5. Biomass Transformation into Chemicals Using Zeolites and MOFs

*Óscar Hernando Laguna Espita,¹ Simona M. Coman,²
Miguel Ángel Centeno Gallego¹ and Vasile I. Pârvulescu²*

¹Institute of Materials Science of Seville, CSIC-University of Seville, Américo Vespucio 49, 41092 Seville, Spain.

²Department of Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4–12 Regina Elisabeta Av., Bucharest, Romania.

Keywords: Cellulose, lignin, biorefinery, platform molecule

1. Introduction

Biomass is referred to as a renewable source of materials and energy, which it is most often associated with plants or plant-based materials that are not used for food or as a feed. From a chemical point of view, interest is focused on the valorization of the dry matter of biomass, commonly known as lignocellulosic biomass. Its total annual production exceeds 100,000 million tons of carbon, which corresponds to an associated energy of 1.5×10^3 to 3×10^3 kW h [1]. Lignocellulosic biomass can be produced quickly and at a low cost and is significantly cheaper than crude oil, generating both important economic and environmental advantages [2].

Lignocellulosic biomass is a tridimensional structure mainly composed of three polymers: cellulose, hemicellulose and lignin, together with small amounts of other components, like acetyl groups, minerals and phenolic substituents (Figure 1). *Cellulose* represents the main crystalline component of lignocellulosic biomass, which is formed by repeating units of the disaccharide cellobiose. The second most abundant polymer is *hemicellulose*, which presents an amorphous structure composed of several heteropolymers, including xylan, galactomannan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan. *Lignin* is the third main component, with a three dimensional structure of phenylpropanoid units including *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.

Figure 1. Lignocellulosic biomass generation and composition. By Khanok Ratanakhanokchai, Rattiya Waenukul, Patthra Pason, Chakrit Tachaapaikoon, Khin Lay Kyu, Kazuo Sakka, Akihiko Kosugi and Yutaka Mori. CC BY-SA 3.0. DOI: 10.5772/51820.

All three components of lignocellulosic biomass have a large quantity of oxygen: almost half for cellulose, $(C_6H_{10}O_5)_n$, and around 30 % for lignin, $(C_9H_{10}O_2)_n$. Nowadays, most feedstocks for the manufacture of commodity chemicals and polymers are obtained from fossil oil [3]. To produce them, an intermediate selective oxidation step is required in many cases. However, this step often has a low environmental (E-) factor and generates CO_2 , contributing to an increase in the greenhouse effect. Therefore, it appears wiser to valorize the oxygen already present in the lignocellulosic biomass for the production of commodity chemicals and polymers, and to devote fossil oil to the production of deoxygenated products.

The main step in chemical valorization of lignocellulosic resources involves, the depolymerization of the macromolecules. While for cellulose an efficient hydrolysis can directly generate monomers, lignin fragmentation is more difficult since the polymers are formed by connecting aromatic entities via both etheric and C-C bonds. Thus, the hydrolysis of cellulose is easier and has been reported by enzymatic [4–6], homogeneous [7] or heterogeneous catalysis [8]. The more complex fragmentation of lignin was carried using multiple approaches like fast pyrolysis [9,10] or homogeneous and heterogeneous catalysis [11] followed by extraction [12]. In this case, the result is a cocktail of small aromatic molecules with different functionalities and masses. Figure 2 depicts the fragmentation of cellulose, along with further chemical valorization.

The solvent is very important in the chemical valorization of biomass. To date, achievements in conversion processes in both water and organic solvents have been reported, including the conversion of biomass to sugars, the conversion of sugars to furanic compounds, and the production of lignin monomers [13]. The solvent influences both conversion and product selectivity as it can affect the solubility of the biomass components, including

Figure 2. Fragmentation of cellulose and further transformations.

cellulose and lignin, and also affect the thermodynamics of reactants, intermediates, products, and/or catalysts. Studies carried in sub- and supercritical water revealed the advantages of working under supercritical conditions [14].

Overall, the aim of this chapter is to discuss the use of zeolites and metal-organic frameworks (MOFs) as catalysts for the fragmentation of cellulose and lignin and for the valorization of the resulting monomers

by producing valuable chemicals. This approach is closely related to the concept of *sustainability* [15]. Both zeolites and MOFs present similar properties which make them perfect candidates for their application in these types of reactions, such as shape selectivity, microporosity, the simultaneous presence of Brønsted and Lewis acid sites, metallic active sites, and related crystal structures, which have been discussed in previous chapters. However, important differences exist between both families of materials in terms of diffusion, adsorption and stability aspects. Besides this, MOFs present a structural versatility that allows the tailored design of a huge variety of different MOF structures, exceeding the number of zeolite structures available. On top of this, zeolites are well-known materials applied since the 1960s in different catalytic processes, while MOFs chemistry is just beginning and only a few families of materials have been employed so far. Thus, our chapter will describe firstly the use of zeolites in the main types of reactions for biomass transformation and, in the second part, the differences between and opportunities for using MOFs.

2. Cellulose transformation into chemicals using zeolites

The fragmentation of cellulose and hemicellulose carbohydrate polymers into their C₅ and C₆ constituent sugars and their subsequent transformation into biorefinery platform molecules for chemical commodities represents a unique means for the production of various oxygenates, such as furfural, 5-hydroxymethylfurfural, xylitol, sorbitol, mannitol, gluconic acid, etc. [16] The use of zeolites as market-accessible solid acid catalysts offers big opportunities.

Zeolites are microporous minerals commonly used as catalysts for acid catalysed reactions. They are also known as ‘molecular sieves’, mainly consisting of Si, Al and O, although the replacement of cations by metals such as Ti, Sn or Zn is also possible. The concomitant presence of two cations in different oxidation states in the structure of these materials requires the compensation by a proton, which induces Brønsted acidity, or by an extra-framework cation, leading to Lewis acidity. Thanks to these properties, zeolites can replace inorganic acids in acid catalysed reactions, with the very important advantages of recyclability and the possibility of tuning the acid strength and type. Working with zeolites eliminates volatile and toxic solvents, and halogenated compounds such as alkylating agents. On this basis they are frequently used for the synthesis of fine chemicals [17], as will be presented in a later chapter, and, somehow related, for the

production of chemicals from biomass [18–20]. This section presents examples of these advantages. They mainly refer to H-zeolites and Sn-Beta zeotype [21]. The processes analysed are depicted in Figure 2.

2.1. Transformation of the primary products of the cellulose fragmentation: sucrose, glucose, fructose, xylose, arabinose, galactose, mannose

The isomerization of glucose into fructose is a large-scale reaction typically performed by enzymes, which have as their main disadvantage deactivation and large reaction volumes [22]. Besides the production of syrups, this reaction is also a potential route for the production of chemicals from biomass. In this regard, recyclable catalysts are necessary.

Ca- and Ba-exchanged A, X and Y zeolites were found less selective in this reaction, whereas those with milder basicity such as Na-X and K-X zeolites were found to achieve the isomerization of glucose into fructose with a selectivity of about 90 %. [23]. However, this high selectivity to fructose is only obtained at low glucose conversions, below 25 %. Furthermore, it was found that a significant amount of the cation leached into water (around 15 % in the case of monovalent ion exchanged X zeolites).

Large-pore zeolite containing tin (Sn-Beta) emerged as particularly effective to catalyse carbohydrate transformations. It is able to isomerize hexoses, pentoses and trioses by intramolecular hydride and carbon shift reactions in various solvents, including aqueous media, with high activity and selectivity. [24–27]. The properties of the large-pore zeolite have a dominant effect on these reactions. The reaction is very slow over Sn-MCM-41 or even does not proceed over a medium-pore zeolite like Sn-MFI [28].

2.2. Hydrolytic hydrogenation of glucose to sugar alcohols or hexitols

The hydrolytic hydrogenation of cellulose/glucose to sugar alcohols offers an alternative to petrochemicals and to the current environmental problems [29]. Such catalytic processes would provide promising platform molecules for oxygenates and liquid alkanes [30]. Sorbitol is an eloquent example. It can be used as a sweetener, dispensing agent and humectant in pharmaceuticals, cosmetics and textiles, as well as for the further chemical synthesis of surfactants [31]. To obtain it, the hydrolytic hydrogenation

of cellulose in the presence of metallic (Ir, Ru, Rh, Pd)/ BEA bifunctional catalysts may produce sorbitol with yields of 55.3–72.8 % [32]. The selectivity to sorbitol correlated with the d-band width of the metal, i.e.: Ir > Ru > Rh > Pd. However, besides the metal nature, both the acid groups of BEA zeolite and in the conversion of monosaccharides, the concentration of adsorbed hydrogen species on the zeolite surface played key roles in the formation of sorbitol. In fact, it was later shown that the rate of hexitol formation increases with the degree of zeolite dealumination [33]. The potential of bifunctional Ru/H-USY catalysts for the total conversion of cellulose to sugar alcohols or hexitols in hot liquid water (HLW) is limited by its physicochemical stability, i.e. the long-term catalytic performance of acid sites and noble metal functionality. Zeolite desilication is the main zeolite degradation mechanism in HLW, in which USY zeolite stability depends on two main parameters – framework and extra-framework aluminium content. The former protects the zeolite lattice by counteracting hydrolysis of framework bonds, and the latter, when located at the external crystal surface, prevents solubilization of the zeolite framework as a result of its low water-solubility.

