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# Hydrolysis of Oligosaccharides Over Solid Acid Catalysts: A Review

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Mild fractionation/pretreatment processes are becoming the most preferred choices for biomass processing within the biorefinery framework. To further explore their advantages, new developments are needed, especially to increase the extent of the hydrolysis of poly- and oligosaccharides. A possible way forward is the use of solid acid catalysts that may overcome many current drawbacks of other common methods. In this Review, the advantages and limitations of the use of heterogeneous catalysis for the main groups of solid acid catalysts (zeolites, resins, carbon materials, clays, silicas, and other oxides) and their relation to the hydrolysis of model soluble disaccharides and soluble poly- and oligosaccharides are presented and discussed. Special attention is given to the hydrolysis of hemicelluloses and hemicellulose-derived saccharides into monosaccharides, the impact on process performance of potential catalyst poisons originating from biomass and biomass hydrolysates (e.g., proteins, mineral ions, etc.). The data clearly point out the need for studying hemicelluloses in natura rather than in model compound solutions that do not retain the relevant factors influencing process performance. Furthermore, the desirable traits that solid acid catalysts must possess for the efficient hemicellulose hydrolysis are also presented and discussed with regard to the design of new catalysts.

## 1. Introduction

Biochemical platform development is in a more advanced stage in comparison to other biorefinery platforms; nevertheless, many improvements are still needed to further advance this concept.[1] Specifically, the development and improvement of biomass fractionation technology and optimizing the fractionation processes to make use of the whole plant are an absolute necessity. Special attention should be given to hemicellulose separation, recovery, and valorization. Usually, hemicellulose is partly hydrolyzed and solubilized during the lignocellulose fractionation. This process, carried out in mild conditions using water (e.g., autohydrolysis, steam explosion), or using dilute acids, such as sulfuric or phosphoric acids,[2] leads to the separation of a solid fraction containing cellulose and lignin and an aqueous fraction containing ex-hemicellulose poly/oligosaccharides (as the borderline between oligosaccharides and polysaccharides cannot be drawn strictly,[3] for the sake of simplicity, oligosaccharides and soluble polysaccharides will be referred to as poly/oligosaccharides) and acetic acid, as well as ex-lignin and ex-proteins compounds (Figure 1).

Hemicellulosic poly/oligosaccharides (e.g., xylo-oligosaccharides) have an important added value for pharmaceutical and food industries and could represent an economic advantage for the biorefinery.[4] Nevertheless, their market volume is not large in comparison to the monosaccharide-derived products. From monosaccharides, even from the pentoses, conversion into bioethanol or biohydrogen is promising[5] as well as the production of important platform molecules such as polyols or other fermentative products, furfural, 5-hydroxymethylfurfural (HMF), and levulinic acids, which are products of dehydration during acid hydrothermal conversion.[6]

Therefore, the hydrolysis of hemicellulose-derived poly/oligosaccharides into monomeric sugars is crucial in an integrated biorefinery framework, but process options are restricted to the use of sulfuric acid as enzymatic processes are still underperforming.[2] However, mineral acids can be advantageously replaced by solid acid catalysts: heterogeneous catalysts can easily be separated, recovered, and reused; they are safe and non-corrosive. That is why they are increasingly used in numerous biorefinery processes.[7] The use of solid acids keeps the advantages of using acid hydrolysis, but improves selectivity towards the glycosidic bonds at the expense of the dehydration of monosaccharides and can lead to higher sugar yield. Moreover, the hydrolysis of soluble oligosaccharides over a solid acid catalyst can be performed in a dynamic flow reactor, allowing for a continuous process and thus decreasing production cost as Kim et al.[8] suggested in the case of corn-fiber valorization. Thus, solid acid catalysts represent an opportunity to develop more efficient and greener hydrolysis processes for soluble poly/oligosaccharides.

Cellulose deconstruction using solid acid catalysts has been studied in detail during the last decade. This is already the topic of several reviews.[9] Comparatively, the catalytic hydroly-

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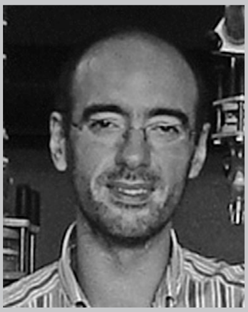

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sis of hemicelluloses or hemicellulosic oligosaccharides is less reported, although a pioneering work was published in the 1980s.[10] However, to the best of our knowledge, there is no recent review focusing on the use of solid acid catalysts for the hydrolysis of soluble oligosaccharides. Cellulose is a solid polysaccharide with a crystalline structure making it very difficult to solubilize and hydrolyze, leading to innovative research strategies including bifunctional catalysis and the use of unconventional media such as supercritical water or ionic liquids.[11] In contrast, oligosaccharides are soluble compounds and are relatively easy to hydrolyze with solid catalysts as there is no solid–solid transfer involved. Therefore, the catalysts and the reaction conditions used in both cases are different and the results obtained on cellulose hydrolysis cannot be transposed to oligosaccharides hydrolysis.

The most often proposed pathway for valorization of pentoses is dehydration into furfural, which is a building block for the synthesis of fuels and chemicals. This topic will not be addressed herein, since high-quality reviews are already available.[6d,12] Other interesting and even more valuable products, such as xylitol, can also be produced from pentoses. That is why hydrolysis of oligosaccharides into pentoses and hexoses without further dehydration into furfural and HMF is critical for numerous processes.

