the rate of fructose and HMF production. As a consequence, the LA yield increases and humins formation reduces significantly.

If we represent the LA yield as a function of the absolute hardness of the Lewis acids [98] (Figure IV.4.6.), we can observe that any cation with absolute hardness superior to 20 will be suitable, no matter the charge of the Lewis acid site or its ionic radii.

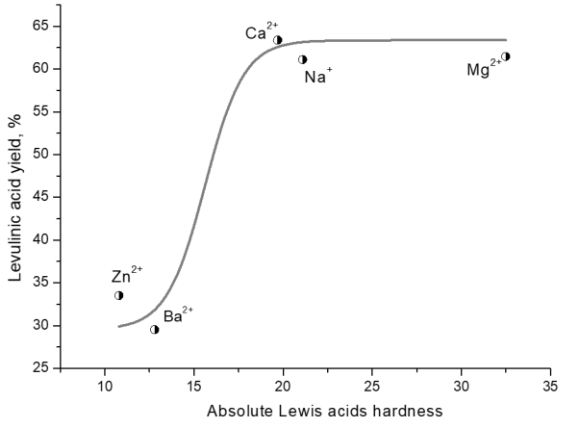


Figure IV.4.6. *LA yield versus metal hardness.*

The effectiveness of the studied inorganic salts must be related to the electron density of their M- glucose' oxygen atoms bond. The hardest acids Mg^{2+} and Ca^{2+} give very similar results in levulinic acid with some excess of humins in the case of Mg^{2+}. The same is true for Na^{+} but with lower humins formation. Finally, the use of barium chloride presents lower conversion and selectivity to its alkali earth homologues.

Based on the obtained results AC-PTSA/$CaCl_2$ system is selected to optimize the reaction parameters, such as time, temperature, heterogeneous/homogeneous component ratio, solvent ratio and catalyst charge. The products yield and distribution dependency on time are presented in Figure IV.4.7.

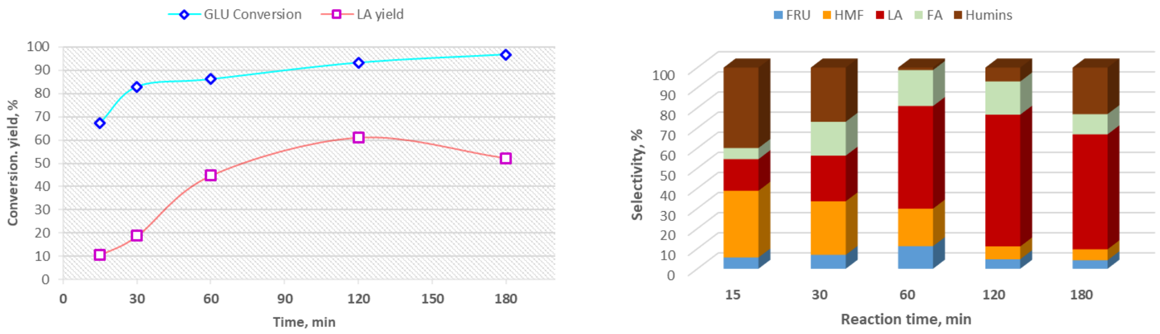


Figure IV.4.7. *Time effect of glucose dehydration over functionalized activated carbon catalysts. Reaction conditions (T=175°C MIBK/*H_2O *3.5/1.5 V/V,* n_{CaCl2} *=5mmol,* $m_{catalyst}$*=40mg)*

Glucose conversion increases progressively with reaction time reaching a maximum at 3 h of reaction. Nevertheless, the LA yield does not follow exactly the same evolution presenting a maximum at 2 h of reaction. After that the selectivity to dehydration products decreases and the system generates a black liquid indicating humins formation. The dominating intermediate is HMF suggesting that the LA is produced after its hydration. Fructose is also detected indicating that at least one part of glucose is transformed via isomerization route. At longer reaction times fructose and HMF are almost totally consumed with a concomitant formation of levulinic acid. Formic acid is also produced with maximum selectivity at 30 min, in lower quantities compared to levulinic acid. The humins selectivity follows down- and- up behavior, reaching a minimum at 60 min. The initial low carbon balance (considered in general as humins formation) could be due also to Ca^{2+}- tautomer complexes formation (not detected by the analysis) or carbon loss by formic acid degradation. The absence of color of the reaction solution supports that idea. Nevertheless, at higher reaction time, the change of color indicates unequivocally humins formation.

The influence of reaction temperature on glucose conversion and products distribution is presented in Figure IV.4.8. Hexose conversion increases linearly with the temperature and temperatures higher than 155 °C are needed to produce LA. At the lowest measured temperature, high amount of fructose and less than 50% total dehydration/rehydration products selectivity is detected being HMF much more present than the targeted LA. At 175 °C, however, LA is the main product accompanied with some fructose, HMF and humins. Further increase to 195 °C provokes an increment of humins suggesting that oligo/polymerization is favored at higher temperatures.

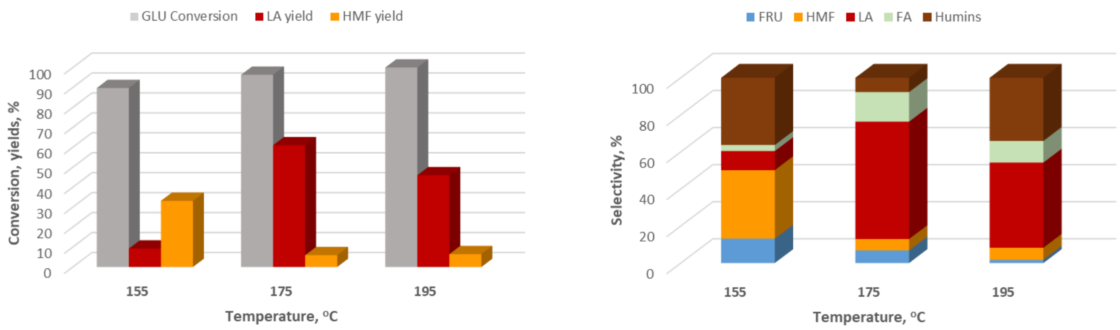


Figure IV.4.8. *Temperature effect on glucose dehydration over functionalized activated carbon catalysts (AC-PTSA) Reaction conditions (time =120min, MIBK/*H_2O *3.5/1.5 V/V,* n_{CaCl2} *=5mmol,* $m_{catalyst}$*=40mg)*

The concentration of the acidic sites has a major impact on the reaction efficiency and viability. The increase of the $CaCl_2$ fraction increases slightly the overall conversion but influences significantly LA productivity from 36% for 0.625 mmol to 61% for 5 mmol of used salt as co-catalyst (Figure IV.8). The increase of the homogeneous component benefits the isomerization reaction facilitating the HMF production and selective conversion to LA. This influences also positively the carbon balance by decreasing the humins yield. HMF is observed as dominated intermediate reaching a maximum yield at 1,25 mmol $CaCl_2$ concentration. One could suggest that the higher the salt concentration the higher the degree of complexation of hexoses tautomer's and higher the dehydration/rehydration rate on active carbon surface.

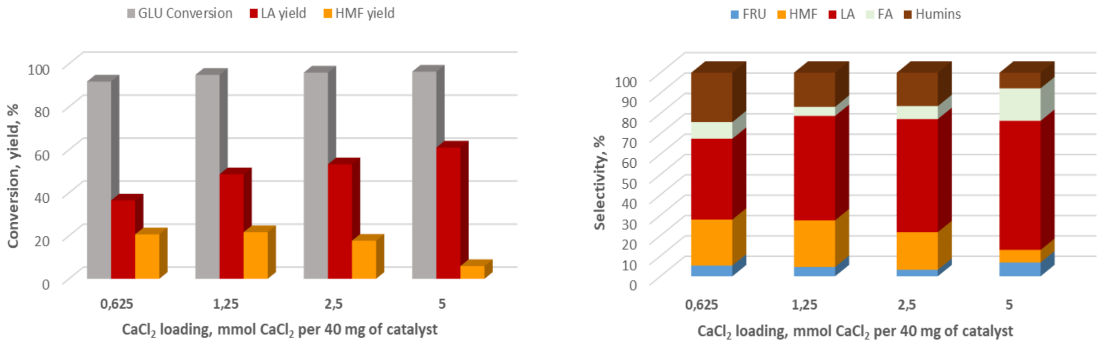


Figure IV.4.8. *Effect of calcium chloride loading over AC-pTSA catalyst. Reaction conditions (time =120min, T=175°C MIBK/H_2O 3.5/1.5 V/V, $m_{catalyst}$=40mg)*

The MIBK/H_2O ratio was studied by increasing the organic fraction keeping constant the aqueous component. The important LA yields at low MIBK/H_2O ratio of 1 and 2.33 (MIBK/H_2O = 1.5/1.5 mL v/v and 3.5/1.5 v/v, respectively) decrease with the increase of the organic fraction (Figure IV.4.9). The decrease of the LA yield in favor to HMF at high MIBK/H_2O ratios suggests that the rate of dehydration/hydration is strictly dependent on the distribution of HMF in both phases. Higher rate of HMF extraction affects negatively the LA yield and increases the humins yield. Strong Brønsted sites interact with MIBK able to extract and prevent HMF from condensation to humins and accelerating its rehydration to LA [99]. At the lowest MIBK/H_2O ratio the organic phase is not enough to extract continuously the intermediate and higher humins fraction is formed. On the contrary, at the highest ratio the aqueous phase appears to be insufficient to equilibrate the dehydration/rehydration reactions and the excess HMF is rapidly converted to humins.