2.3. Production of HMF, furfural and 2,5-furandicarboxylic acid

5-Hydroxymethylfurfural (HMF), furfural and 2,5-furandicarboxylic acid (FDCA) are derivatives of furan compounds, which were listed among the top 10 value-added bio-based chemicals by the US Department of Energy [34]. To obtain it from cellulose, from a mechanistic point of view, glucose needs to be isomerized to fructose, followed by dehydration to HMF. Accordingly, the process requires an isomerization catalyst for the transformation of glucose to fructose and a second component able to catalyse the dehydration [35].

Dehydration of fructose into HMF was found to depend on both acidic and structural properties of the zeolites used [36]. H/Y faujasites and H-Mordenites with Si/Al ratios of 15 and 11 were used. Shape-selective properties and, particularly, the absence of cavities are very important, allowing selectivities over 90–95 % for H-Mordenites [37].

Dehydration of D-xylose into furfural was also reported in liquid-phase over various H-zeolites (H-furrieries, H-Beta, H-ZSM-5, H-Y and H-Mordenite) with various Si/Al molar ratios in different solvent systems: water, dimethyl sulfoxide (DMSO), and a mixture of water and toluene [38]. Conversion and furfural yield generally decreased with an increasing Si/Al

molar ratio, which was closely related to the accessibility of the acid sites, and depended on the solvent: water/toluene > DMSO > water. Thus, H-Beta (25) showed the highest furfural selectivity in water and water/toluene, while H-Mordenite (20) showed the highest furfural selectivity in DMSO. Phase modifiers like DMSO and poly(1-vinyl-2-pyrrolidinone) also helped to suppress undesired side reactions [39]. However, the catalyst should also show high stability in highly acidic aqueous environments to allow coupling the isomerization with other acid-catalysed reactions, namely, the dehydration of the isomerized product. Sn-Beta zeotype has also been reported to catalyse the isomerization of xylose [40].

DFT calculations explained the role of Sn in these reactions [41], indicating that its main contribution is to promote the transformation of the acyclic glucose to a deprotonated fructose intermediate. The catalytic cycle is completed by the closure of the fructofuranose ring and the protonation of the anionic carbohydrate intermediate bound to the Sn site. These steps are facilitated by water molecules, which mediate the proton transfer reactions between the different oxygen-containing moieties of the carbohydrate. According to these calculations, the Sn(IV) tetrahedral lattice site and the hydroxylated SnOH species exhibit very similar reactivity.

The conversion of cellulose to HMF using a complex acid catalyst composed of CrCl_2 /Zeolite/BMIMCl (ionic liquid 1-butyl-3-methylimidazolium chloride) was reported to be active at low catalyst loading and low temperature (<120 °C) [42]. The role of zeolite in this process was to promote cellulose hydrolysis and to slow down the decomposition of the HMF product. Its effect varied in the order: H-Y > H-Beta > H-MOR > H-ZSM-5.

Mesoporous $\text{Nb}_x\text{W}_{8-x}$ oxides synthesized by an evaporation-induced self-assembly method created large amounts of Lewis and Brønsted acid sites, which promoted the isomerization of glucose to fructose as well as its following dehydration to HMF. Mannose was also formed through the epimerization of glucose [43].

5-benzyl-2-furoic acid derivatives are important intermediates for the preparation of a variety of compounds with biological activity [44]. In the classic protocols they are produced by a Friedel-Crafts alkylation with chlorinated acid derivatives using AlCl_3 or ZnCl_2 as Lewis acid catalysts. To obtain methyl 5-hydroxymethyl-2-furoate from HMF, a heterogeneous catalytic alternative comprises consecutive reactions using a two-component catalyst (Au/TiO_2 and an acid catalyst). Au/TiO_2 catalyses the oxidative esterification of HMF, followed by its conversion into methyl 5-benzyl-2-furoate by alkylation of the benzene derivative of interest

Figure 3. The production of 5-benzyl-2-furoate in the presence of a two-dimensional zeolite. (HMF = 5-hydroxymethylfurfural, HMFE = 5-hydroxymethyl furoic acid methyl ester, DOBMF = dimethyl 5,5'-(oxybis(methylene))bisfuran-2-carboxylate). Reprinted with permission from ref. [45]. Copyright 2016 American Chemical Society.

over the solid acid catalyst (Figure 3). For this last step, a number of zeolites with similar Si/Al ratios including H-Beta (Si/Al=12 and 14), MCM-22 (Si/Al=15), USY (Si/Al=12), 2D zeolite ITQ-2 (Si/Al=15), and a hierarchical mesoporous zeolite USY-HYM zeolite (Si/Al=5.3) were considered [44]. The catalytic results demonstrated the need for a balance between acidity and diffusional constraints. Large pore tridimensional zeolites, such as Beta and USY, showed an adequate acidity to carry out the reaction but they presented strong product diffusion limitations that led to rapid deactivation. On the other hand, MCM-41 had pores large enough to allow an easy product diffusion but exhibited a too low acidity for this reaction. Finally, delaminated ITQ-2 zeolite combined both requirements and thus allowed high reaction rates and selectivity.

2.4. Cellulose to levulinic acid

Levulinic acid (LA) represents a versatile bio-based chemical product of the valorization of cellulose and is an important feedstock for the production of many chemical commodities (Figure 4) [45]. It can be obtained by HMF transformation and the presence of a carbonyl and a carboxylic acid group confers to this molecule the properties of a building block for various chemicals [46]. On this basis, the catalytic conversion of carbohydrates to LA over solid catalysts has received much attention over the last few decades. Since these reactions require the presence of strong Brønsted acids, H-zeolites have been largely investigated. Zeolite

Figure 4. Chemical commodities produced from levulinic acid [45].

catalysts like H-ZSM-5 have economic advantages over resin catalysts, in particular, they can be easily regenerated by a calcination treatment after they are deactivated [47]. However, employing these catalysts may result in significantly lower LA yields, especially when high LA concentrations are desired in the product stream. This disadvantage can be eliminated by utilising biphasic systems: an aqueous layer that contains the zeolite and an organic layer to extract the LA produced [47]. 2-*sec*-butylphenol, 4-*n*-hexylphenol and 4-propylguaiaicol already demonstrated to be effective extracting agents for the production of furfural and LA in these biphasic systems [47]. Another advantage of the solvents is that they can be synthesized directly from biomass (i.e. lignin). Hybrid catalysts consisting of a homogeneous (CrCl_3) and a heterogeneous (zeolite Y) catalyst have been indicated as effective in this reaction as well [48,49].

The efficient production of levulinate esters is another important reaction in the valorization of biomass. Zeolites were largely investigated for this esterification because of their adjustable acidity, easy recyclability, and potential economic and environmental benefits. However, levulinic acid esterification with ethanol to ethyl levulinate over H-USY, H-BEA, H-ZSM-5, H-MOR indicated that they are not active enough to be considered in an industrial application [50]. Esterification on these materials occurred with smaller yields compared to other functionalized porous structures, like sulfonic-acid-functionalized SBA-15 catalyst [51].

Figure 5. Reaction pathway for the microwave-assisted hydrogenation of LA in presence of FA using Pd/C catalyst. Adapted from [53]. CC BY 4.0.

2.5. Levulinic acid hydrogenation to γ -valerolactone

Levulinic acid can be transformed to a series of other valuable chemicals. Among these, γ -valerolactone (GVL) is one of the most important. Several catalytic approaches to produce it have been reported. Qi and Horváth [52] demonstrated that working with a homogeneous catalyst with GVL as solvent it is possible to produce GVL directly from fructose having HMF and levulinic acid as the only intermediates.