Herein, we review the use of solid acid catalysts for the hydrolysis of poly/oligosaccharides into sugars. The advances on the kinetics and mechanism of oligosaccharides hydrolysis are briefly reported. Then, we report the use of solid acid catalysts for hydrolysis of commercial disaccharides as model compounds, with an emphasis on the performances and on the recyclability of the catalysts. The hydrolysis of more complex soluble oligosaccharides is also reviewed. Only a few authors have shown the impact of real oligosaccharides liquors on the catalysts; their work is reviewed in a fourth part. The last part of this Review provides an outlook on the hydrolysis of raw materials with solid acid catalysts.

## 2. Hydrolysis Reaction—Kinetic and Mechanistic Considerations

The hydrolysis of polysaccharides can be seen as a sequence of three first order reactions: first, the polysaccharides are hydrolyzed into oligosaccharides and, subsequently, into monosaccharides; then, the monosaccharides are dehydrated into products such as HMF, furfural, and carboxylic acids.[13] For example, in the absence of catalyst, glucose is dehydrated into HMF around 130 °C.[14] The efficiency of the hydrolysis process depends on the ratio of the kinetic constants $\alpha = (k_1 + k_2)/k_3$: when $\alpha$ increases, the monosaccharide selectivity increases (Scheme 1).

The value of the kinetic constants $(k_1 + k_2)$ is correlated to the effective acidity, that is, the acid sites available and accessible in aqueous medium.[15] Thus, it is important to take into account the water effect on Brønsted acid sites[16] and the diffusion limitations due to the size of the biggest poly/oligosaccharides.

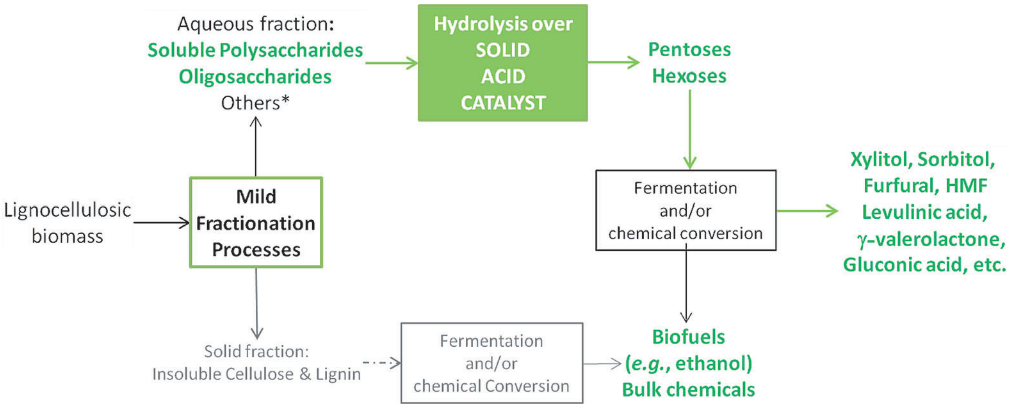

**Figure 1.** Schematic representation of a biomass upgrading strategy highlighting the relevance of solid acid catalysts for hemicellulose upgrade. Potential added-value products are represented in green. Note: *includes soluble phenolics from lignin, acetic acid from hemicellulosic acetyl groups, mineral ions, proteic compounds, and other extractives from the biomass source.

$$\text{Polysaccharides} \xrightarrow{k_1} \text{Oligosaccharides} \xrightarrow{k_2} \begin{array}{c}\text{Monosaccharides}\\ \text{(sugars)}\end{array} \xrightarrow{k_3} \begin{array}{c}\text{Dehydration}\\ \text{products}\end{array}$$

**Scheme 1.** Polysaccharide hydrolysis reaction.

The value of $(k_1+k_2)$ is also dependent of the reactant: the reactivity of the ether linkage depends on its environment. For example, poly/oligosaccharides with a low polymerization degree are more easily hydrolyzed into monomeric sugars than those with a high polymerization degree;[17] α-Anomers are more easily hydrolyzed than β-anomers, this effect being attributed to the adsorption step; furanoses are more easily hydrolyzed than pyranoses (e.g., arabinose is easier to recover than xylose); branched monomers are more easily cleaved than skeletal monomers. The ranking of reactivity of ether linkage is thus: arabinoside > xyloside > galactoside > mannoside > glycoside.[13d] In the case of disaccharides, the following ranking by decreasing reactivity was established in the presence of acid solids: sucrose ≫ maltose > cellobiose,[18] and corresponds to α-(1→2) linkage (Glc–Fru) ≫ α-(1→4) linkage (Glc–Glc) > β-(1→4) linkage (Glc–Glc).

Concerning the mechanism, the most common hypothesis is the adsorption of poly/oligosaccharides using oxygen electron lone pairs or hydroxyl groups, then protonation of the oxygen atom of the ether linkage, followed by the insertion of a water molecule, leading to a C–O bond cleavage. A proton is then released (Figure 2). This mechanism occurs randomly on the poly/oligosaccharides chain.[15] Brønsted acid sites are required for the hydrolysis reaction.[19] Admittedly, strong acidity is necessary ($\mathrm{p}K_a < 4$),[20] but strong mineral acids may lead to high yields in dehydration products. Thus, it is proposed that the acid strength should be chosen carefully to permit hydrolysis reactions and limit degradation reactions. As an example, maleic acid ($\mathrm{p}K_a = 1.9$; 4.4) exhibited better performances than $H_2SO_4$ ($\mathrm{p}K_a = -3$; 2) for homogeneously catalyzed cellobiose hydrolysis.[21]

Alternatively, Charmot and Katz[22] suggest that an acid–base pair is necessary to cleave a glycosidic bond: the base adsorbs the poly/oligosaccharides using the hydroxyl groups and the acid cleaves the ether linkage.