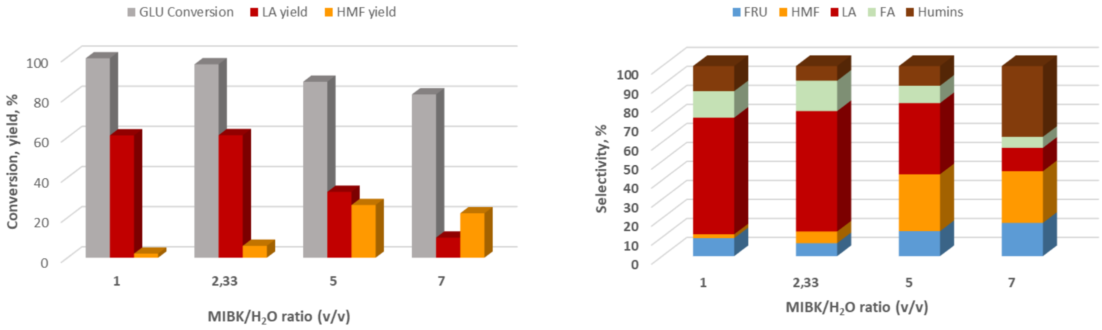


Figure IV.9. *MIBK/H2O ratio effect over AC-pTSA catalyst Reaction conditions: (time =120min, T=175°C MIBK/H_2O V/V, n_{CaCl2} =5mmol, $m_{catalyst}$=40mg)*

Catalyst recycling

The reusability of the heterogeneous catalysts is the main advantages over the homogeneous catalysts. The recyclability of AC-PTSA/$CaCl_2$ catalyst is investigated and the corresponding results are presented in Figure IV.4.10. Compared with the fresh catalyst, the glucose conversion does not change significantly over the cycles and obviously related to the presence of calcium chloride. Nevertheless, the LA yield and selectivity gradually decrease in favor to HMF. This decrease may be caused either by surface blocking by humins deposition or the slight leaching of SO_3H groups of the PTSA. In any case, the presence of a renewable homogeneous component maintains the conversion but the product yield appears affected by the changes produced on the heterogeneous component of the catalytic system.

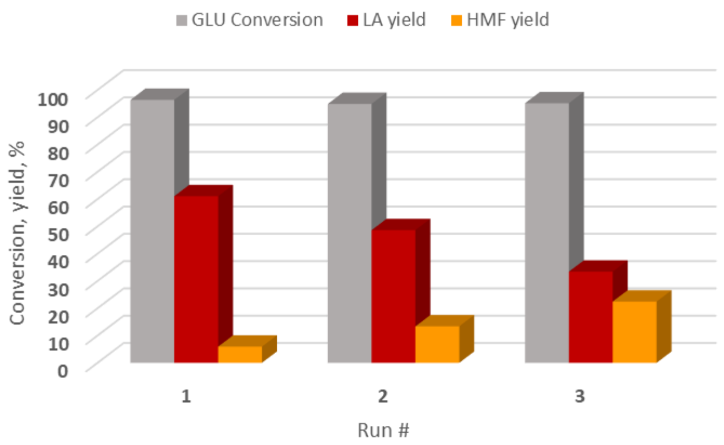


Figure IV.10. *Glucose dehydration reaction recycling over AC-pTSA catalyst. Reaction conditions (time =120min, T=175°C MIBK/H_2O 3.5/1.5 V/V, nCaCl2 =5mmol, mcatalyst=40mg)*

Partial conclusion

Co-catalytic systems having Brønsted/Lewis acid sites are clearly efficient for the production of levulinic acid from glucose monomer. Combining homogeneous catalysts such as PTSA+$CaCl_2$ results in high glucose conversion values with important levulinic acid yields and remarkably low humins percentage. On the other hand, their heterogeneous homologues showed an improved dehydration behaviour but suffered from higher humins formation. The PTSA heterogenization through its immobilization on activated charcoal, AC-PTSA, allow us to move a step forward to a half heterogeneous catalytic system without compromising the positive results obtained over the homogeneously mixed catalysts (61% of LA yield and negligible humins production). Sulfonation of activated carbon by sulfuric and sulfanilic acids increases levulinic acid and HMF yields in respect to the bare AC, but the efficiency is far from that of AC-PTSA catalyst which seems to be ascribed to a combination of great density of sites along with high surface and pore volume. No matter the alkaline/alkali-earth metal used, its presence increases the LA yield being suitable any cation with absolute hardness superior to 20, whatever the site's charge or ionic radii.

At the studied conditions, LA yield reaches a maximum after 2h of reaction being 175 ºC the preferred temperature in the 155 - 195 ºC range. The increase of the homogeneous component benefits LA yield, also favoring the carbon balance (less humins formation). MIBK/H_2O ratio has an important impact in the product distribution, being established 2.33 as a limit to maintain reasonable LA yield. Finally, heterogeneous AC-PTSA is efficiently separated from reacted mixture and reused, maintaining glucose conversion (compared to the bare AC-PTSA) but gradually decreasing the LA yield and selectivity in favor to HMF probably caused by leaching of SO_3H groups of the pTSA or by a surface blocking by humins deposition.

[37] J. Liu, M. Yang, C. Gong, S. Zhang, K. Sheng, X. Zhang, Insights into the glucose isomerization mechanism of Al-hydrochar catalyst probed by Al-oxide species transformation, Journal of Environmental Chemical Engineering. 9 (2021) 106721. https://doi.org/10.1016/j.jece.2021.106721.

[38] Valorization of biomass to hydroxymethylfurfural, levulinic acid, and fatty acid methyl ester by heterogeneous catalysts - ScienceDirect, (n.d.). https://www.sciencedirect.com/science/article/abs/pii/S1385894717311658 (accessed November 20, 2021).

[39] R. Weingarten, A. Rodriguez-Beuerman, F. Cao, J.S. Luterbacher, D.M. Alonso, J.A. Dumesic, G.W. Huber, Selective Conversion of Cellulose to Hydroxymethylfurfural in Polar Aprotic Solvents, ChemCatChem. 6 (2014) 2229–2234. https://doi.org/10.1002/cctc.201402299.

[40] B. Song, Y. Yu, H. Wu, Tuning glucose decomposition in hot-compressed gamma-valerolactone/water mixtures: From isomerization to dehydration reactions, Fuel. 238 (2019) 225–231. https://doi.org/10.1016/j.fuel.2018.10.065.

[41] R. Zhong, B.F. Sels, Sulfonated mesoporous carbon and silica-carbon nanocomposites for biomass conversion, Applied Catalysis B: Environmental. 236 (2018) 518–545. https://doi.org/10.1016/j.apcatb.2018.05.012.

[42] X. Xiong, I.K.M. Yu, L. Cao, D.C.W. Tsang, S. Zhang, Y.S. Ok, A review of biochar-based catalysts for chemical synthesis, biofuel production, and pollution control, Bioresource Technology. 246 (2017) 254–270. https://doi.org/10.1016/j.biortech.2017.06.163.

[43] C.G.S. Lima, E.Y.C. Jorge, L.G.S. Batinga, T. de M. Lima, M.W. Paixão, ZSM-5 zeolite as a promising catalyst for the preparation and upgrading of lignocellulosic biomass-derived chemicals, Current Opinion in Green and Sustainable Chemistry. 15 (2019) 13–19. https://doi.org/10.1016/j.cogsc.2018.08.001.