As an alternative to noble metal catalysts, supported iron oxide nanoparticles on Al- and Zr-SBA-15 were investigated for the hydrogenation of levulinic acid to γ -valerolactone [53]. Reactions were carried out under continuous flow, with formic acid as the hydrogen donating agent to effectively replace high pressure H_2 . Since α -angelicalactone can suffer an isomerization to β -angelicalactone leading to pentenoic acid isomers and valeric acid (Figure 5), the control of the selectivity is very important in this reaction.

2.6. Oxidation of glucose to gluconic acid, glucuronic acid, tartaric acid, glycolic acid, and glyceric acid

The use of redox zeolites and redox pillared clays for the valorization of biomass was suggested long ago [54]. The oxidation of D-glucose to gluconic acid, glucuronic acid, tartaric acid, glycolic acid and glyceric acid may also occur with hydrogen peroxide as oxidant over several zeolites and Ti-containing zeolites, like TS-1 or Ti-MCM-41 [55]. Using zeolites (ZSM-5, L, Y, Mordenite) gluconic acid is the main reaction product, having glucuronic and tartaric acids as main by-products. The presence of titanium preserves the high selectivity to gluconic acid but the oxidation by-products change to glycolic acid.

2.7. Production of lactic acid and methyl lactate

Lactic acid is an important platform molecule in the synthesis of a wide range of chemicals [56,57]. Lactic acid fermentation is typically performed by lactic acid bacteria, which convert simple carbohydrates like glucose, sucrose, or galactose to lactic acid.

Lewis acidic Sn-Beta zeotype also allowed the direct formation of methyl lactate from common sugars [58]. The conversion of sucrose in methanol at 160 °C afforded methyl lactate with a yield of 68 %. The conversion of pentoses and hexoses into methyl lactate over Sn-Beta showed a dependence on the nature of the saccharide. Pentoses are converted to methyl lactate in slightly lower yields (~40 %) than those obtained from hexoses (~50 %), but higher yields of glycolaldehyde dimethyl acetal are observed from pentoses. This finding agrees with a reaction pathway involving the retro aldol condensation of the sugars to yield triose and glycolaldehyde from pentoses, and two trioses from hexoses. When reacting glycolaldehyde (formally a C₂-sugar) in the presence of Sn-Beta, aldol condensation occurs, leading to the formation of methyl lactate, methyl vinylglycolate and methyl 2-hydroxy-4-methoxybutanoate. By contrast, when converting the sugars in water at low temperature (100 °C), Sn-Beta catalyses the isomerization of sugars (ketose-aldose epimers) rather than the formation of lactates [59].

High selectivity to the desired lactate product was achieved with an ordered mesoporous material (OMM) Sn-MCM-41 [60]. However, a more elaborated Lewis acid zeotype catalyst consisting of two components (MCM-41 filled with a porous polyaromatic hydrocarbon network) improved the performance in this reaction (Figure 6) [61]. Modification of the organic part with functional groups exhibiting mild Brønsted acidity and of the inorganic part by grafting Lewis acid Sn(IV) enabled a catalyst able to transform trioses and aldo- and ketohexoses (fructose) into lactic acid in aqueous medium (R = H) or into alkyl lactates (A) in alcoholic solvents (R = alkyl). Yields to lactate correlate with the length of the alcohol radical, octanol providing the highest values.

In aqueous solutions without alkali, the efficient preparation of lactic acid through the direct catalysis of sugars is hindered by the dehydration side reaction to 5-hydroxymethylfurfural. This is due to Brønsted acidity, which originates from organic acids [62]. It was suggested that this could be avoided by using Zn-Sn-Beta prepared via solid-state ion exchange. In water under ambient air pressure, without a base, a sucrose conversion exceeding 99 % with a lactic acid yield of 54 % was achieved within 2 hours at 190 °C. Studies of the acid and base properties of the Zn-Sn-Beta zeolite

Figure 6. Conversion of monosaccharides like trioses and aldo- and ketohexoses (fructose) into lactic acid in aqueous medium ($R = H$) or into alkyl lactates (A) in alcoholic solvents ($R = \text{alkyl}$). The side reaction leading to the formation of pyruvic aldehyde dialkyl acetal (B) is undesired –LA = Lewis acid; BA = Brønsted acid. Reprinted with permission from ref. [61]. Copyright 2012 American Chemical Society.

suggest that the introduction of Zn into the Sn-Beta zeolite enhanced both the Lewis acid and base sites. The base sites inhibited a series of side reactions related to fructose dehydration to 5-hydroxymethylfurfural and its subsequent decomposition.

Indeed, Sn-Beta zeolite was also found to be a highly active catalyst for the conversion of triose sugars (1,3-dihydroxyacetone in Figure 6) to lactic acid. In water, once they are produced, isomerization takes place to form

lactic acid in very high yields at 125 °C [63]. Methanol reaction at 80 °C, is also followed by esterification, leading to methyl lactate in quantitative yields. H-USY (Si/Al = 6) is also reasonably active in this reaction [64].

2.8. Aldol condensation of fural aldehydes

Zeolites have also been considered for aldol condensation of fural aldehydes. Nitrided zeolite Y was used in the aldol condensations of furaldehydes with acetone and propanal, showing comparable activity to MgO–ZrO₂ and much higher than that over NaY [65]. However, under reaction conditions part of the nitrogen leached, resulting in the loss of catalytic activity [65]. H-zeolites of different structural types also showed appreciable activity in the aldol condensation of furfural with acetone and resulted in the formation of products, which are usually obtained using basic catalysts [66,67]. However, the reaction on these zeolites can continue with the dimerization of the classical condensation products. Large-pore three-dimensional BEA and FAU zeolites afforded higher furfural conversion than medium-pore MFI or large-pore mono-dimensional MOR [66]. Another disadvantage of these catalysts is the quick formation of coke inside the zeolite pores, requiring regeneration of the catalysts.

3. Lignin valorization

Catalytic valorization of lignin for the production of renewable chemicals has been recently reviewed [11]. The participation of zeolites in this effort is merely associated with biomass fast-pyrolysis. Such technology upgrades solid biomass as it yields products with higher energy density, and is also more economical than the alternative technologies of gasification [68,69]. The composition of the produced bio-oil depends on the origin of the lignin. Softwood lignins yielded exclusively guaiacyl derivatives, coniferaldehyde and coniferyl alcohol, hardwood lignins gave rise to guaiacyl and syringyl derivatives, among which syringaldehyde, coniferyl alcohol and sinapyl alcohol were the most abundant. Grass lignins, represented by bamboo lignin, yielded *p*-vinylphenol as the main compound. In addition, other guaiacyl and syringyl pyrolysis products were identified, too [70].

In situ electron paramagnetic resonance (EPR) measurements and model compounds studies reveal two main decomposition routes in this process – firstly, the homolytic fission of the weakest bond-forming radicals

Figure 7. Zeolite transformation of the pyrolysis oil. Copyright © Swiss Chemical Society: CHIMIA, ref. [71]. DOI: <https://doi.org/10.2533/chimia.2015.597>

and, secondly, the radical initiation leading to different radicals, which further rearrange or recombine depending on the nature of the radicals [71]. However, there is a significant potential to control the selectivity by varying catalysts and reaction conditions [72–74]. The formation of aromatic hydrocarbons is enhanced over zeolite-supported Co and Ni catalysts, (Figure 7). The intermediates are stabilized by adsorption on the pores in materials without acidity, such as silicalite, thus increasing the yield of liquid without changing the liquid products distribution. In the presence of strongly acidic zeolites, such as H-USY and H-ZSM5 of low Si/Al ratio, complex reactions, such as dehydration, decarboxylation, dealkylation, cracking, isomerization and oligomerization are involved.

To preserve the catalyst activity, the establishment of a step of pyrolytic lignin deposition at 400 °C avoids the blockage of the on-line catalytic bed and attenuates the deactivation of a HZSM-5 zeolite based catalyst used for hydrocarbon production [75]. As mentioned above, the stability of the zeolites is a critical issue in these processes. One of the major concerns is their hydrothermal stability in the presence of steam or hot water. Therefore, given the high water content in pyrolysis oils and biomass as a whole, as well as in aqueous processes, the selection of H-USY and H-ZSM5 is reasonable. These materials, exhibit a good stability in liquid water between 150 and 200 °C regardless of their Si/Al ratio [76].

Biomass pyrolysis oil contains oxygenate compounds that may be partially transformed to hydrocarbons on acid catalysts to obtain raw a material for the petrochemical industry (light olefins and benzene, toluene,

and xylene). The utilization of a catalyst based on HZSM-5 zeolite led to a product distribution similar to that obtained from the transformation of light alcohols [77,78].