To overcome dehydration reaction of the sugars, the transformation of sugars in situ into less reactive products is often proposed and leads to higher yields in final products. This means the formation of polyols such as xylitol (from xylose),[28] arabitol and galactitol (from arabinose and galactose, respectively),[29] or sorbitol (from glucose)[9a, 30] in reductive conditions or the formation of gluconic acid (from glucose) in oxidative conditions.[31]

## 3. Acid Catalysts for Hydrolysis of Model Disaccharides

Heterogeneous acid catalysts have been widely used for a long time, particularly in oil refinery processes such as fluid catalytic cracking, isomerization among others.[32] Corma et al. extensively revised their application in biomass conversion processes.[33] Nevertheless, the traditional solid acid catalysts were not designed to be water resistant. With the development of biorefineries and new processes involving soluble compounds such as sugars in water at low temperature, understanding the behavior of acid catalysts in aqueous medium became impor-

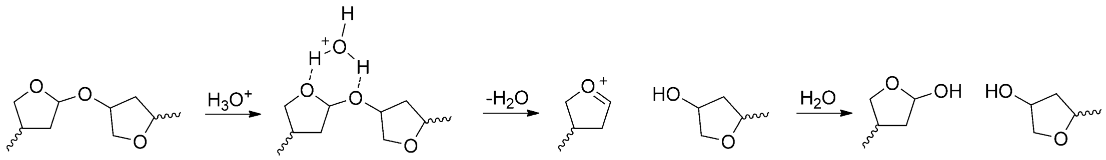

**Figure 2.** Mechanism of acid hydrolysis of hemicellulose glycosidic bonds. The hydrogen and hydroxyl groups are omitted for clarity. Adapted from [9b].

tant since it is known that water modifies the strength and number of acid sites of solid acid catalysts.[34]

Table 1. Hydrolysis of disaccharides using zeolites.

| Entry | Catalyst | Reactant | Operating conditions[a] | Catalyst/substrate mass ratio [*w*/*w*] | Conversion [%] | Sugar yield [%] | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | H-Y (Si/Al = 27) | sucrose | 70 °C, 8 h | 0.1 | $<5$ | – | [23] |
| 2 | H-Y (Si/Al = 55) | | | | $<5$ | – | |
| 3 | H-Y (Si/Al = 110) | | | | 90 | – | |
| 4 | H-Y (Si/Al = 15) | sucrose | 95 °C, 3 h | 0.01 | 100 | – | [24] |
| 5 | organic matrix-USY | sucrose | 80 °C, 1 h | 0.025 | – | 36 | [25] |
| 6 | organic matrix-beta | | | | – | 30 | |
| 7 | H-ZSM5 | sucrose | 80 °C, 1 h | 0.2 | – | $<1$ | [26] |
| 8 | H-ZSM5 | cellobiose | 95 °C, 1 h | | – | 0 | |
| 9 | H-BEA | cellobiose | 120 °C, 24 h | 1 | 1.6 | 0.8 | [27] |
| 10 | H-MOR | maltose | 130 °C, 24 h, 10 bar $N_2$ | 0.5 | 60–70 | 66 | [14] |
| 11 | H-beta | | | | 45–85 | 81 | |
| 12 | H-Y (Si/Al = 15) | sucrose | 100 °C, 1.5 h, fixed-bed reactor | – | 100 | – | [24] |

[a] The tests were carried in batch reactor, under atmospheric pressure, unless otherwise specified.

In the following sections, we present and discuss the major groups of solid acid catalysts and their relation to the hydrolysis of model disaccharides. The aims of these studies are the hydrolysis of sucrose into glucose and fructose, used in food industry, the hydrolysis of maltose as a model compound for starch and of cellobiose as a model compound for cellulose. None of these disaccharides are present in hemicellulose or in ex-hemicellulose oligosaccharides. However, they provide interesting information on the solid acid catalysts behavior during hydrolysis reaction.

### 3.1. Zeolites

Zeolites are crystalline aluminosilicates with complex tridimensional structures creating different levels of porosity: mesopores (5–50 nm) and micropores ($<5$ nm). Their surfaces, acid strength, and acid sites concentrations can be finely tuned by several preparation methods. However, the stability of zeolites in the presence of water is a questionable issue. Ravenelle et al.[42] reported recently that faujasite H-Y zeolites deactivate around 200 °C in liquid water in a few hours, whereas Dimitrejvic's work shows that the same catalysts are stable up to 160 °C.[43] The ultrastable zeolites H-USY could overcome this issue: this type of zeolite is treated by steaming to improve the stability. These materials are able to hydrolyze xylan in water at 140 °C.[44]

Zeolites have been studied for the hydrolysis of various disaccharides (Table 1). They can easily convert disaccharides into monomer sugars at temperatures between 80 and 140 °C. Interestingly, several authors report a very low activity of H-ZSM5, perhaps due to the low temperature of the reaction (Table 1, entries 7 and 8). Even if, theoretically, they can catalyze dehydration reactions such as fructose dehydration into HMF, in most of the cases the yield in dehydration products is low. The adsorption of HMF on the zeolite was reported by Moreau et al.[24] and could explain its absence in the reaction medium.