[44] M. Stöcker, Biofuels and Biomass-To-Liquid Fuels in the Biorefinery: Catalytic Conversion of Lignocellulosic Biomass using Porous Materials, Angewandte Chemie International Edition. 47 (2008) 9200–9211. https://doi.org/10.1002/anie.200801476.

[45] Q. Hou, M. Zhen, L. Liu, Y. Chen, F. Huang, S. Zhang, W. Li, M. Ju, Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid, Applied Catalysis B: Environmental. 224 (2018) 183–193. https://doi.org/10.1016/j.apcatb.2017.09.049.

[46] S.-S. Wang, G.-Y. Yang, Recent Advances in Polyoxometalate-Catalyzed Reactions, Chem. Rev. 115 (2015) 4893–4962. https://doi.org/10.1021/cr500390v.

[47] X. Zhang, D. Zhang, Z. Sun, L. Xue, X. Wang, Z. Jiang, Highly efficient preparation of HMF from cellulose using temperature-responsive heteropolyacid catalysts in cascade reaction, Applied Catalysis B: Environmental. 196 (2016) 50–56. https://doi.org/10.1016/j.apcatb.2016.05.019.

[48] B.M.E. Russbueldt, W.F. Hoelderich, New sulfonic acid ion-exchange resins for the preesterification of different oils and fats with high content of free fatty acids, Applied Catalysis A: General. 362 (2009) 47–57. https://doi.org/10.1016/j.apcata.2009.04.019.

[49] N. Aljammal, C. Jabbour, J.W. Thybaut, K. Demeestere, F. Verpoort, P.M. Heynderickx, Metal-organic frameworks as catalysts for sugar conversion into platform chemicals: State-of-the-art and prospects, Coordination Chemistry Reviews. 401 (2019) 213064. https://doi.org/10.1016/j.ccr.2019.213064.

[50] X. Zhao, J. Xu, A. Wang, T. Zhang, Porous carbon in catalytic transformation of cellulose, Chinese Journal of Catalysis. 36 (2015) 1419–1427. https://doi.org/10.1016/S1872-2067(15)60942-1.

[51] B. Zou, X. Chen, C. Zhou, X. Yu, H. Ma, J. Zhao, X. Bao, Highly-efficient and low-cost synthesis of 5-hydroxymethylfurfural from monosaccharides catalyzed by surface treated biomass, Can. J. Chem. Eng. 96 (2018) 1337–1344. https://doi.org/10.1002/cjce.23077.

[52] R.S. Thombal, V.H. Jadhav, Biomass derived β-cyclodextrin-SO 3 H carbonaceous solid acid catalyst for catalytic conversion of carbohydrates to 5-hydroxymethylfurfural, Applied Catalysis A: General. 499 (2015) 213–216. https://doi.org/10.1016/j.apcata.2015.04.021.

[53] Aluminium-biochar composites as sustainable heterogeneous catalysts for glucose isomerisation in a biorefinery - Green Chemistry (RSC Publishing), (n.d.). https://pubs.rsc.org/en/content/articlelanding/2019/gc/c8gc02466a/unauth#!divAbstract (accessed November 13, 2019).

[54] X. Li, K. Peng, Q. Xia, X. Liu, Y. Wang, Efficient conversion of cellulose into 5-hydroxymethylfurfural over niobia/carbon composites, Chemical Engineering Journal. 332 (2018) 528–536. https://doi.org/10.1016/j.cej.2017.06.105.

[55] A. Rusanen, R. Lahti, K. Lappalainen, J. Kärkkäinen, T. Hu, H. Romar, U. Lassi, Catalytic conversion of glucose to 5-hydroxymethylfurfural over biomass-based

activated carbon catalyst, Catalysis Today. (2019). https://doi.org/10.1016/j.cattod.2019.02.040.

[56] A. Berman, M. Epstein, The kinetic model for carboreduction of zinc oxide, J. Phys. IV France. 09 (1999) Pr3-319-Pr3-324. https://doi.org/10.1051/jp4:1999349.

[57] S.A. Schmidt, M. Peurla, N. Kumar, K. Eränen, D.Yu. Murzin, T. Salmi, Preparation of selective ZnCl 2 /alumina catalysts for methyl chloride synthesis: Influence of pH, precursor and zinc loading, Applied Catalysis A: General. 490 (2015) 117–127. https://doi.org/10.1016/j.apcata.2014.11.008.

[58] S.A. Schmidt, N. Kumar, A. Shchukarev, K. Eränen, J.-P. Mikkola, D.Yu. Murzin, T. Salmi, Preparation and characterization of neat and ZnCl2 modified zeolites and alumina for methyl chloride synthesis, Applied Catalysis A: General. 468 (2013) 120–134. https://doi.org/10.1016/j.apcata.2013.08.039.

[59] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B. 61 (2000) 14095–14107. https://doi.org/10.1103/PhysRevB.61.14095.

[60] J.L. Santos, M. Alda-Onggar, V. Fedorov, M. Peurla, K. Eränen, P. Mäki-Arvela, M.Á. Centeno, D.Yu. Murzin, Hydrodeoxygenation of vanillin over carbon supported metal catalysts, Applied Catalysis A: General. 561 (2018) 137–149. https://doi.org/10.1016/j.apcata.2018.05.010.

[61] C.M. Subramaniyam, N.R. Srinivasan, Z. Tai, H.K. Liu, S.X. Dou, Enhanced capacity and cycle life of nitrogen-doped activated charcoal anode for the lithium ion battery: a solvent-free approach, RSC Adv. 7 (2017) 16505–16512. https://doi.org/10.1039/C6RA27836A.

[62] R. Weingarten, G.A. Tompsett, W.C. Conner, G.W. Huber, Design of solid acid catalysts for aqueous-phase dehydration of carbohydrates: The role of Lewis and Brønsted acid sites, Journal of Catalysis. 279 (2011) 174–182. https://doi.org/10.1016/j.jcat.2011.01.013.

[63] Y.J. Pagán-Torres, T. Wang, J.M.R. Gallo, B.H. Shanks, J.A. Dumesic, Production of 5-Hydroxymethylfurfural from Glucose Using a Combination of Lewis and Brønsted Acid Catalysts in Water in a Biphasic Reactor with an Alkylphenol Solvent, ACS Catal. 2 (2012) 930–934. https://doi.org/10.1021/cs300192z.

[64] H. Wang, C. Zhu, D. Li, Q. Liu, J. Tan, C. Wang, C. Cai, L. Ma, Recent advances in catalytic conversion of biomass to 5-hydroxymethylfurfural and 2, 5-

dimethylfuran, Renewable and Sustainable Energy Reviews. 103 (2019) 227–247. https://doi.org/10.1016/j.rser.2018.12.010.

[65] B.F.M. Kuster, 5-Hydroxymethylfurfural (HMF). A Review Focussing on its Manufacture, Starch/Stärke. 42 (1990) 314–321. https://doi.org/10.1002/star.19900420808.

[66] W. Yang, C. Zhang, C. Li, Z.Y. Huang, X. Miao, Pathway of 5-hydroxymethyl-2-furaldehyde formation in honey, J Food Sci Technol. 56 (2019) 2417–2425. https://doi.org/10.1007/s13197-019-03708-7.

[67] V. Vasudevan, S.H. Mushrif, Insights into the solvation of glucose in water, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and N,N-dimethylformamide (DMF) and its possible implications on the conversion of glucose to platform chemicals, RSC Adv. 5 (2015) 20756–20763. https://doi.org/10.1039/C4RA15123B.

[68] C. Zhou, J. Zhao, A.E.A. Yagoub, H. Ma, X. Yu, J. Hu, X. Bao, S. Liu, Conversion of glucose into 5-hydroxymethylfurfural in different solvents and catalysts: Reaction kinetics and mechanism, Egyptian Journal of Petroleum. 26 (2017) 477–487. https://doi.org/10.1016/j.ejpe.2016.07.005.

[69] W. Weiqi, W. Shubin, Experimental and kinetic study of glucose conversion to levulinic acid catalyzed by synergy of Lewis and Brønsted acids, Chemical Engineering Journal. 307 (2017) 389–398. https://doi.org/10.1016/j.cej.2016.08.099.