4. Metal-organic frameworks for the upgrading of biomass

So far, we have demonstrated the use of zeolites in different reactions involved in the production of platform molecules derived from biomass. This is due to the structural properties of these porous materials that present a 3D framework with high surface areas and suitable porous structures, as well as chemical and thermal stabilities. The 3D structure leaves confined spaces with limited dimensions where only certain substrates, transition states or products are allowed, resulting in a control of the process called shape selectivity [79]. Moreover, zeolites, which have coordinatively unsaturated metal sites, present strong Lewis acidity and can also have Brønsted acidity, both of them useful for biomass reactions such as hydrolysis. Nevertheless, despite the advantages of zeolites and the wide number of possible structures [80], higher chemical adaptability of the zeolite-based catalysts is required to improve yields and selectivities in biomass upgrading and to allow one-pot syntheses. Additionally, textural properties of zeolites also require a more specific design to control the transport phenomena during the catalytic reactions and to enhance the density of active sites. Therefore, a step forward is required in the design of catalysts for reactions such as hydrolysis, pyrolysis, condensation, isomerization, deoxygenation, hydrogenation, and oxidation, working under complex chemical environments with multiple functional groups and in the presence of water.

In this sense, a new type of porous materials, with a huge potential for catalysis, has been developed over the last 25 years. These are metal-organic frameworks (MOFs), also named porous coordination polymers (PCPs), which are composed of metal ions and various organic ligands [81–87]. MOFs can be classified into different families according to the inorganic framework, as was highlighted by Farrusseng et al. [87]. There are different systems, such as a) open-framework coordination polymers made from 0D inorganic, hybrid or isolated metal clusters connected by bridging organic polytopic ligands, or organic-inorganic hybrid materials in which the inorganic moieties can be organized into b) 1D chains or c) 2D layers separated by organic pillars. These materials have demonstrated their high potential to outperform even zeolites in some reactions due to their tunability provided by the different compositions of organic ligands and metallic clusters [87].

Table 1. MOFs vs zeolites: a comparison of the main properties of both types of materials. Adapted from references [79,80].

Properties	MOFs	Zeolites
Thermal stability	Stable below 300 °C	Stable above 450 °C
Chemical stability	Limited chemical stability specially to H ₂ O in most cases	Stable to solvents, acids, oxidizing and reducing agents
BET surface area	Around 1,000–10,000 m ² g ⁻¹	Around 200–500 m ² g ⁻¹
Pore volume	Over 1 cm ³	0.1–0.5 cm ³
Metal site density	High	Low
Lewis acidity	Accessible framework metal ions	Accessible framework metal ions
Brønsted acidity	Introducible through organic linker	Bridging Si(OH)/Al hydroxyl groups
Basicity	Introducible through organic linker	From framework oxygen atoms
Active site environment	More hydrophobic, but linker-dependent	Mostly hydrophilic but can be made hydrophobic
Additional features	Chiral functionalities, flexible and stimuli responsive behaviour	–
Reactivation	Washing procedures; thermal treatment not possible	By thermal treatment

Strengths
 Weaknesses
 Comparable properties
 No weakness at all

The application of MOF catalysts is recent [80], and the use of MOFs-based catalysts for the upgrading of lignocellulosic biomass is even more recent. In 2011, Akiyama et al. [88] presented one of the first works on the synthesis of a new PCP decorated with sulfonic acid functional groups for the hydrolysis of cellulose. Recently, Herbst and Janiak have presented a comprehensive review about the use of MOF catalysts in the transformation of biomass into valuable fine chemicals [80]. This includes the state of the art as well as the challenges and perspectives in this field of MOF applications. Furthermore, this review not only summarizes the few works devoted to this end but also deeply analyses the advantages and drawbacks of these types of materials and compares them to zeolites. Given the scope of this book, we have adapted some of the main relevant contrasts made by these authors in Table 1.

The application of MOFs in the transformation of biomass is not easy since, although over 20,000 types have been reported in literature, only water-stable MOFs would be applicable in the sort of reactions cited above. Furthermore, certain thermal and chemical stabilities are required, thus reducing the number of suitable MOF-based catalysts considerably [80,89,90]. Thus, the stability of MOFs is an important issue that has to be controlled and carefully addressed, especially when reactions are carried out in the presence of water, which is a typical situation for the reactions involving biomass-derived feedstocks [80,90]. Concerning the relevance of the stability of MOFs for catalytic applications, Burtch et al. [91] have presented a comprehensive review defining some concepts on the water stability of MOFs, which can be considered during the design of MOF catalysts for the transformation of biomass. In this review, a broad classification of the huge number of MOFs that have been experimentally characterized after water exposure is presented, taking into account thermodynamic and kinetic stabilities. Thermodynamic stability considers chemical aspects, such as the metal-ligand bond strength or the lability in water and the possible variables that may affect them during the reactions. On the other hand, kinetic stability deals with aspects such as access to the active sites. From both, the hydrophobicity and the steric factors will determine if the MOF-based catalysts are suitable for reactions including water [91].

Another remarkable advantage of MOF catalysts is their high adsorption capacity and the possibility of achieving controlled pore sizes. In fact, to process the big molecules derived from the biomass deconstruction, materials with big pores are required to enhance the selectivity in the adsorption of reactants and in the desorption of products to allow one-pot procedures. In their review, Farrusseng et al. [87] presented the influence of the porous architecture on selectivity in different reactions. In this sense, the superior adsorption abilities of MOF catalysts over zeolites is demonstrated from results like those by Kruger et al. [92]. In this work, the pore sizes of different zeolite catalysts and the diameter of platform molecules were compared by means of simulations. While the zeolite structure with the largest pore sizes is H-Y with 7.5 Å, some of the most suitable MOFs systems for the upgrading of biomass present larger pore diameters. For instance, MIL-101Cr has pores of 29 and 34 Å and pore windows of 12 to 15 Å [92], which made this system suitable for glucose recovery [93]. The unusual adsorption abilities of some MOFs has also been confirmed by Yabushita et al. [94], who observed that NU-1000 MOF adsorbs cellobiose and lactose dimers from aqueous solution in amounts exceeding 1250 mg g⁻¹ while completely excluding adsorption of the glucose monomer. The high

selectivity of the adsorption process in these materials, which results in a selective molecular recognition, seems to be due to the number of favourable CH- π interactions between the sugar with pyrene units and the studied MOF.

4.1. Transformation of cellulose and hemicellulose carbohydrate polymers using MOF catalysts

As remarked above, the work by Akiyama and coworkers [88] addressed the high potential of MOF catalysts for transforming biomass-derived products into biofuels or high added value chemicals. This will contribute to the development of biorefineries, aiming to transform residual biomass feedstocks rather than those derived from food crops so avoiding competition with the food supply. In this work, the authors modified the structure of a typical MIL-101 MOF introducing sulfonic acid groups on its pore surface for use in cellulose hydrolysis [88]. After comparing the catalytic performance of this system with that of different acid catalysts, such as Amberlyst-15, this MOF catalyst demonstrated clean catalytic activity and high Brønsted acidity but low yields to mono- and disaccharides due to the low solubility of crystalline cellulose in water. However, the MOF catalyst exhibited a considerable robustness in boiling water and strongly acidic conditions. Further studies from this research team about the use of functionalized MIL-101 catalysts have confirmed that the high stability and availability of its acid centres and the open metal sites resulted in the enhancement of glucose-to-fructose conversion [95]. In addition, the structural features in coordination of the chromium sites in this type of materials led to performances comparable to those of homogeneous catalysts, demonstrating the high specificity that can be achieved with these materials [80,95].

Chen et al. presented a different approach to the conversion of cellulose, starting from a MIL-101 MOF but with different modifications [96]. In this case, water-tolerant phosphotungstic acid (PTA)/MOF-supported Ru catalysts are bifunctional (metal/acid) catalysts for obtaining cellulose- and cellobiose-derived alcohols. The metal/acid balance was studied in order to establish optimal conditions for the production of alcohols: selectivities to sorbitol of 57.9 % and 95.1 % were achieved in the conversion of cellulose and cellobiose, respectively [96].

Recently, Huang et al. [97] reported the use of a new 3D MOF/graphene catalyst prepared by in situ growth of zeolitic imidazolate framework (ZIF-8)

nanoparticles inside the pores of a hydrogel. In this case, cellulose was dissolved in alkaline aqueous solution and consequently degraded over the catalyst under hydrothermal conditions, reaching total conversion with formic acid as the main product, along with oxalic and acetic acids.