The Si/Al ratio is an essential property of zeolites. Basically, when the Si/Al ratio increases, the number of Brønsted acid sites decreases, and the average acid strength increases. This leads to an increased activity of zeolites in disaccharides hydrolysis (Table 1, entries 1–3). The adsorption of the reactant seems to be favored by a decreasing aluminum content.[23]

Abaddi et al.[14] observed a partial deactivation of zeolites H-mordenite and H-beta during hydrolysis of maltose at 130 °C: a slight leaching of Al and Si led to the presence of homogeneous complexes and to the decrease of heterogeneous catalytic activity.

It is interesting to note that, in the case of the hydrolysis of disaccharides (sucrose or maltose), the diffusion of the reactant into the zeolite pores is not an issue.[14] It was suggested that some disaccharides such as sucrose have a high affinity for the polar surface of zeolites.[23]

### 3.2. Resins and polymers

Resins are organic polymers synthesized as beads. They can contain a macroreticular structure with an important specific surface area and microporosity. Their high ion-exchange capacity is used for the adsorption of cations. Resins are also used in organic synthesis as acid catalysts.[45] Their acidity is due to the presence of sulfonic groups ($-SO_3H$). One of the most common resins is the Rohm and Haas Amberlyst-15. Resins have been widely used in the hydrolysis of various disaccharides (Table 2) since the 1970s.[46] They have the advantage of converting disaccharides into monomeric sugars at low temperatures (40–130 °C). At 80–90 °C, for example, they are more active than zeolites.[39–41,47]

The main drawback of resins is their poor temperature stability. For example, the Amberlyst resins are designed for temperatures lower than 130 °C (from Rohm and Haas data). This can be a major issue for disaccharides hydrolysis in which the temperature can be close to 130 °C[14] or above. However, Kim et al.[8] suggest that Amberlyst-35W could be stable until 160 °C despite the commercial recommendation.

Thus, resins can be useful for hydrolysis processes at low temperatures. Their adsorption and ion-exchange properties can also be used to remove impurities before the fermentation process, such as cations, proteins, furfural, HMF, aliphatic acids, or lignin derivatives.[48]

Polymers such as polystyrene grafted with sulfonic groups can also be interesting for low temperature hydrolysis.[49] The main advantage of polymers is that they can be adapted to various shapes (beads, membranes, etc.).

**Table 2.** Hydrolysis of disaccharides using resins.

| Entry | Catalyst | Reactant | Operating conditions[a] | Catalyst/substrate mass ratio [*w*/*w*] | Conversion [%] | Sugar yield [%] | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | Amberlite IR-120 H | sucrose | 170 °C, 1 h | 2.6 | 85–100 | – | [35] |
| 2 | Amberlite 200C | sucrose | 80 °C, 3 h | 1.6 | 100 | 98 | [36] |
| 3 | Amberlite IR-120 H | sucrose | 79 °C, 1.5 h, $N_2$ | 3.6 | 100 | – | [37] |
| 4 | Amberlyst-35W | cellobiose | 110-130 °C, 2 h | 166 | 80–100 | 70 | [8] |
| 5 | Nafion NR50 | cellobiose | 100 °C, 4 h | 2 | – | 6.7 | [38] |
| 6 | Amberlyst-15 | | | | – | 7 | |
| 7 | Amberlyst-15 | cellobiose | 90 °C, 24 h | 0.8 | 62 | 62 | [39] |
| 8 | Amberlite A120 | sucrose | 80 °C, 4 h, recirculating fixed-bed reactor | – | 91 | 82 | [18] |
| 9 | Amberlite A200 | | | | 100 | 95 | |
| 10 | Amberlite A120 | maltose | 80 °C, 50 h, recirculating fixed-bed reactor | | 33 | 29 | |
| 11 | Amberlite A200 | | | | 19 | 15 | |
| 12 | Amberlite A120 | cellobiose | | | 22 | 18 | |
| 13 | Amberlite A200 | | | | 6 | $<5$ | |
| 14 | Dowex50×2-100 | maltose | 120 °C, 26 h, 5 bar $N_2$ | 0.5 | $>95$ | – | [14] |
| 15 | Amberlyst-15 | sucrose | 80 °C, 2 h | 0.2 | – | 75 | [40] |
| 16 | Nafion NR50 | | | | – | 30 | |
| 17 | Amberlyst-15 | cellobiose | 100 °C, 2 h | 0.2 | – | 87 | |
| 18 | Nafion NR50 | | | | – | 75 | |
| 19 | Amberlyst-15 | sucrose | 80 °C, 4 h | 0.5 | 88 | 88 | [41] |
| 20 | Nafion–$SiO_2$ | | | | 28 | 27 | |

[a] The tests were carried in batch reactor, under atmospheric pressure, unless otherwise specified.

### 3.3. Carbon materials

Activated carbon, char or carbon nanotubes are carbon materials used as catalysts or sorbents. Their specific surface areas are usually very high (more than 500 $m^2 g^{-1}$), with an important microporous volume. In heterogeneous catalysis, they are used as metal supports or as acid catalysts in various processes.[50] In the latter case, they can be acid-treated for example in fuming $H_2SO_4$ which forms sulfonic ($-SO_3H$) groups at the carbon surface. Activated carbons also contain hydroxyl and carboxyl groups.

In the biorefinery context, it is interesting to note that activated carbons and char can be easily prepared from raw or treated biomass. Wood chips, peanut hulls,[51] orange skin,[52] olive stone,[53] and hemp fiber,[54] even glucose[19] can be used as starting materials for the preparation of activated carbons.