[70] K. Kumar, S. Pathak, S. Upadhyayula, 2nd generation biomass derived glucose conversion to 5-hydroxymethylfurfural and levulinic acid catalyzed by ionic liquid and transition metal sulfate: Elucidation of kinetics and mechanism, Journal of Cleaner Production. 256 (2020) 120292. https://doi.org/10.1016/j.jclepro.2020.120292.

[71] W. Wei, S. Wu, Experimental and kinetic study of glucose conversion to levulinic acid in aqueous medium over Cr/HZSM-5 catalyst, Fuel. 225 (2018) 311–321. https://doi.org/10.1016/j.fuel.2018.03.120.

[72] C. Antonetti, D. Licursi, S. Fulignati, G. Valentini, A. Raspolli Galletti, New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock, Catalysts. 6 (2016) 196. https://doi.org/10.3390/catal6120196.

[73] I.K.M. Yu, D.C.W. Tsang, Conversion of biomass to hydroxymethylfurfural: A review of catalytic systems and underlying mechanisms, Bioresour Technol. 238 (2017) 716–732. https://doi.org/10.1016/j.biortech.2017.04.026.

[74] W. Guo, Z. Zhang, J. Hacking, H.J. Heeres, J. Yue, Selective fructose dehydration to 5-hydroxymethylfurfural from a fructose-glucose mixture over a sulfuric acid catalyst in a biphasic system: Experimental study and kinetic modelling, Chemical Engineering Journal. 409 (2021) 128182. https://doi.org/10.1016/j.cej.2020.128182.

[75] Kinetics and Reaction Engineering of Levulinic Acid Production from Aqueous Glucose Solutions - Weingarten - 2012 - ChemSusChem - Wiley Online Library, (n.d.). https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/cssc.201100717 (accessed April 18, 2021).

[76] L. Kupiainen, J. Ahola, J. Tanskanen, Kinetics of glucose decomposition in formic acid, Chemical Engineering Research and Design. 89 (2011) 2706–2713. https://doi.org/10.1016/j.cherd.2011.06.005.

[77] V. Bokade, H. Moondra, P. Niphadkar, Highly active Brønsted acidic silicon phosphate catalyst for direct conversion of glucose to levulinic acid in MIBK–water biphasic system, SN Appl. Sci. 2 (2019) 51. https://doi.org/10.1007/s42452-019-1827-z.

[78] G. Portillo Perez, A. Mukherjee, M.-J. Dumont, Insights into HMF catalysis, Journal of Industrial and Engineering Chemistry. 70 (2019) 1–34. https://doi.org/10.1016/j.jiec.2018.10.002.

[79] X. Hu, S. Wang, R.J.M. Westerhof, L. Wu, Y. Song, D. Dong, C.-Z. Li, Acid-catalyzed conversion of C6 sugar monomer/oligomers to levulinic acid in water, tetrahydrofuran and toluene: Importance of the solvent polarity, Fuel. 141 (2015) 56–63. https://doi.org/10.1016/j.fuel.2014.10.034.

[80] M. Mikola, J. Ahola, J. Tanskanen, Production of levulinic acid from glucose in sulfolane/water mixtures, Chemical Engineering Research and Design. 148 (2019) 291–297. https://doi.org/10.1016/j.cherd.2019.06.022.

[81] D. Garcés, L. Faba, E. Díaz, S. Ordóñez, Aqueous-Phase Transformation of Glucose into Hydroxymethylfurfural and Levulinic Acid by Combining Homogeneous and Heterogeneous Catalysis, ChemSusChem. 12 (2019) 924–934. https://doi.org/10.1002/cssc.201802315.

[82] Enhanced Levulinic Acid Production from Cellulose by Combined Brønsted Hydrothermal Carbon and Lewis Acid Catalysts | Industrial & Engineering Chemistry Research, (n.d.).

https://pubs.acs.org/doi/pdf/10.1021/acs.iecr.8b05332?rand=9cb24k4r (accessed April 18, 2021).

[83] M. Sajid, Y. Bai, D. Liu, X. Zhao, Conversion of Glucose to 5-Hydroxymethylfurfural by Co-catalysis of p-Toluenesulfonic Acid (pTSA) and Chlorides: A Comparison Based on Kinetic Modeling, Waste Biomass Valor. (2020). https://doi.org/10.1007/s12649-020-01215-x.

[84] J. Feng, L. Tong, Y. Xu, J. Jiang, C. Hse, Z. Yang, H. Pan, Synchronous conversion of lignocellulosic polysaccharides to levulinic acid with synergic bifunctional catalysts in a biphasic cosolvent system, Industrial Crops and Products. 145 (2020) 112084. https://doi.org/10.1016/j.indcrop.2019.112084.

[85] L.J. Konwar, P. Mäki-Arvela, E. Salminen, N. Kumar, A.J. Thakur, J.-P. Mikkola, D. Deka, Towards carbon efficient biorefining: Multifunctional mesoporous solid acids obtained from biodiesel production wastes for biomass conversion, Applied Catalysis B: Environmental. 176–177 (2015) 20–35. https://doi.org/10.1016/j.apcatb.2015.03.005.

[86] C.E. Bounoukta, C. Megías-Sayago, S. Ivanova, A. Penkova, F. Ammari, M.A. Centeno, J.A. Odriozola, Effect of the sulphonating agent on the catalytic behavior of activated carbons in the dehydration reaction of fructose in DMSO, Applied Catalysis A: General. 617 (2021) 118108. https://doi.org/10.1016/j.apcata.2021.118108.

[87] C.E. Bounoukta, C. Megías-Sayago, F. Ammari, S. Ivanova, A. Monzon, M.A. Centeno, J.A. Odriozola, Dehydration of glucose to 5-Hydroxymethlyfurfural on bifunctional carbon catalysts, Applied Catalysis B: Environmental. 286 (2021) 119938. https://doi.org/10.1016/j.apcatb.2021.119938.

[88] R.-J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, Chem Rev. 113 (2013) 1499–1597. https://doi.org/10.1021/cr300182k.

[89] B.F.M. Kuster, H.J.C.D.V. Steen, Preparation of 5-Hydroxymethylfurfural Part I. Dehydration of Fructose in a Continuous Stirred Tank Reactor, Starch - Stärke. 29 (1977) 99–103. https://doi.org/10.1002/star.19770290306.

[90] Y. Román-Leshkov, J.A. Dumesic, Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts, Top Catal. 52 (2009) 297–303. https://doi.org/10.1007/s11244-008-9166-0.

[91] L. Shuai, J. Luterbacher, Organic Solvent Effects in Biomass Conversion Reactions, ChemSusChem. 9 (2016) 133–155. https://doi.org/10.1002/cssc.201501148.

[92] M.A. Mellmer, C. Sanpitakseree, B. Demir, K. Ma, W.A. Elliott, P. Bai, R.L. Johnson, T.W. Walker, B.H. Shanks, R.M. Rioux, M. Neurock, J.A. Dumesic, Effects of chloride ions in acid-catalyzed biomass dehydration reactions in polar aprotic solvents, Nature Communications. 10 (2019) 1132. https://doi.org/10.1038/s41467-019-09090-4.

[93] J. Wang, H. Cui, Y. Wang, R. Zhao, Y. Xie, M. Wang, W. Yi, Efficient catalytic conversion of cellulose to levulinic acid in the biphasic system of molten salt hydrate and methyl isobutyl ketone, Green Chem. 22 (2020) 4240–4251. https://doi.org/10.1039/D0GC00897D.

[94] I.I. Junior, M.A. do Nascimento, R.O.M.A. de Souza, A. Dufour, R. Wojcieszak, Levoglucosan: a promising platform molecule?, Green Chem. 22 (2020) 5859–5880. https://doi.org/10.1039/D0GC01490G.

[95] Y. Yang, S. Zhang, L. Gu, S. Shao, W. Li, D. Zeng, F. Yang, S. Hao, Stable yolk-structured catalysts towards aqueous levulinic acid hydrogenation within a single Ru nanoparticle anchored inside the mesoporous shell of hollow carbon spheres, Journal of Colloid and Interface Science. 576 (2020) 394–403. https://doi.org/10.1016/j.jcis.2020.05.039.

[96] C. García-Sancho, I. Fúnez-Núñez, R. Moreno-Tost, J. Santamaría-González, E. Pérez-Inestrosa, J.L.G. Fierro, P. Maireles-Torres, Beneficial effects of calcium chloride on glucose dehydration to 5-hydroxymethylfurfural in the presence of alumina as catalyst, Applied Catalysis B: Environmental. 206 (2017) 617–625. https://doi.org/10.1016/j.apcatb.2017.01.065.