Although the use of MOF catalysts for the transformation of biomass is an emerging topic, most works have focused on the transformation of molecules derived from cellulose and hemicellulose rather than lignin. This is due to the complex transformation of the lignin molecule, as a result of its complex structure and multiple possibilities of selective rupture in smaller molecules. Table 2 presents a comprehensive summary of works devoted to the transformation of cellulose/hemicellulose-derived molecules using MOF catalysts. It includes all the references cited by Herbst and Janiak [80] and the newer works presented up until now. As can be inferred from the table, two families of MOFs have principally been studied as catalysts for these reactions: MIL-101(Cr) and UiO-66 – due to the thermal and water stability in both cases, as well as the contribution of strong and stable acid sites.

Lignin is also a potential source of renewable organics with high a content of oxygenated functional groups. However, the strong chemical bonds comprising this polymer make its transformation particularly difficult. Furthermore, the complexity of the obtained mixtures of products is also important because in such a multi-functional chemical environment oxygenated molecules may tend to re-polymerize. Despite this, the development of efficient heterogeneous catalysts for the selective cleavage of C-O aromatic bonds in lignin has been recently demonstrated [98]. This verifies the first report by Stavila et al. [99] concerning the use of MOF-based catalysts for the hydrogenolysis of carbon-oxygen ether bonds, which are common linkages in oxygenated molecules derived from lignin.

4.2. Transformation of lignin over MOF catalysts

To date, only vanillin has been analysed as a model to explore the hydrogenation and deoxygenation routes of lignin. Recently, Zhang et al. [114] have studied the properties of $\text{SO}_3\text{H-MIL-101(Cr)}$, encapsulated Pd nanoparticles in the mesoporous cages of the catalysts and obtained an efficient catalyst for the hydrodeoxygenation of vanillin. In this case, the developed Pd/ $\text{SO}_3\text{H-MIL-101(Cr)}$ catalysts presented high catalytic activity in tandem hydrogenation-deoxygenation reactions, and could be recycled several times without any apparent loss in activity or selectivity. The high

Table 2. Studies regarding the transformation of cellulose/hemicellulose derived molecules using MOF catalysts.

Main process	Reactions	Studied MOFs	Highlights	Ref.
Cellulose to glucose and fructose	Glucose-to-fructose isomerization reaction	MIL-101Cr-SO ₃ H	Pioneer work using MOFs for the transformation of biomass	[88]
			High stability to boiling water	
			Strong Brønsted acid sites	
	Catalytic isomerization from glucose to fructose	MIL-101-H	In general, the MIL-101 framework is suitable for glucose-to-fructose isomerization due to the large pores allowing transportation of the molecules	
Cellulose to formic acid		MIL-101-NH ₂	The catalytic activity can be tuned by the acidity of open metal sites depending on the functional groups of the linkers	[95]
		MIL-101-H		
		MIL-101-(CH ₃) ₂		
		MIL-101-NO ₂		
		MIL-101-SO ₃ H	The -SO ₃ H modified MOF presents high conversion as well as high selectivity towards fructose.	
	Cellulose to formic acid, acetic acid and oxalic acid	3D ZIF-8/rGO	The hydrogel nanocomposite presents micropores and mesopores with acidic sites	
			High stability in alkaline solution	[97]
			High catalytic performance during the conversion of cellulose in its homogeneously aqueous solution, reaching a 93.66 %yield of formic acid	

Cellulose to sorbitol	Aqueous hydrogenation reaction conditions	Ru-PTA/MIL-101(Cr)	Yields in sorbitol of 95.1 % and 57.9 % can be achieved in the conversion of cellobiose and ball-milled cellulose respectively.	[96]
		PTA/MIL-101(Cr)	Lower crystallinity of cellulose can promote the formation of sorbitol	
		MIL-101(Cr)	Acid site density to the number of metal surface atoms ratio between 8.84 and 12.90 results in the maximum conversion of cellulose and cellobiose into hexitol. Relevance of the balance between hydrogenation – hydrolysis functions has been demonstrated.	
Cellulose to ethylene glycol	Hydrolysis and hydrogenation reactions	Ru/NENU-3 (NENU-3 is an hybrid phosphotungstic acid (PTA) and HKUST-1)	Ethylene glycol yield of 50.2 % can be obtained from cellulose.	[100]
			The presence of PTA sites (for the cellulose hydrolysis) and the metallic clusters (Ru) for the hydrogenation are determinant for the production of ethylene glycol from cellulose.	
			A relatively low formation rate of cellulose-derived sugars favours a high yield of ethylene glycol.	
Fructose to 5-HMF	Dehydration of fructose to 5-HMF in DMSO	PTA/MIL-101	The catalytic activity depends on the PTA loadings	[101]
			The reaction was proton catalyzed	
			The exchange of protons between the immobilized PTA and the organic cations of the ionic liquid led to the presence of partial protons in the ionic liquid medium.	

Table 2. (Continued)

Main process	Reactions	Studied MOFs	Highlights	Ref.
Fructose to 5-HMF	Dehydration of fructose to 5-HMF in DMSO	MIL-101(Cr)-PMAI-Br	The catalysts could be recycled under the same reaction conditions.	[102]
			Vinyl monomers and cross-linkers impregnated within MOF pores undergo free-radical polymerization to form a network threading through the MOF porous structure	
			The stability of the composite was provided by the parental stability of the MOF as well as the design of the polymeric network.	
			The included polymeric units can be functionalized.	
Fructose to 5-HMF	Dehydration of fructose to 5-HMF in DMSO	MIL-101(Cr)	The composite is recyclable within the reaction conditions.	[103]
			A superior HMF yield of up to 90 % with a full fructose conversion was obtained with the MIL-101(Cr)-SO ₃ H catalyst.	
			The concentration of -SO ₃ H in the MOFs and the contribution of Brønsted acidity of the modified MOFs can be precisely tuned by -SO ₃ H grafting rate of MOF-SO ₃ H.	
			In all cases the sulfonic acid groups are equivalent regardless of precursors.	
		UIO-66(Zr)	The most active system seems to follow a pseudo-first-order kinetic and can be recovered and reused.	
		UIO-66(Zr)-SO ₃ H MIL-53(Al) MIL-53(Al)-SO ₃ H		

Fructose to 5-HMF	Dehydration of fructose to 5-HMF in DMSO	NUS-6(Hf)	The catalysts exhibit excellent stability and can retain their porosity under vigorous activation at 150 °C.	[104]
		NUS-6(Zr)	The MOFs present decent CO ₂ capture performance.	
			Hf-containing system presents better reaction kinetics and chemoselectivity with quantitative fructose conversion and a HMF yield of 98 %.	
Glucose to 5-HMF	Dehydration of glucose to 5-HMF	MIL-101(Cr)-PMAi-Br	The superior performance of the Hf-containing MOF is due to the superior Brønsted acidity as well as the more suitable pore size that inhibits side reactions.	[102]
			Poor yield during the process near to 16%	
			The activity is mainly ascribed to PMAi-Br rather than the MOF.	
Glucose to 5-HMF	Dehydration of glucose to 5-HMF	MIL-101Cr	MIL-SO ₃ H gives the highest yield of 5-HMF from glucose of 29%, which is below of the yields achieved with other acid catalysts.	[105]
		MIL-NO ₂	The reaction only proceeds with a small amount of water.	
		MIL-NO ₂ /SO ₃ H	In pure THF, no product formation is observed.	
		MIL-SO ₃ H(0.33) MIL-SO ₃ H	From 5-HMF, a poor production of levulinic acid is observed, in contrast of the results using H ₂ SO ₄ or Amberlyst-70	
Glucose to 5-HMF	Dehydration of glucose to 5-HMF	MIL-101(Cr)-SO ₃ H	The batch heterogeneous reaction gives a 5-HMF of 44.9 % and selectivity of 45.8%.	[106]

Table 2. (Continued)

Main process	Reactions	Studied MOFs	Highlights	Ref.
Sucrose to methyl lactate	Dehydration of glucose to 5-HMF	HKUST-1 MIL-53Al MIL-101Cr	Reaction kinetics suggests that the glucose isomerization in GVL with 10 wt.% follows a second-order reaction.	[107, 108]
			The catalyst is highly stable in the continuous reaction in the fixed bed reactor, providing a steady 5-HMF yield.	
			Poor methyl lactate yields below 5 %.	
Sucrose to methyl lactate	Dehydration of glucose to 5-HMF	ZIF-8 ZIF-67	Both systems have different activity due to the presence of Zn in the ZIF-8 and Co in the ZIF-67.	[107]
			ZIF-8 demonstrates higher activity with yield to methyl lactate 42 %	
			ZIF-8 was reused in four catalytic cycles.	
Furfural to furfuryl alcohol and 5-HMF to 2,5dihydroxymethyltetrahydrofuran	Selective hydrogenation	MIL-101(Al)-NH ₂ Pd/MIL-101-NH ₂	The presence of free amine moieties in the frameworks of MIL-101(Al)-NH ₂ seems to play a key role on the formation of uniform and well dispersed Pd nanoparticles.	[109]
			Amine-functionalized MOFs show preferential adsorption to hydrogenation intermediate DHMF than in the case of HMF.	