Sulfonated carbons and chars were reported to catalyze the hydrolysis of various disaccharides with good performances (Table 3, entries 1–4). Their hydrophilic behavior, due to hydroxyl surface groups, could explain their high activity: the weak acid sites present on the carbon surface (hydroxyl and carboxyl groups) adsorb easily the carbohydrates.[19,38,39,55]

Ormsby et al.[51] prepared chars from biomass which exhibited a higher activity for cellobiose hydrolysis than Amberlyst-15 resin.

Carbons are known to be stable in aqueous media,[56] but the sulfonated surface groups are sometimes leached during hydrolysis reactions.[51] The deactivation of sulfonated carbon does not occur at low temperature (90 °C).[39] Thus, the recyclability of such catalysts should be studied carefully.

As for resins, some authors suggest to use chars as adsorbents for fractionation processes impurities.[8,57]

### 3.4. Functionalized silica

Silica is a class of catalysts with a wide range of porosities and surface areas, from mesoporous materials (e.g., amorphous silica) to microporous materials (e.g., SBA-15, MCM-41). Their intrinsic acidity is not very interesting, but they can be modified by treatments involving sulfone or sultone compounds and then include sulfonic ($-SO_3H$) groups. As in the case of carbon materials, they can bear hydroxyl or carboxylic groups.

Sulfonated silicas have been tested for the hydrolysis of several soluble disaccharides (Table 3, entries 5–12). Bootsma and Shanks[20] suggested that sulfonic groups release protons in the aqueous medium to hydrolyze cellobiose, that is, the reactant is not in close contact with the solid catalyst and the diffusion rate does not limit the reaction kinetics. Several authors reported good stability of sulfonated silica during disaccharides hydrolysis.[41,58] Lai et al.[58,59] improved the catalyst recovery by adding paramagnetic iron species on SBA-15-$SO_3H$. This process was also applied to nanoparticles $CoFe_2O_4$-$SiO_2$-$SO_3H$ for cellobiose hydrolysis,[60] with glucose yields reaching 50 % for a 80 % cellobiose conversion.

### 3.5. Other oxides

Inorganic oxides are widely used in heterogeneous catalysis as pure compounds, as supports for metals or other promoters, or as mixed oxides.

Abbadi et al.[14] tested silica–alumina for maltose hydrolysis (Table 3, entry 16). The major drawback is that the basic sites of alumina enhance glucose dehydration into HMF and decrease sugar yield.

**Table 3.** Hydrolysis of disaccharides using various solid catalysts.

| Entry | Catalyst | Reactant | Operating conditions[a] | Catalyst/substrate mass ratio [*w*/*w*] | Conversion [%] | Sugar yield [%] | Ref. |
|---|---|---|---|---|---|---|---|
| 1 | carbon-$SO_3H$ | cellobiose | 90 °C, 24 h | 0.8 | 85 | 85 | [39] |
| 2 | biochar-$SO_3H$ | cellobiose | 123 °C, 7 h | 10 | 97 | 80 | [51] |
| 3 | activated carbon-$SO_3H$ | | | | 95 | 18 | |
| 4 | magnetic porous carbon-$SO_3H$ | sucrose | 80 °C, 2.5 h | 0.3 | 100 | 94 | [63] |
| 5 | silica-R-$SO_3H$ | cellobiose | 175 °C, 2 h | 0.2 | 100 | – | [20] |
| 6 | silica-R-COOH | | | | 30 | – | |
| 7 | MCM-41 | maltose | 130 °C, 24 h | 0.5 | 74 | – | [14] |
| 8 | SBA-15-COOH | sucrose | 80 °C, 4 h | 0.5 | 68 | – | [64] |
| 9 | MCM-41 | | | | 50 | – | |
| 10 | $SiO_2$-$SO_3H$ | sucrose | 80 °C, 4 h | 0.5 | 90 | 90 | [41] |
| 11 | $ZrO_2$-$SO_3H$/SBA-15 | cellobiose | 160 °C, 1.5 h, 20 bar $N_2$ | 0.2 | 80 | 54 | [61] |
| 12 | SBA-15 | | | | 20 | 15 | |
| 13 | $Fe_3O_4$–SBA-15-$SO_3H$ | cellobiose | 120 °C, 1 h | 1.5 | 98 | 96 | [58] |
| 14 | $ZrO_2$-$SO_3H$ | cellobiose | 160 °C, 1.5 h, 20 bar $N_2$ | 0.2 | 64 | 15 | [61] |
| 15 | Al-SBA-15 | | | | 39 | 20 | |
| 16 | $SiO_2$–$Al_2O_3$ | maltose | 130 °C, 24 h | 0.5 | 45–83 | | [14] |
| 17 | $WO_3/ZrO_2$ | cellobiose | 97 °C, 32 h | 0.1 | 9 | 7.5 | [65] |
| 18 | $SiO_2$–$Al_2O_3$ | sucrose | 80 °C, 4 h, recirculating fixed-bed reactor | - | 28 | 9 | [18] |
| 19 | $SiO_2$–$ZrO_2$ | sucrose | | | 11 | $<5$ | |
| 20 | $Nb_2O_5$ | sucrose | | | 20 | 10 | |
| 21 | $Nb_2O_5$–$PO_4$ | sucrose | | | 62 | 62 | |
| 22 | $CoFe_2O_4$–$SiO_2$-$SO_3H$ | cellobiose | 175 °C, 1 h | 0.2 | 80 | 50 | [60] |
| 23 | $H_4SiW_{10}O_{40}$ | cellobiose | 150 °C, 24 h | 1 | 61 | 53 | [27] |
| 24 | $H_3PMo_{12}O_{40}$ | | | | 83 | 48 | |
| 25 | $H_4SiMo_{12}O_{40}$ | | | | 75 | 42 | |

[a] The tests were carried in batch reactor, under atmospheric pressure, unless otherwise specified.