[97] C. Lin, C. Chai, Y. Li, J. Chen, Y. Lu, H. Wu, L. Zhao, F. Cao, K. Chen, P. Wei, P. Ouyang, $CaCl_2$ molten salt hydrate-promoted conversion of carbohydrates to 5-hydroxymethylfurfural: an experimental and theoretical study, Green Chem. 23 (2021) 2058–2068. https://doi.org/10.1039/D0GC04356G.

[98] Absolute hardness: companion parameter to absolute electronegativity | Journal of the American Chemical Society, (n.d.). https://pubs.acs.org/doi/10.1021/ja00364a005 (accessed April 18, 2021).

[99] V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, T.A. Nijhuis, The effect of solvent addition on fructose dehydration to 5-hydroxymethylfurfural in biphasic system

over zeolites, Journal of Catalysis. 287 (2012) 68–75. https://doi.org/10.1016/j.jcat.2011.12.002.

General conclusions and perspectives

Although at the end of each chapter, a series of partial conclusions are made this part summarize the most relevant general conclusions of this thesis project.

This work results in the adaptation of an experimental protocol for carbonaceous materials application starting with its production, functionalization and final use as catalyst or support. The carbons used in this thesis are produced from residual biomass (cotton stalks) by pyrolysis and compared to commercially available materials (activated carbon or carbon nanofibers). Then the functionalization is carried out where the most appropriate conditions (nature of the functionalizing agent, temperature, time, heating rate and precursor amount) are determined by evaluation of all materials in reaction of biomass (glucose/fructose) valorization to HMF and levulinic acid, two of the most important platform molecules.

Furthermore, HMF and HMF-derived levulinic acid are used as starting materials for the production of value-added chemicals by hydrodeoxygenation reaction to DMF and GVL respectively. Three different metals (Pt, Ru and Pd) are employed as active sites for this reaction supported on carbonaceous materials.

The structure and surface properties of all designed catalysts are investigated by several different physicochemical characterization technics confirming in all cases the success of the functionalization treatment and the changes produced on material' textural or chemical properties.

Fructose dehydration over sulphonated carbons seems affected by the total sulfur content, support's textural properties and nature of solvent. The different sulphonation methods convert successfully the commercial activated carbon in Brønsted acid catalyst with moderate strength functional groups, active in carbohydrates dehydration to HMF.

Although attractive from green chemical point of view, the solvent free reaction leads to low HMF yields and favors the secondary reactions like HMF rehydration and oligo/polymerization. The switch to a reaction in DMSO media increases significantly fructose conversion which remains unaltered for temperatures superior to 80 ºC whatever the changes of reaction conditions (time or substrate/catalyst ratio). The conversion is ruled mainly by the presence of DMSO (active in absence of catalyst) and the catalyst porosity whereas the selectivity and HMF yield depends on the nature of sulphonating agent. The *p*-toluenesulphonic acid is chosen as the best agent of functionalization and the modified carbons with it show almost complete fructose conversion. On the other hand, the ionic liquids ILs and organoslicates are immobilized and used as heterogeneous catalysts. The functionalization of the CNF by ILs is rather unsuccessful, regarding the poor catalytic performance of the later, suggesting that the introduction of sulfonic Brønsted acid groups to the ILs is highly desirable for dehydration. However, the presence of silicate as Lewis acid with sulfonic groups enhance the catalytic activity to HMF under sustainable conditions using MIBK/H_2O mixture as solvent.

As for glucose, the functionalization of the carbons with alkali earth chlorides shows a good potential for carbon treatment and catalyst activity in the isomerization reaction to fructose. The presence of metal oxide such as MgO on the surface of the catalyst seems to be the responsible for the good activity of the catalysts.

A commercial activated carbon (AC) is used as raw material for the preparation of bifunctional Bronsted/Lewis tandem site solid catalysts for the direct conversion of glucose to HMF in biphasic water - methyl isobutyl ketone (MIBK) system. A series of mono/bifunctional catalysts based on AC are designed and their functionality is chosen on the base of Lewis and/or Brønsted acid sites addition. The former is introduced by impregnation and activation of metal halides (Zn and Ca chlorides) and the later by the introduction of *p*-toluenesulfonic acid (pTSA). On monofunctional catalyst, the results reveal a superior activity of Ca-containing samples while the bifunctional pTSA-Ca/AC catalyst present important efficiency and stability in 5 cycles of catalyst reuse.

Co-catalytic heterogeneous/homogeneous system, pTSA/AC-$CaCl_2$ contains finely balanced population of Brønsted/Lewis acid sites very efficient for levulinic acid production from glucose. A difference to the heterogeneous system the main product on this hybrid catalyst is levulinic acid instead of HMF.

For the hydrodeoxygenation (HDO) of levulinic acid the homemade carbon materials from cotton stalks biomass shows better performance as supports than the commercially available materials. The highest mesoporous surface and specific area of the biocarbons promote the anchoring of the active Ru metal resulting in low particle size and as a consequence high accessibility and HDO activity. The presence of ash and/or hydrophobic character are revealed as limiting activity factors. On the contrary, bigger Ru particle size and higher microporous surface are promoters of activity deactivation caused either by pore blocking or by leaching.

Organosilane immobilization on nanostructured CNF surface helps significantly the ruthenium nanoparticles size diminution and reflects in excellent results in the reaction of levulinic acid (LA) HDO to γ-valerolactone (GVL). This encourages the development of green catalyst hybrid.

Regarding the used active metal, it appears that Pd based catalyst is better for the HDO of 5-hydroxymethylfurfural to dimethylfurane(DMF) in organic solvent medium, while Ru is better to transform LA to GVL in aqueous media. Higher support surface allows also a higher activity for the DMF production. In this reaction a bimetallic PdCo catalyst is applied to test the idea to search for transition metal substitute of the noble metal.

Where the future points are?

Taking into account that the biorefinery concept is still viewed as a new sustainable way to produce chemical commodities in all described field in this thesis still much work is needed. Although the important knowledge received over carbon properties and functionalization a systematic characterization during the reaction or after the reaction is absolutely needed to understand the reasons for catalyst’ deactivation.

The carbon materials are very interesting for biorefinery reaction purposes due to their capability of surface exchange, functionalization and control on hydrophilicity/phobicity. More future application must be explored as they provide the possibility to combine multiple active sites. One possible process is the direct formation of HMF from cellulose.

The potential of the ILs/carbon and organosilica/carbon hybrids is still pending for exploration. The influence of ILs and organosilica nature must be investigated together with the reaction parameters optimization.

The solvent free method of dehydration is also interesting to explore, although some alternative ways of catalyst heating, as microwave or sonication treatment, must be envisaged.

The use of green alternative sources for hydrogenation as formic acid for example formed during the reaction is also an attractive field to be explored.

Conclusions générales y perspectives.

Dans cette thèse, un protocole expérimental pour la synthèse, la fonctionnalisation et l'application catalytique de divers matériaux carbonés a été établi : charbons biomorphes préparés par pyrolyse de biomasse résiduelle (tiges de coton), charbon actif (AC) et nanofibres de carbone commerciales (CNF).

Les conditions de fonctionnalisation ont été optimisées en ajustant différents paramètres tels que la nature de l'agent modifiant, la température, le temps, la vitesse de chauffage et la quantité de précurseur. Les matériaux obtenus dans cette étude ont été testés dans les réactiones de valorisation de la biomasse, tels que d'isomérisation et déshydratation du glucose et fructose pour obtenir le 5-hydroxyméthylfurfural (HMF) et l'acide lévulinique, deux des molécules plateformes les plus intéressantes. Les meilleurs catalyseurs selon cette étude ont été utilisés dans l'hydrodésoxygénation du HMF et de l'acide lévulinique pour produir des composés chimiques à haute valeur ajoutée tels que le 2,5-diméthylfurane (DMF) et la gamma-valérolactone. Comme phase métallique active, trois métaux nobles ont été utilisés, Pt, Ru, Pd.

Les propriétés texturales et structurales de tous les catalyseurs preparés ont été étudiées par différentes techniques de caractérisation physico-chimique qui confirment, dans tous les cas, le succès de la fonctionnalisation et les modifications des propriétés de surface et chimie des matériaux.