5-HMF to 2,3-diformyl furan	MIL-53 (Al)	The hydrophilic nature of DHMF and its interaction with the support by means of the hydrogen bonding enhancing the hydrogenation reaction to DHMTHF.	Levulinic acid (LA) to γ-valero lactone (GVL)
	Pd/MIL-53 (Al) MIL-53 (Al)-NH ₂ MIL-101 (Cr) Pd/MIL-101 (Cr)	The higher selectivity towards DHMTHF is due to a cooperation between metallic sites and free amine moieties on the MOF support, especially in the case of the Pd/MIL-101 (Al)-NH ₂ .	
	UiO-66	The Ru nanoparticles were smaller than 3 nm	
	UiO-67	Ru/UiO-66 presented the highest catalytic activity and the systems could be used during five cycles.	
	Zr6-NDC	The catalytic activity is closely related to the easy reduction of Ru	
	MIL-140A MIL-140B MIL-140C	The strong interaction between the RuO _x nanoparticles and the Zr-MOF results in the decrease of the catalytic performance of these systems	
	FeCo/C starting from MIL-45B	The FeCo/C materials were highly active and selective during the oxidation of 5-HMF affording the desired product DFF in >99 % yield.	
	Aerobic oxidation	The obtained structure allowed a favoured adsorption of 5-HMF and a quick desorption of DFF from the catalysts surface.	
	Hydrogenation	The catalysts were recovered and used six times without any significant loss in reactivity.	
	MIL-101 (Cr)	Pd supported on these acidic materials showed bifunctional catalytic roles in the conversion of GVL	

Table 2. (Continued)

Main process	Reactions	Studied MOFs	Highlights	Ref.
Levulinic acid (La) to ethyl levulinate (EL)	Esterification of LA	MIL-101(Cr)-SO ₃ H	With increasing acid site density the ring opening activity of GVL increases and subsequently hydrogenation of C=O bond led to ethyl pentenoate, which is finally hydrogenated by Pd clusters to form ethyl valerate.	[113]
		Pd/MIL-101(Cr)	High temperature and loading of Pd are required for achieving hydrogenation of ethyl pentenoate.	
		Pd/MIL-101(Cr)-SO ₃ H	Pd sintering is observed at high temperatures.	
			The amount of -SO ₃ H influences the size of the Pd nanoparticles.	
			MIL-101(Cr)-SO ₃ H also influences the selectivity during the process.	
		Ui-66	In general, the studied catalysts are active and reusable for the esterification of LA with various alcohols.	
		Ui-66-NH ₂	In Ui-66-NH ₂ , a dual acid-base activation mechanism is proposed.	
		Ui-66Zr	LA is activated on Zr sites and the alcohol in the amino groups.	
		Ui-66Zr-NH ₂	Variations of the catalytic activity from batch to batch suggest that the active sites are located at defect positions associated with ligand deficiency of solids.	
			Particle size seems to have a minor impact only in the case of UiO-66-NH ₂	

performance of the catalyst was attributed to the stability of the support, which maintained a high dispersion of the Pd nanoparticles. Additionally, the electronic activation of the reactants and the good dispersion of the catalyst in the water media were evidenced [114]. The same research team also reported the use of MOF catalysts based on the UiO-66 structure in the hydrodeoxygenation of vanillin [115]. The catalysts were prepared by introducing ultra-small Pd nanoparticles (1.5–2.5 nm) into a highly porous and hydrothermally stable amine-functionalized UiO-66 (NH_2 -UiO-66). The stable and leaching-resistant dispersion of the Pd nanoparticles was attributed to the presence of free amine moieties in the framework of the catalyst. Consequently, the amine/Pd ratio should be optimized.

To the best of our knowledge, the most recent work devoted to the transformation of vanillin proposed the use of a hybrid support consisting of MOF crystals and partially reduced graphene oxide (PRGO) nanosheets to disperse metal nanoparticles. The Ce-based MOF was wrapped with thin PRGO nanolayers, and the obtained 5 wt.% Pd/PRGO/Ce-MOF catalyst exhibited high catalytic activity in the tandem hydrogenation-deoxygenation reactions. Furthermore, it could be reused at least four times without any loss of activity or selectivity. The inclusion of PRGO seems to promote the selectivity of the process towards the production of 2-methoxy-4-methylphenol, which is an important phenol-type compound with high added value. In addition, PRGO provides stability and acidic sites that promote the hydrogenolysis reaction.

5. Concluding remarks

Zeolites and MOFs are very suitable materials to be used in reactions of biomass-to-chemicals. The chemical valorization of the lignocellulosic biomass involves a sequence of different catalytic processes, such as depolymerization, hydrolysis, hydrogenation, dehydration, isomerization, and oxidation reactions, among others. Thus, the high versatility of these materials, which extends to different porous structures (pore dimension and void volume), shape selectivity, number and nature of active sites (single or multiple), etc., makes them ideal for these applications by means of adjusting their structures to the desired reaction.

Literature reports have largely evidenced the strong capabilities of zeolites for the transformation of lignocellulosic biomass feedstocks, whereas the application of MOF-based catalysts goes almost unexplored. Few works on MOFs have been published so far, and only two MOF families (MIL-101

and UiO-66) have demonstrated their stability under typical reaction conditions involving water and strongly acidic environments. Therefore, the design of novel MOFs is necessary, at the same time aiming to adapt the properties of the catalysts to the particular reaction under study. To this end, the tunability of Lewis and Brønsted acidity, as well as the nature of the open metal sites or the control of the hydrogen bonding interactions through the linkers are parameters amenable to modification. Furthermore, the hydrophilicity/hydrophobicity must be optimized to control the adsorption processes during the reactions [80].

Apart from these considerations, the evolution of MOF-based catalysts for lignocellulosic biomass transformation must follow the principles of green chemistry [116]. One of these principles is the efficient utilization of raw materials. Thus, MOF catalysts need to be designed for the deconstruction of residual lignocellulosic biomass, which avoids competing with the food supply. However, this is a challenging task, since the processing of real residual biomass presents a huge complexity, including the presence of strongly deactivating species, such as sulphur- and nitrogen-containing compounds. Despite this, the success in using MOFs for this purpose would contribute both to the remediation of biomass waste and to the decreasing of the CO₂ footprint as bio-derived fuels and fine chemicals would come from renewable carbon sources. Another approach that would improve the efficient use of resources would be the use of molecules derived from other transformations of lignocellulosic biomass in a biorefinery. This would also contribute to the decrease of CO₂ emissions and would bring economic and environmental benefits.

Acknowledgments

The authors thank the support from the Spanish Ministerio de Economía y Competitividad (MINECO) (ENE2015-66975-C3-2-R and ENE2013-47880-C3-2-R) co-financed by FEDER funds from the European Union. Financial support from the Junta de Andalucía to the Surface Chemistry and Catalysis research group (TEP106) is specifically acknowledged.

References

- [1] Field, C.B., Behrenfeld, M.J., Randerson, J.T., Falkowski, P. *Science* 1998, 281, 237.
- [2] Huber, G.W., Iborra, S., Corma, A. *Chem. Rev.* 2006, 106, 4044.
- [3] Dodds, D.R., Gross, R.A. *Science* 2007, 318, 1250.