Sulfated zirconia led also to a low activity during cellobiose hydrolysis (Table 3, entry 14). The low surface area of sulfated zirconia can be increased by dispersing it in a SBA-15 matrix.[61] The interactions between silica and zirconia create strong Brønsted acid sites useful for cellobiose hydrolysis, with a glucose yield of 60% (Table 3, entry 11).

Phosphates are also known as acidic promoters for oxides. Nevertheless, $Nb_2O_5$–$PO_x$ is not very active during disaccharides hydrolysis: its weak Brønsted acid sites are occupied by water and its strong Lewis acid sites are unable to hydrolyze ether osidic bonds (Table 3, entries 20, 21).[18] $Nb_2O_5$ and mixed oxides including niobium ($Nb_2O_5$–$SiO_2$) exhibited low activity for sucrose hydrolysis for the same reasons.[18,62]

Mixed oxides of niobium and tantalum or tungsten were evaluated during the conversion of sucrose (80 °C) and cellobiose (95 °C): their catalytic performances are better than resins and zeolites for the same conditions.[26,47,66] The authors attribute this high activity to the presence of strong acid sites due to amorphous tungsten on the catalyst surface.

Indeed, tungstated zirconias are known as efficient acid catalysts, bearing Lewis and/or Brønsted acid sites depending on the tungsten content and dispersion.[67] They are active and stable during cellobiose hydrolysis if the tungsten condensation is high enough to form strong Brønsted acid sites, validating the role of Brønsted and Lewis acidities in the hydrolysis reaction (Table 3, entry 17).[65]

Layered mixed transition metal oxides ($HNbMoO_6$, $HTiNbO_5$ and $HTaMoO_6$) have been presented by Takagaki et al.[26,40,47,66,68] as very interesting catalysts for the hydrolysis of cellobiose: their layered structure and polar surface permit the adsorption of disaccharides and water in the intercalary space (Figure 3). Then, the strong acid sites present in the intercalar space can easily hydrolyze the ether linkages, with glucose yield reaching 100% in 2 h at 100 °C during cellobiose conversion over nanosheets $HNbMoO_6$.[40]

### 3.6. Heteropolyacids

Heteropolyacids (HPAs) are protonic acids that incorporate polyoxometalate anions having metal–oxygen octahedral as the basic structural units into the complex cluster.[69]

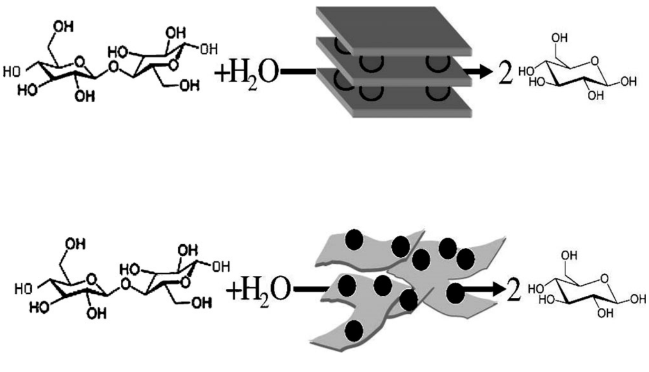

**Figure 3.** Layered (up) and nanosheets (bottom) mixed transition metal oxides. Reprinted from [68a] with permission.

Micellar heteropolyacids are efficient for sucrose hydrolysis: the micellar structure facilitates the interactions acid site-reactant.[70] Moreover, this catalyst is stable in the reaction medium. HPAs can hydrolyze cellobiose into glucose at 150 °C (Table 3, entries 23–25).

Many HPAs exhibit super acidity. For example, $H_2PW_{12}O_{40}$ is a stronger acid than $H_2SO_4$ or $CF_3SO_3H$. The drawback is their solubility in polar solvents but they can be supported on silica,[71] carbon or acidic ion-exchange resins.

The study of the hydrolysis of disaccharides provides useful information on the solid acid catalysts behavior. The hydrolysis reaction is usually carried out between 80 and 120 °C, with times on stream between 1 and 24 h. Several types of solid acids are able to hydrolyze disaccharides into monosaccharides with a good selectivity and limited side reactions. However, the nature of the disaccharide influences the rate of hydrolysis, corroborating the activity order, sucrose $>$ maltose $\gg$ cellobiose, already presented in Section 2. A key element of the catalyst behavior is the stability in the aqueous reaction medium. However, two thirds of the reviewed articles do not present data on the catalyst stability or recyclability. When the recyclability is studied, most of the catalysts exhibit an activity decrease over three runs as for example MCM-41[14,64] or Amberlyst-15.[39] Indeed, there is no report of the recyclability of a resin catalyst for a disaccharide hydrolysis reaction. In contrast, sulfonated carbon can be stable at low temperature,[39] as well as sulfonated silica[41] or layered mixed transition metal oxides.[47,68a]