La déshydratation du fructose sur les carbones sulfonés semble être affectée par la teneur totale en soufre, les propriétés texturales du support et la nature du solvant. Différentes méthodes de sulfonation convertissent avec succès le charbon actif commercial en catalyseur acide de Brønsted avec des groupes fonctionnels de force modérée, actifs dans la déshydratation des monosaccharides dans le HMF.

Bien que le procédé soit attractif du point de vue de la chimie verte, la réaction sans solvant conduit à de faibles rendements en HMF et favorise les réactions secondaires telles que la réhydratation de l'HMF et son oligo/polymérisation. Le passage à une réaction en milieu organique utilisant le DMSO comme solvant, augmente significativement la conversion du fructose, qui reste sans chamgment a partir des températures supérieures à 80°C, quelles que soient les conditions de réaction (durée ou rapport substrat/catalyseur). La conversion est principalement régie par la présence de DMSO (actif en l'absence de catalyseur) et la porosité du materiau, tandis que la sélectivité et le rendement en HMF dépendent de l'agent de sulfonation. L'acide *p*-toluènesulfonique (pTSA) s'avère être le meilleur, avec une conversion presque complète du fructose. D'autre part, les liquides ioniques (Lis) et les organosilanes sont immobilisés sur le support carboné et utilisés comme catalyseurs hétérogènes. La fonctionnalisation des CNF par les LIs est plutôt inefficace, vue les mauvais résultats catalytiques obtenus à partir de ces derniers, ce qui suggère la nécessité d'introduire des groupements sulfoniques de Brønsted pour favoriser la déshydratation. Cependant, la présence de silanols comme acides de Lewis avec des groupes sulfoniques comme acides de Brønsted améliore l'activité catalytique en utilisant un mélange de MIBK / H_2O comme solvant.

Concernant le glucose, la fonctionnalisation du charbon avec des chlorures alcalino-terreux présente un grand potentiel. De plus, la présence d'oxyde métallique, tel que MgO, à la surface du catalyseur améliore encore plus son activité.

Le charbon actif (AC) commercial a été utilisé pour la préparation de catalyseurs bifonctionnels Brønsted/Lewis pour la conversion directe du glucose à HMF dans un système biphasique MIBK/H_2O. Les sites actifs de Lewis et Brønsted ont été introduits par imprégnation de chlorures métalliques (chlorures de Zn et de Ca) et d'acide p-toluènesulfonique (pTSA), respectivement.

Parmi les catalyseurs monofonctionnels, celui qui contient du Ca montre de bons résultats, bien que c’est le catalyseur bifonctionnel pTSA-Ca/AC qui présente des rendements très élevés et une stabilité importante en 5 cycles de réutilisation.

L'association d'un catalyseur hétérogène, pTSA/AC, avec un catalyseur homogène, $CaCl_2$, conduit à une quantité bien équilibrée de sites acides de Brønsted/Lewis très efficaces pour la production d'acide lévulinique à partir de glucose. Une différence importante entre le système combiné hétérogène/homogène et l'utilisation d'un système hétérogène est que le produit principal de la réaction c’est l'acide lévulinique au lieu du HMF.

Les métaux nobles supportés sur des matériaux carbonés synthétisés à partir de tiges de coton (biochar) sont les meilleurs catalyseurs dans la réaction d'hydrodésoxygénation (HDO) de l'acide lévulinique. La surface mésoporeuse supérieure du biochar favorise l'incorporation du métal actif, la réduction de la taille des particules et, par conséquent, augmente l’ accessibilité de sites actifs et leur activité en HDO. En revanche, une taille de particule de Ru plus grande et une surface microporeuse plus élevée sont des promoteurs de la désactivation catalytique provoquée par le blocage des pores ou frittage. La présence d'impuretés métalliques ou de composés hydrophobes limite également l'activité du catalyseur.

L'immobilisation des organosilanes à la surface du CNF favorise significativement la réduction de la taille des particules de ruthénium, se traduisant en excellents résultats dans la réaction HDO de l'acide lévulinique (LA) à γ-valérolactone (GVL).

Concernant le métal actif utilisé, il semble que le catalyseur à base de Pd soit meilleur pour l'HDO du 5-hydroxyméthylfurfural en diméthylfurane (DMF) en milieu organique, tandis que le Ru est meilleur pour transformer l'acide lévulinique en GVL en milieu aqueux. Une augmentation de la surface spécifique du support permet une plus grande activité pour la production de DMF.

Enfin, l'étude d'une série de catalyseurs bimétalliques PdCo a permis de vérifier la faisabilité d'une substitution partielle du métal noble par un métal de transition, afin de réduire les coûts de production des catalyseurs.

Perspectives

Considérant que la bioraffinerie est un nouveau concept pour l'obtention de produits chimiques à haute valeur ajoutée, il reste encore beaucoup de travail à faire. Les matériaux carbonés s'avèrent très intéressants pour ces procédés car il est possible de moduler leur surface spécifique, de contrôler leur hydrophilie/hydrophobie et de les fonctionnaliser avec des sites actifs d'intérêt.

Dans cette thèse, des informations importantes sur les propriétés et la fonctionnalité du materiux carbones ont été acquises, mais une caractérisation systématique pendant et après la réaction est absolument nécessaire pour comprendre les raisons de la désactivation du catalyseur.

D'autres applications catalytiques peuvent être explorées, puisque le charbone offre la possibilité de combiner plusieurs sites actifs. Une réaction possible est la formation directe de HMF à partir d la cellulose.

Le plein potentiel des hybrides LI/charbone et organosilanes/charbone reste à explorer, et l'influence de la nature de l'organosilane et l'optimisation des paramètres de réaction devraient être étudiées plus en détail.

Entre autres points qu'il serait intéressant d'étudier, on peut mettre en évidence la méthode de déshydratation du fructose/glucose sans utilisation de solvant organique ; des moyens alternatifs de chauffage, tels que le traitement par micro-ondes ou sonication, ou l'utilisation de sources d’ hydrogène alternatives pour l'hydrogénation/hydrodésoxygénation telles que l'acide formique.

Conclusiones generales y perspectivas.

En esta tesis doctoral se ha establecido un protocolo experimental de síntesis, funcionalización y aplicación catalítica de diversos materiales carbonosos: carbones biomorficos preparados por pirolisis de la biomasa residual (tallos de algodón), carbón activo (AC) y nanofibras de carbono (CNF) comerciales.

Las condiciones de funcionalización han sido optimizadas ajustando diversos parámetros como naturaleza del agente modificante, temperatura, tiempo, velocidad de calentamiento y cantidad de precursor. Los materiales obtenidos en este estudio han sido ensayados en la reacción de valorización de biomasa, isomerización y deshidratación de glucosa y fructosa para obtener 5- hidroximetilfurfural (HMF) y ácido levulínico, dos de las moléculas plataforma de mayor interés. Los mejores catalizadores de acuerdo a este estudio han sido empleados en la hidrodesoxigenacion de HMF y ácido levulínico para obtener compuestos químicos de alto valor añadido como 2,5-dimetilfurano (DMF) y gamma-valerolactona. Como fase metálica activa se emplean tres metales nobles, Pt, Ru, Pd.

Las propiedades texturales y estructurales de todos los catalizadores diseñados han sido estudiadas por varias técnicas de caracterización físico-química que confirman, en todos los casos, el éxito de la funcionalización y las modificaciones en las propiedades superficiales y químicas del material.

La deshidratación de fructosa en carbonos sulfonados parece afectada por el contenido total de azufre, las propiedades texturales del soporte y la naturaleza del disolvente. Los diferentes métodos de sulfonación convierten con éxito el carbono comercial activado en catalizador ácido de Brønsted con grupos funcionales de fuerza moderada, activos en la deshidratación de monosacáridos en HMF.

Aunque el proceso es atractivo desde el punto de vista de la química verde, la reacción sin disolvente conduce a bajos rendimientos de HMF y favorece reacciones secundarias como la rehidratación de HMF y su oligo/polimerización. El paso a una reacción en medio orgánico usando DMSO como disolvente, aumenta significativamente la conversión de la fructosa, que permanece inalterada a temperaturas superiores a 80 ºC, cualesquiera que sean las condiciones de reacción (tiempo o relación substrato/catalizador). La conversión se rige principalmente por la presencia de DMSO (activo en ausencia de catalizador) y la porosidad del catalizador, mientras que la selectividad y el rendimiento en HMF dependen del agente de sulfonación. El ácido *p*-toluenosulfónico (pTSA) resulta ser el mejor, con una conversión de fructosa casi completa. Por otra parte, los líquidos iónicos LIs y los organosilanos son inmovilizados en el soporte carbonoso y utilizados como catalizadores heterogéneos. La funcionalización del CNF con LIs es más bien ineficaz, en cuanto a los malos resultados catalíticos obtenidos de este último, lo que sugiere la necesidad de introducir grupos sulfónicos de Brønsted para favorecer la deshidratación. Sin embargo, la presencia de silanoles como ácidos de Lewis junto con grupos sulfónicos como ácidos de Brønsted mejora la actividad catalítica utilizando una mezcla de MIBK/H_2O como disolvente.