- [4] Bailey, M., Enari, T.M., Linko, M., Halliwell, G. In *SITRA Symposium on Enzymatic Hydrolysis of Cellulose*, Finland, 1975.
- [5] Fan, L.T., Gharpuray, M.M., Lee, Y.H. *Cellulose Hydrolysis*, Springer, 1987.
- [6] Devendra, L.P., Kumar, K.M., Pandey, A. *Biores. Technol.* 2016, 213, 350.
- [7] Serrano-Ruiz, J.C., Luque, R., Sepulveda-Escribano, A. *Chem. Soc. Rev.* 2011, 40, 5266.
- [8] Lin, H., Strull, J., Liu, Y., Karmiol, Z., Plank, K., Miller, G., Guo, Z., Yang, L. *Energy J. Environ. Sci.* 2012, 5, 9773.
- [9] Nowakowski, D.J., Bridgwater, A.V., Elliott, D.C., Meier, D., de Wild, P.J. *J. Anal. Appl. Pyrolysis* 2010, 88, 53.
- [10] Liu, C., Wang, H., Karim, A.M., Sun, J., Wang, Y. *Chem. Soc. Rev.* 2014, 43, 7594.
- [11] Zakzeski, J., Bruijninx, P.C.A., Jongerius, A.L., Weckhuysen, B.M. *Chem. Rev.* 2010, 110, 3552.
- [12] Björkman, A. *Sven. Papperstidn* 1956, 59, 477.
- [13] Shuai, L., Luterbacher, J. *ChemSusChem* 2016, 9, 133.
- [14] Piqueras, C.M., Cabeza, A., Gallina, G., Cantero, D.A., Garcia-Serna, J., Cocero, M.J. *Chem. Eng. J.* 2017, 308, 110.
- [15] Corma, A., Iborra, S., Velty, A. *Chem. Rev.* 2007, 107, 2411.
- [16] Zhang, X., Wilson, K., Lee, A.F. *Chem. Rev.* 2016, 116, 12328.
- [17] Climent, M.J., Corma, A., Iborra, S. *Zeolites and Catalysis: Synthesis, Reactions and Applications*, Wiley-VCH, 2010.
- [18] Dapsens, P.Y., Mondelli, C., Perez-Ramirez, J. *ACS Catal.* 2012, 2, 1487.
- [19] Ennaert, T., Van Aelst, J., Dijkmans, J., De Clercq, R., Schutyser, W., Dusselier, M., Verboekend, D., Sels, B.F. *Chem. Soc. Rev.* 2016, 45, 584.
- [20] Li, H., Yang, S., Riisager, A., Pandey, A., Sangwan, R.S., Saravanamurugan, S., Luque, R. *Green Chem.* 2016, 18, 5701.
- [21] Corma, A., Nemeth, L.T., Renz, M., Valencia, S. *Nature* 2001, 412, 423.
- [22] Bhosale, S.H., Rao, M.B., Deshpande, V.V. *Microbiol. Mol. Biol. Rev.* 1996, 60, 280.
- [23] Moreau, C., Durand, R., Roux, A., Tichit, D. *Appl. Catal., A* 2000, 193, 257.
- [24] Moliner, M., Roman-Leshkov, Y., Davis, M.E. *PNAS* 2010, 107, 6164.
- [25] Roman-Leshkov, Y., Moliner, M., Labinger, J.A., Davis, M.E. *Angew. Chem. Int. Ed.* 2010, 49, 8954.
- [26] Gunther, W.R., Wang, Y., Ji, Y., Michaelis, V.K., Hunt, S.T., Griffin, R.G., Roman-Leshkov, Y. *Nat. Commun.* 2012, 3.
- [27] van der Graaff, W.N.P., Tempelman, C.H.L., Li, G., Mezari, B., Kosinov, N., Pidko, E.A., Hensen, E.J.M. *ChemSusChem* 2016, 9, 3145.
- [28] Lew, C.M., Rajabbeigi, N., Tsapatsis, M. *Micropor. Mesopor. Mater.* 2012, 153, 55.
- [29] Kobayashi, H., Komano, T., Guha, S.K., Hara, K., Fukuoka, A. *Appl. Catal., A* 2011, 409, 13.
- [30] Huber, G.W., Chheda, J.N., Barrett, C.J., Dumesic, J.A. *Science* 2005, 308, 1446.
- [31] Deng, W., Tan, X., Fang, W., Zhang, Q., Wang, Y. *Catal. Lett.* 2009, 133, 167.
- [32] Negoi, A., Triantafyllidis, K., Parvulescu, V.I., Coman, S.M. *Catal. Today* 2014, 223, 122.
- [33] Ennaert, T., Geboers, E., Gobechiya, E., Courtin, C.M., Kurttepel, M., Houthoofd, K., Kirschhock, C.E.A., Magusin, P.C.M.M., Bals, S., Jacobs, P.A., Sels, B.F. *ACS Catal.* 2015, 5, 754.
- [34] Bozell, J.J., Petersen, G.R. *Green Chem.* 2010, 12, 539.
- [35] Teong, S.P., Yi, G., Zhang, Y. *Green Chem.* 2014, 16, 2015.
- [36] Moreau, C., Durand, R., Pourcheron, C., Razigade, S. *Ind. Crops Prod.* 1994, 3, 85.
- [37] Moreau, C., Durand, R., Peyron, D., Duhamet, J., Rivalier, P. *Ind. Crops Prod.* 1998, 7, 95.
- [38] Kim, S.B., You, S.J., Kim, Y.T., Lee, S., Lee, H., Park, K., Park, E.D. *Korean J. Chem. Eng.* 2011, 28, 710.
- [39] Roman-Leshkov, Y., Chheda, J.N., Dumesic, J.A. *Science* 2006, 312, 1933.
- [40] Choudhary, V., Pinar, A.B., Sandler, S.I., Vlachos, D.G., Lobo, R.F. *ACS Catal.* 2011, 1, 1724.
- [41] Yang, G., Pidko, E.A., Hensen, E.J.M. *ChemSusChem* 2013, 6, 1688.

- [42] Tan, M., Zhao, L., Zhang, Y. *Biomass Bioenergy* 2011, 35, 1367.
- [43] Guo, J., Zhu, S., Cen, Y., Qin, Z., Wang, J., Fan, W. *Appl. Catal. B* 2017, 200, 611.
- [44] Arias, K.S., Climent, M.J., Corma, A., Iborra, S. *ACS Sustain. Chem. Eng.* 2016, 4, 6152.
- [45] Yan, K., Jarvis, C., Gu, J., Yan, Y. *Renew. Sustain. Energy Rev.* 2015, 51, 986.
- [46] Chen, H., Yu, B., Jin, S. *Biores. Technol.* 2011, 102, 3568.
- [47] Guerbuez, E.I., Wettstein, S.G., Dumesic, J.A. *ChemSusChem* 2012, 5, 383.
- [48] Ya'aini, N., Amin, N.A.S., Asmadi, M. *Biores. Technol.* 2012, 116, 58.
- [49] Ya'aini, N., Amin, N.A.S., Endud, S. *Micropor. Mesopor. Mater.* 2013, 171, 14.
- [50] Fernandes, D.R., Rocha, A.S., Mai, E.F., Mota, C.J.A., Teixeira da Silva, V. *Appl. Catal., A* 2012, 425–426, 199.
- [51] Saravanamurugan, S., Riisager, A. *Catal. Commun.* 2012, 17, 71.
- [52] Qi, L., Horvath, I.T. *ACS Catal.* 2012, 2, 2247.
- [53] Yopez, A., De, S., Salud Climent, M., Romero, A.A., Luque, R. *Appl. Sci.* 2015, 5, 532.
- [54] Sheldon, R.A. *Stud. Surf. Sci. Catal.* 1991, 59, 33.
- [55] Velarde, A.M., Bartl, P., Nießen, T.E.W., Hoelderich, W.F. *J. Mol. Catal. A Chem.* 2000, 157, 225.
- [56] Dusselier, M., Van Wouwe, P., Dewaele, A., Makshina, E., Sels, B.F. *Energy Environ. Sci.* 2013, 6, 1415.
- [57] Maki-Arvela, P., Simakova, I.L., Salmi, T., Murzin, D.Y. *Chem. Rev.* 2014, 114, 1909.
- [58] Holm, M.S., Saravanamurugan, S., Taarning, E. *Science* 2010, 328, 602.
- [59] Holm, M.S., Pagan-Torres, Y.J., Saravanamurugan, S., Riisager, A., Dumesic, J.A., Taarning, E. *Green Chem.* 2012, 14, 702.
- [60] Li, L., Stroobants, C., Lin, K., Jacobs, P.A., Sels, B.F., Pescarmona, P.P. *Green Chem.* 2011, 13, 1175.
- [61] de Clippel, F., Dusselier, M., Van Rompaey, R., Vanelderen, P., Dijkmans, J., Makshina, E., Giebel, L., Oswald, S., Baron, G.V., Denayer, J.F.M., Pescarmona, P.P., Jacobs, P.A., Sels, B.F. *J. Am. Chem. Soc.* 2012, 134, 10089.
- [62] Dong, W., Shen, Z., Peng, B., Gu, M., Zhou, X., Xiang, B., Zhang, Y. *Sci. Rep.* 2016, 6, 26713.
- [63] Taarning, E., Saravanamurugan, S., Holm, M.S., Xiong, J., West, R.M., Christensen, C.H. *ChemSusChem* 2009, 2, 625.
- [64] West, R.M., Holm, M.S., Saravanamurugan, S., Xiong, J., Beversdorf, Z., Taarning, E., Christensen, C.H. *J. Catal.* 2010, 269, 122.
- [65] Shen, W., Tompsett, G.A., Hammond, K.D., Xing, R., Dogan, F., Grey, C.P., Conner Jr, W.C., Auerbach, S.M., Huber, G.W. *Appl. Catal., A* 2011, 392, 57.
- [66] Kikhtyanin, O., Kelbichová, V., Vitvarová, D., Kubů, M., Kubička, D. *Catal. Today* 2014, 227, 154.
- [67] Kikhtyanin, O., Chlubna, P., Jindrova, T., Kubicka, D. *Dalton Trans.* 2014, 43, 10628.
- [68] Kubička, D., Kikhtyanin, O. *Catal. Today* 2015, 243, 10.
- [69] Kubicka, D., Kubickova, I., Cejka, J. *Catal. Rev. Sci. Eng.* 2013, 55, 1.
- [70] Saiz-Jimenez, C., Deleeuw, J.W. *Org. Geochem.* 1986, 10, 869.
- [71] Ma, Z., Custodis, V., Hemberger, P., Baehrle, C., Vogel, F., Jeschke, G., van Bokhoven, J.A. *Chimia* 2015, 69, 597.
- [72] Ma, Z., Troussard, E., van Bokhoven, J.A. *Appl. Catal., A* 2012, 423–424, 130.
- [73] Ma, Z., van Bokhoven, J.A. *ChemCatChem* 2012, 4, 2036.
- [74] Ma, Z., Custodis, V., van Bokhoven, J.A. *Catal. Sci. Technol.* 2014, 4, 766.
- [75] Gayubo, A.G., Valle, B., Aguayo, A.T., Olazar, M., Bilbao, J. *J. Chem. Technol. Biotechnol.* 2010, 85, 132.
- [76] Hicks, J.C. *J. Phys. Chem. Lett.* 2011, 2, 2280.
- [77] Gayubo, A.G., Aguayo, A.T., Atutxa, A., Prieto, R., Bilbao, J. *Energy Fuels* 2004, 18, 1640.
- [78] Deng, S.M., Fan, M.H., Wang, T.J., Li, Q.X. *Chinese J. Chem. Phys.* 2014, 27, 361.