## 4. Acid Catalysts for Hydrolysis of Model Hemicellulosic Oligosaccharides

The catalytic hydrolysis of hemicellulosic oligosaccharides derived from xylan, arabinogalactan, and *O*-acetyl-galactoglucomannan has also been studied in a few papers (Table 4). As a general trend, the hydrolysis of such complex oligosaccharides requires more severe operating conditions, that is, longer reaction times, up to 100 h (entries 1 and 2), higher temperatures (140–185 °C) (entries 5, 7, 13–20), or high catalyst loadings (entries 6 and 7). In these conditions, the hydrolysis reaction gives monomeric sugars in yields as high as 80 %. Disaccharides and small oligosaccharides are also produced, indicating a random cleavage of the glycosidic bonds. Nevertheless, mass-transfer limitations are observed, for example, with an Amberlyst-15 resin catalyst.[72] This is due to the slow diffusion of the reactant into the pores of microporous (zeolites) or mesoporous catalysts, which could be overcome by using added pressure (entries 5, 13-30).[25] The catalyst structure has also an impact on the oligosaccharides diffusion inside the pores. For example, the resin cross-linkage degree increases mass-transfer limitations. Fibrous resins (Smopex-101, entries 1, 3) are suitable to facilitate the reactant and products transfers to the catalytic sites.[72] Because of their microporosity, activated carbons can also lead to diffusion limitations. To avoid these issues, the use of carbon materials structured as randomly oriented sheets is a good option.[39,55]

Among the catalysts tested, resins are the most used (entries 1–4, 7, 22–25). These catalysts present a high number of acid sites (around 4–5 $mmol_{H^+}\,g^{-1}$ for Amberlyst-15), but their stability in aqueous media is uncertain. Carà et al. show that Amberlyst-35 and Purolite D5082 are not recyclable over three runs for xylan hydrolysis.[73] The lack of stability of Amberlyst-15 was already discussed in Section 3; this result is corroborated by a recyclability test over xylan hydrolysis.[51]

Zeolites are also popular for complex oligosaccharides hydrolysis, despite of their microporosity (entries 12–16, 27–30). They present a medium number of acid sites (between 0.5 and 1.2 $mmol_{H^+}\,g^{-1}$), but can hold strong acid sites, as, for example, H-ferrierite.[73] It is interesting to note that H-ZSM5 can present a medium hydrolysis activity for complex oligosaccharides, whereas its activity for disaccharides hydrolysis was null (see Section 3). This result is probably explained by the added pressure used for complex oligosaccharides hydrolysis, which permits a better internal diffusion of the reactants. Concerning the recyclability, when reported, the zeolites H-ferrierite and H-USY are recyclable.[73–74]

Mesoporous silicas (entries 5 and 8), silica–alumina (entries 17 and 18), and silica gel (entry 26), sulfonated or not, have also been studied for arabinogalactan and xylan hydrolysis. The sulfonated catalysts present a high number of acid sites and a high conversion rate. However, their stability in aqueous medium is questionable, since the sulfonated groups can be easily leached. The sulfonated silica gel synthesized by Carà et al. was not recyclable over three runs, for example.[73] The non-sulfonated silica–alumina Al-MCM-41 and Al-SBA-15 do not hold enough active acid sites to be interesting for xylan hydrolysis. However, Kusema et al. obtained good results in arabinogalactan hydrolysis over MCM-48, probably because of the high temperature.[29]

Other oxides, such as titania and zirconia (entries 9–11)[75] or alumina and niobia (entries 19 and 20), have been tested for xylan hydrolysis and have shown a medium activity. Sulfated oxides are most of the time unstable in aqueous medium, the sulfates groups being leached and giving homogeneous active species, for example in the case of $ZrO_2$–$SO_4$.[61,75] The main product of xylan hydrolysis was furfural, and only small amounts of xylose. Actually, in the case of titania and zirconia, furfural and HMF were the target compounds, sugars were considered by-products.

To the best of our knowledge, there is only one publication reporting the activity of a clay (K-10, acid-activated montmorillonite) for the hydrolysis of hemicelluloses.[74] The clay exhibited an activity comparable to zeolites at 170 °C. However, a fast deactivation was observed for this catalyst (severe loss of surface area).

The reported results of catalytic hydrolysis of hemicellulosic oligosaccharides underline the importance of two major parameters. First, the mass-transfer limitations induced by the molecular dimensions of complex oligosaccharides lead to selection of different operating conditions, including higher temperature (generating higher water autogenous pressure), and added pressure of inert gas to facilitate the internal diffusion. Secondly, in these more drastic conditions, the catalyst stability