En cuanto a la glucosa, la funcionalización del carbón con cloruros alcalinotérreos muestra un gran potencial para el tratamiento del carbono. Además, la presencia de óxido metálico, como MgO, en la superficie del catalizador favorece aún más su reactividad.

El carbón activo comercial (AC) se ha usado como materia prima para la preparación de catalizadores bifuncionales Brønsted/Lewis para la conversión directa de glucosa a HMF en un sistema bifásico MIBK/H_2O. Los sitios activos de Lewis y Brønsted se introdujeron por impregnación de cloruros metálicos (cloruros de Zn y Ca) y ácido *p*-toluenosulfónico (pTSA), respectivamente.

Entre los catalizadores monofuncionales, el que contiene Ca muestra buenos resultados, aunque es el catalizador bifuncional pTSA-Ca/AC el que presenta rendimientos muy altos y una estabilidad importante en 5 ciclos de reutilización.

La combinación de un catalizador heterogéneo, pTSA/AC, con otro homogéneo, $CaCl_2$, resulta en una cantidad equilibrada de sitios ácidos Brønsted/Lewis muy eficaz para la producción de ácido levulínico a partir de glucosa. Una diferencia importante del sistema combinado heterogéneo/homogéneo con respecto al uso de un sistema heterogéneo es que el producto principal de la reacción es el ácido levulínico en lugar de HMF.

Los metales nobles soportados sobre materiales carbonosos sintetizados a partir de los tallos del algodón resultan mejores catalizadores en la reacción de hidrodesoxigenación (HDO) del ácido levulínico que los soportados sobre materiales comerciales. La superficie mesoporosa más alta de los biochar favorece la incorporación del metal activo, la disminución de su tamaño de partícula y, por consiguiente, aumenta su accesibilidad y actividad en HDO. Por el contrario, un mayor tamaño de partículas de Ru y una superficie microporosa más elevada son promotores de desactivación catalítica causada por bloqueo de poros o por sinterización. La presencia de impurezas metálicas o de compuestos de carácter hidrófobo limita también la actividad del catalizador.

La inmovilización de los organosilanos en la superficie de CNF promueve significativamente la disminución del tamaño de las nanopartículas de rutenio, reflejándose en unos resultados excelentes en la reacción de HDO de ácido levulínico (LA) a γ-valerolactona (GVL).

Por lo que se refiere al metal activo utilizado, parece que el catalizador a base de Pd es mejor para la HDO de 5-hidroximetilfurfural a dimetilfurano (DMF) en medio orgánico, mientras que Ru es mejor para transformar ácido levulínico en GVL en medios acuosos. Un aumento de la superficie específica del soporte permite una mayor actividad para la producción de DMF.

Finalmente, el estudio de una serie de catalizadores bimetálicos PdCo nos ha permitido comprobar la viabilidad de una posible sustitución parcial del metal noble con un metal de transición, con el fin de disminuir los costes de producción de catalizador.

Perspectivas

Teniendo en cuenta que la biorrefinería sigue considerándose un concepto nuevo para la obtención de productos químicos de alto valor añadido, aún queda mucho trabajo por hacer. Los materiales carbonosos resultan ser muy interesantes para los procesos de biorrefinería debido a que es posible modular su superficie específica, controlar su hidrofilicidad/hidrofobicidad y funcionalizarlos con especies de interés.

En esta tesis, se han obtenido conocimientos importantes sobre las propiedades y la funcionalidad del carbón, pero es absolutamente necesario realizar una caracterización sistemática durante la reacción y después de ella para comprender las razones de la desactivación del catalizador.

Se pueden explorar otras aplicaciones catalíticas, ya que el carbón ofrece la posibilidad de combinar varios sitios activos. Una posible reacción es la formación directa de HMF a partir de la celulosa.

Queda pendiente de exploración el potencial total de los híbridos LI/carbono y organosilanos/carbono, debiendo investigarse con más detalle la influencia de la naturaleza del organosilano y la optimización de los parámetros de la reacción.

Entre otros puntos que sería interesante estudiar pueden destacarse el método de deshidratación de fructosa/glucosa sin el uso de disolvente orgánico; medios alternativos de calefacción, como el tratamiento por microondas o de sonicación.o el uso de fuentes alternativas de hidrogeno para la hidrogenación/hidrodesoxigenación como, por ejemplo, el ácido fórmico.

Publications lists

G. Delgado Martin, **C.E. Bounoukta**, F. Ammari, M.I. Domínguez, A. Monzón, S. Ivanova, M.Á. Centeno, Fructose dehydration reaction over functionalized nanographitic catalysts in MIBK/H_2O biphasic system, **Catal. Today**. (2020) S0920586120301334.

C.E. Bounoukta, C. Megías-Sayago, F. Ammari, S. Ivanova, A. Monzon, M.A. Centeno, J.A. Odriozola, Dehydration of glucose to 5-Hydroxymethlyfurfural on bifunctional carbon catalysts, **Applied Catalysis B: Environmental**. 286 (2021) 119938.

C.E. Bounoukta, C. Megías-Sayago, S. Ivanova, A. Penkova, F. Ammari, M.A. Centeno, J.A. Odriozola, Effect of the sulphonating agent on the catalytic behavior of activated carbons in the dehydration reaction of fructose in DMSO, **Applied Catalysis A: General**. 617 (2021) 118108.

Charf Eddine Bounoukta, Cristina Megías-Sayago, Svetlana Ivanova, Fatima Ammari, Miguel Angel Centeno, Jose Antonio Odriozola. Homogeneous vs. heterogeneous catalysts for glucose transformation to levulinic acid and the effect of their co-action. **Submitted to ACS Catalysis.**

Abstract

The worldwide demand of energy and its excessive consumption will lead soon to fuel reserve deficiencies and harmful effects over the climate. All this items have caused a shift of the research interest toward new long-term, green, and sustainable energy sources. Such alternative is the catalytic conversion in liquid phase of carbohydrates originated from the renewable lignocellulosic biomass in biofuels and industrial commodities of high added value. To achieve this is necessary to develop an active, robust, and cost-efficient catalyst for carbohydrates chemical valorization trough dehydration, isomerization and hydrodeoxygenation reactions. In this thesis, commercial and homemade (from residual biomass) carbon materials are functionalized and employed as supports and catalysts in the aforementioned reactions. The material's structure and reaction parameters are modified in order to obtain high process efficiency: high conversion and desired product yields. Some kinetic aspects of the reaction are also studied as well as the viability of the catalysts in biorefinery processing at large scale.

Keywords

Glucose/fructose, 5-hydroxymethylfurfural, carbon, isomerization, dehydration, hydrodeoxygenation.

Résumé

La demande mondiale et la surconsommation d'énergie vont entrainer bientôt un épuisement des réserves de carburant et une aggravation de la situation climatique. Cela a amené les chercheurs à se concentrer sur de nouvelles sources d'énergie durables et vertes. La conversion catalytique en phase liquide d'hydrates de carbone issus de la biomasse lignocellulosique est une alternative idéale pour la production de biocarburants et de produits industriels à haute valeur ajoutée. Pour atteindre cet objectif, il est nécessaire de développer un procédé catalytique actif, efficace et rentable de valorisation des carbohydrates par les réactions de déshydratation, isomérisation ou hydrodésoxygénation. Dans cette thèse, des matériaux carbonés commerciaux et préparés en laboratoire à partir de biomasse résiduelle ont été fonctionnalisés. Ces matériaux ont été utilisés comme supports et catalyseurs dans les réactions mentionnées au-dessus. La structure des matériaux et les paramètres de réaction ont été modifiés afin d'obtenir une haute efficacité du procédé à la fois en conversion et en rendement en produits souhaités. Certains aspects cinétiques ont été évalués et la viabilité des carbones fonctionnalisés dans les processus de bioraffinerie à grande échelle a été étudiée.