- [79] Dhakshinamoorthy, A., Alvaro, M., Corma, A., Garcia, H. *Dalton Trans.* 2011, 40, 6344.
- [80] Herbst, A., Janiak, C. *Cryst. Eng. Comm.* 2017.
- [81] Kitagawa, S., Kitaura, R., Noro, S. *Angew. Chem. Int. Ed.* 2004, 43, 2334.
- [82] Ferey, G. *Chem. Soc. Rev.* 2008, 37, 191.
- [83] Bloch, E.D., Britt, D., Lee, C., Doonan, C.J., Uribe-Romo, F.J., Furukawa, H., Long, J.R., Yaghi, O.M. *J. Am. Chem. Soc.* 2010, 132, 14382.
- [84] Deng, H., Doonan, C.J., Furukawa, H., Ferreira, R.B., Towne, J., Knobler, C.B., Wang, B., Yaghi, O.M. *Science* 2010, 327, 846.
- [85] Volklinger, C., Cohen, S.M. *Angew. Chem. Int. Ed.* 2010, 49, 4644.
- [86] Bernt, S., Guillermin, V., Serre, C., Stock, N. *Chem. Commun.* 2011, 47, 2838.
- [87] Farrusseng, D., Aguado, S., Pinel, C. *Angew. Chem. Int. Ed.* 2009, 48, 7502.
- [88] Akiyama, G., Matsuda, R., Sato, H., Takata, M., Kitagawa, S. *Adv. Mater.* 2011, 23, 3294.
- [89] Furukawa, H., Cordova, K.E., O'Keeffe, M., Yaghi, O.M. *Science* 2013, 341, 1230444.
- [90] Qadir, N.U., Said, S.A.M., Bahaidarah, H.M. *Micropor. Mesopor. Mater.* 2015, 201, 61.
- [91] Burtch, N.C., Jasuja, H., Walton, K.S. *Chem. Rev.* 2014, 114, 10575.
- [92] Kruger, J.S., Nikolakis, V., Vlachos, D.G. *Curr. Opin. Chem. Eng.* 2012, 1, 312.
- [93] Gupta, K.M., Zhang, K., Jiang, J.W. *Sci. Rep.* 2015, 5.
- [94] Yabushita, M., Li, P., Bernales, V., Kobayashi, H., Fukuoka, A., Gagliardi, L., Farha, O.K., Katz, A. *Chem. Commun.* 2016, 52, 7094.
- [95] Akiyama, G., Matsuda, R., Sato, H., Kitagawa, S. *Chem. Asian J.* 2014, 9, 2772.
- [96] Chen, J., Wang, S., Huang, J., Chen, L., Ma, L., Huang, X. *ChemSusChem* 2013, 6, 1545.
- [97] Huang, P., Yan, L.F. *Chinese J. Chem. Phys.* 2016, 29, 742.
- [98] Allendorf, M.D., Stavila, V., Ramakrishnan, P., Davis, R. Sandia Report 2014, SAND2014-18259, prod.sandia.gov/techlib/access.
- [99] Stavila, V., Parthasarathi, R., Davi, R.W., El Gabaly, F., Sale, K.L., Simmons, B.A., Singh, S., Allendorf, M.D. *ACS Catal.* 2016, 6, 55.
- [100] Wang, S., Chen, J., Chen, L. *Catal. Lett.* 2014, 144, 1728.
- [101] Zhang, Y., Degirmenci, V., Li, C., Hensen, E.J.M. *ChemSusChem* 2011, 4, 59.
- [102] Bromberg, L., Su, X., Hatton, T.A. *Chem. Mater.* 2014, 26, 6257.
- [103] Chen, J., Li, K., Chen, L., Liu, R., Huang, X., Ye, D. *Green Chem.* 2014, 16, 2490.
- [104] Hu, Z., Peng, Y., Gao, Y., Qian, Y., Ying, S., Yuan, D., Horike, S., Ogiwara, N., Babarao, R., Wang, Y., Yan, N., Zhao, D. *Chem. Mater.* 2016, 28, 2659.
- [105] Herbst, A., Janiak, C. *New J. Chem.* 2016, 40, 7958.
- [106] Su, Y., Chang, G., Zhang, Z., Xing, H., Su, B., Yang, Q., Ren, Q., Yang, Y., Bao, Z. *AIChE J.* 2016, 62, 4403.
- [107] Park, K.S., Ni, Z., Cote, A.P., Choi, J.Y., Huang, R., Uribe-Romo, F.J., Chae, H.K., O'Keeffe, M., Yaghi, O.M. *PNAS* 2006, 103, 10186.
- [108] Murillo, B., Zornoza, B., de la Iglesia, O., Tellez, C., Coronas, J.J. *Catal.* 2016, 334, 60.
- [109] Chen, J., Liu, R., Guo, Y., Chen, L., Gao, H. *ACS Catal.* 2015, 5, 722.
- [110] Yuan, Q., Zhang, D., van Haandel, L., Ye, F., Xue, T., Hensen, E.J.M., Guan, Y. *J. Mol. Catal. A Chem.* 2015, 406, 58.
- [111] Fang, R., Luque, R., Li, Y. *Green Chem.* 2016, 18, 3152.
- [112] Zhang, D., Ye, F., Guan, Y., Wang, Y., Hensen, E.J.M. *RSC Adv.* 2014, 4, 39558.
- [113] Cirujano, F.G., Corma, A., Llabres i Xamena, F.X. *Chem. Eng. Sci.* 2015, 124, 52.
- [114] Zhang, F., Jin, Y., Fu, Y., Zhong, Y., Zhu, W., Ibrahim, A.A., El-Shall, M.S. *J. Mater. Chem. A* 2015, 3, 17008.
- [115] Zhang, F., Zheng, S., Xiao, Q., Zhong, Y., Zhu, W., Lin, A., El-Shall, M.S. *Green Chem.* 2016, 18, 2900.
- [116] Sheldon, R.A. in *Ionic Liquids in the Biorefinery Concept: Challenges and Perspectives*, p 258, The Royal Society of Chemistry, 2016.