Mots clés : Glucose/fructose, 5-hydroxymethylfurfural, charbon, isomérisation, déshydrations, hydrodésoxygénation

Resumen

La demanda mundial y el consumo excesivo de energía conducirán pronto a un agotamiento de las reservas de combustible y a un empeoramiento de la situación climática. Esto ha causado que los investigadores fijen su interés en nuevas fuentes de energía sostenibles y ecológicas. La conversión catalítica en fase líquida de carbohidratos originados a partir de biomasa lignocelulósica es una alternativa ideal para la producción de biocombustibles y productos industriales de alto valor añadido. Para lograr este objetivo, es necesario desarrollar un proceso catalítico activo, eficiente y rentable para la valorización de carbohidratos a través de su deshidratación, isomerización o hidrodesoxigenación. En esta tesis, se han funcionalizado materiales de carbono tanto comerciales como preparados en el laboratorio a partir de biomasa residual. Dichos materiales se han empleado como soportes y catalizadores en las reacciones antes mencionadas. La estructura de los materiales y los parámetros de reacción se han modificado con el fin de obtener una alta eficiencia del proceso tanto en conversión como en rendimiento a los productos deseados. Se han evaluado algunos aspectos cinéticos y se ha estudiado la viabilidad de los carbonos funcionalizados en procesos de biorrefinería a gran escala.

Palabras clave

Glucosa / fructosa, 5-hidroximetilfurfural, carbono, isomerización, deshidratación, hidrodesoxigenación.

الملخص

يؤدي الطلب المتزايد على الطاقة واستهلاكها المفرط إلى نقص في الوقود وزيادة مستمرة المخاطر المتعلقة بالاحتباس الحراري

يعد تحويل الكربوهيدرات التي تمثل الجزء الاكبر من الكتلة الحيوية المتجددة الى وقود موارد كيميائية سائلة حلا . مثاليا .السكريات تشكل بدائل مستدامة للطاقة الحفرية و الكثير من المنتجات الصناعية المستخرجة من البترول.

لذلك من الضروري ,و بصفة خاصه تطوير الطرق التحفيزية من اجل تثمين الكربو هيدرات عبر عدة تفاعلات كيميائية والمتمثلة في التماكب ,البلهمة و الهدرجة .في هذه الاطروحة يتم إستعمال مواد كربونية صلبة مصنعة و تجارية تم تفعيلها لاستخدامها كعناصر داعمة و/أو محفزة فالتفاعلات السالفة الذكر.

يتم التحكم جيدا في بنية المواد المصنعة وانظمه التفاعل لتحقيق مردودعالي في عملية التحويل اي منسوب غالي في المنتجات وضبط آلية كل تفاعل .تقدم هذه الأطروحة أيضا عدة نقاط بارزة لاستدامة الكربون الهجين كمحفز غير متجانس في الكيمياء الصناعية والاستعمال الواسع النطاق للمصفاة الحيوية

الكلمات الرئيسية: الجلوكوز/الفركتوز ,البلهمة ,الهدرجة ,HMF

Abstract

The diminishing reserves of fossil resources calls for the exploration of alternative and sustainable feedstocks. Due to its abundance, renewable nature and neutral relation to global warming, conversion of biomass for the production of fuels and chemicals has emerged as an important area of research. Hexoses represent the majority of carbohydrates which are most abundant monosaccharides found in nature, and a fundamental resource to bio-chemicals. Synthesis of HMF through dehydration of hexoses is extensively studied due to importance of HMF as a platform chemical. In fact, HMF is one of the top ten value-added bio-based chemicals listed by the US Department of Energy. The main objective of this work is the catalytic design based on functionalized carbon, for producing two prominent bio-based chemicals, hydroxymethylfurfural (HMF) and levulinic acid (LA) from glucose. Further, using HMF-derived levulinic acid as starting materials for the production of value added molecules by hydrodeoxygenation reaction, are also investigated by noble metal supported on activated carbon. The results reveals a superior activity of Ca-containing samples, the bifunctional catalysts pTSA-Ca/AC reveals as efficient and stable system maintaining HMF yield during 5 cycles of catalyst reuse. For levulinic acid LA synthesis, an important result of LA yield was obtained using catalyst based on AC-pTSA prometed by calcium chloride. Also, excellent results of valorization HMF-derived levulinic acid to γ-valerolactone (GVL), are obtained.

Key words: HMF, LA, glucose, functionalized carbon, dehydration

Résumé

La diminution des réserves de ressources fossiles exige l'exploration de matières premières alternatives et durables. En raison de son abondance, de sa nature renouvelable et de sa relation neutre avec le réchauffement planétaire, la conversion de la biomasse pour la production de combustibles et de produits chimiques est devenue un domaine de recherche important. Les hexoses représentent la majorité des glucides qui sont les monosaccharides les plus abondants dans la nature, et une ressource fondamentale pour les produits bio-chimiques. La synthèse du HMF par déshydratation des hexoses est largement étudiée en raison de l'importance du HMF comme produit chimique plateforme. En fait, le HMF est l'un des dix principaux produits chimiques à valeur ajoutée provenant de la biomasse, énumérés par le ministère de l'Énergie des États-Unis. Le principal objectif de ce travail est la conception catalytique basée sur charbon fonctionnalisé, pour produire deux produits chimiques importants, l'hydroxyméthylfurfural (HMF) et l'acide lévulinique (LA) à partir du glucose. De plus, l'utilisation de l'acide lévulinique dérivé du HMF comme matière de départ pour la production de molécules à valeur ajoutée, par réaction d'hydrodésoxygénation est également étudiée sur catalyseur à base d'un métal noble supporté sur charbon actif. Les résultats révèlent une activité supérieure des échantillons contenant du Ca, les catalyseurs bifonctionnels pTSA-Ça/AC révèlent comme système efficace et stable maintenant le rendement du HMF pendant 5 cycles de réutilisation du catalyseur. Pour la synthèse de l'acide lévulinique LA, d'important résultat du rendement en LA a été obtenu sur catalyseur à base de AC-pTSA favorisé par le chlorure de calcium. D'excellents résultats de valorisation de l'acide lévulinique dérivé du HMF en γ-valerolactone (GVL), ont aussi obtenus.

Mots clés : HMF, LA, glucose, charbon fonctionnalisé, déshydratation

ملخص

يتطلب استنفاد إحتياطيات الوقود الأحفوري استكشاف مواد خام بديلة ومستدامة. نظرًا لوفرة الكتلة الحيوية وطبيعتها المتجددة وعلاقتها المحايدة بالاحترار العالمي ، فقد أصبح تحويل الكتلة الحيوية لإنتاج الوقود والمواد الكيميائية مجالًا مهمًا للبحث. تمثل الهكسوز غالبية الكربوهيدرات التي تعد أكثر السكريات الأحادية وفرة في الطبيعة، وموردًا أساسيًا للمواد الكيميائية الحيوية. تمت دراسة تركيب HMF عن طريق تجفيف hexoses على نطاق واسع بسبب أهمية HMF كمنصة كيميائية. في الواقع ، هي واحدة من أفضل عشر مواد كيميائية ذات قيمة مضافة من الكتلة الحيوية، مدرجة من قبل وزارة الطاقة الأمريكية. الهدف الرئيسي من هذا العمل هو التصميم التحفيزي القائم على الكربون الوظيفي ، لإنتاج مادتين كيميائيتين مهمتين، هيدروكسي ميثيل فورفورال HMF وحمض الليفولينك LA من الجلوكوز. بالإضافة إلى ذلك ، يتم أيضًا دراسة استخدام حمض الليفولينك المشتق من HMF كمادة أولية لإنتاج جزيئات ذات قيمة مضافة، عن طريق تفاعل الأكسجة الهيدروجينية على محفز يعتمد على معدن نبيل مدعوم بالكربون المنشط. تظهر النتائج نشاطًا أعلى للعينات المحتوية على الكالسيوم، تظهر محفزات AC/Ca-pTSA ثنائية الوظيفة كنظام فعال ومستقر يحافظ على إنتاجية HMF خلال 5 دورات من إعادة استخدام المحفز. لتخليق حمض الليفولينك LA ، تم الحصول على نتيجة مهمة لعائد LA على محفز يعتمد على pTA-AC المعزز بواسطة كلوريد الكالسيوم. كما تم الحصول على نتائج ممتازة من ترقية حمض المشتق من HMF إلى ɤ-valerolactone (GVL).

الكلمات الأساسية : HMF، LA، الجلوكوز، الفحم الوظيفي، الجفاف