**Table 4.** Hydrolysis of soluble hemicellulosic poly/oligosaccharides using various solid catalysts.

| Entry | Catalyst | Reactant | Target compound(s) | Operating conditions[a] | Catalyst/substrate ratio [*w*/*w*] | Acid-site number [$mmol_{H^+}\,g^{-1}$] | Conversion [%] | Sugar yield [%] | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Smopex-101 | *O*-acetyl-galactoglucomannan | glucose, mannose, galactose | 90 °C, 72 h | – | – | 60 | – | [81] |
| 2 | Amberlyst-15 | | | 90 °C, 100 h | – | – | 50 | – | |
| 3 | Smopex-101 | arabino-galactan | arabinose | 90 °C, 24 h | – | – | – | 85 | [72] |
| 4 | Amberlyst-15 | | | | | – | – | 50 | |
| 5 | MCM-48 | arabino-galactan | arabinose, galactose | 185 °C, 24 h, 20 bar $H_2$ | 0.5 | 0.12[b] | 100 | 65 | [29] |
| 6 | biochar-$SO_3H$ | xylan | xylose | 123 °C, 2 h | 13 | 5.65[c] | 80 | – | [51] |
| 7 | Amberlyst-15 | | | | | – | 80 | – | |
| 8 | SBA-15-$SO_3H$ | xylan | xylose | 180 °C, 2 h | 0.16 | 2.8[c] | 95 | 35 | [80] |
| 9 | $TiO_2$ | xylan | furfural | 250 °C, 5 min | 1 | 0.16[d] | 55–62 | 12–13 | [75] |
| 10 | $ZrO_2$ | | | | | 0.23 | 40–50 | 7–9 | |
| 11 | $ZrO_2$-$SO_4$ | | | | | 0.76 | 60 | 12 | |
| 12 | H-USY-oxalic acid treated | xylan | reducing sugars | 140 °C, 7 h | | 0.05[d] | – | 56 | [44] |
| 13 | H-USY | xylan | | 170 °C, 3 h, 50 bar $N_2$ | 0.5 | 0.55[d] | 53 | 41 | [74] |
| 14 | H-beta (Si/Al=19) | | | | | 0.91 | 43 | 38 | |
| 15 | H-mordenite | | | | | 1.18 | 42 | 37 | |
| 16 | clay K-10 | | | | | 0.42 | 41 | 29 | |
| 17 | Al-MCM-41 (Si/Al=50) | | | | | 0.14 | 18 | 15 | |
| 18 | Al-SBA-15 (Si/Al=100) | | | | | 0.08 | 7 | 5 | |
| 19 | $Al_2O_3$ | | | | | 3.74 | 32 | 20 | |
| 20 | $Nb_2O_5$ | | | | | 0.3 | 28 | 20 | |
| 22 | Amberlyst-70 | xylan | xylose, arabinose | 120 °C, 4 h, 10 bar Ar | 1 | 2.55 | – | 75 | [73] |
| 23 | Amberlyst-35 | | | | | – | – | 80 | |
| 24 | D5081 | | | | | – | – | 55 | |
| 25 | D5082 | | | | | – | – | 70 | |
| 26 | sulfonated silica gel | | | | | – | 100 | 48 | |
| 27 | H-ZSM5 (Si/Al=50) | | | | | – | – | 33 | |
| 28 | H-ZSM5 (Si/Al=80) | | | | | – | – | 29 | |
| 29 | H-Y | | | | | – | – | 20 | |
| 30 | H-ferrierite | | | | | – | – | 43 | |

[a] The tests were carried in batch reactor, under atmospheric pressure, unless otherwise specified. [b] Determined by FTIR-pyridine. [c] Determined by acid-base titration. [d] Determined by temperature programmed desorption of ammonia (TPD-$NH_3$).

is crucial. However, this parameter is not systematically studied. Another important element is the number and strength of acid sites. The methods used to determine the acid sites concentration varies from one article to another [e.g., temperature-programmed desorption of ammonia (TPD-$NH_3$), titration, etc.], making a global comparison difficult. Nevertheless, it seems that a high acid-site number and available strong Brønsted acid sites favor the hydrolysis rate.

## 5. Catalytic Hydrolysis of Hemicelluloses and Ex-Hemicellulose Oligosaccharide-Rich Liquor

Catalytic studies on ex-hemicellulose oligosaccharide-rich liquors are very rare in the literature. To the best of our knowledge, there are only two papers reporting the use of solid catalysts for the transformation of oligosaccharides liquor. The first concerns the use of sulfonated resins to hydrolyze the oligosaccharides present in the aqueous stream of corn-fiber pretreatment.[8] A sugar yield of 61 % is obtained at 130 °C in less than 2 h, for a conversion superior to 90 %. The other article is related to the hydrolysis of the oligosaccharides contained in the waste stream of distillers' grains, using functionalized silica holding sulfonic groups.[76] The glucose–xylose–arabinose global yield reaches 60 % at 175 °C in 1 h.

Both papers underline the negative role of proteins on the hydrolysis rate. These proteins can cover the surface of catalysts and lead to deactivation issues. A protein adsorbent made of resins or activated carbon is suggested by Bootsma et al.[76] to limit this deactivation.

For both studies, the necessary temperature for a good conversion is higher than for most of the model disaccharides, around 170 °C. This observation is in accordance with a lower kinetic rate of hydrolysis due to the high polymerization degree. Moreover, Bootsma et al. suggest that the temperature has a positive effect on the ratio hydrolysis/dehydration rates.[76]

The importance of impurities for the catalyst activity and stability present in, for example, autohydrolysis effluents has hardly been studied in the literature. It is important to note that oligosaccharide liquors contain carboxylic acids, mainly acetic acid coming from acetyl groups of hemicelluloses, furfural, HMF,[77] ex-lignin organic compounds (e.g., phenols, terpenes),[78] but also inorganic compounds (e.g., ions released during catalyst leaching) and, eventually, proteins coming from the raw lignocellulosic material. All these compounds can interact with acid catalysts and increase their deactivation, for example, by an ion-exchange reaction between the dissolved cations and the Brønsted acid sites of the catalyst, by poisoning, or by favoring the leaching of mineral compounds from the catalysts.

The presence of impurities after hydrolysis should also be taken into account: the subsequent fermentation of pentoses is a very sensitive process.[78] Thus, performance of catalytic hydrolysis must be evaluated not only on the sugars yield but also on the degradation products yield and primarily, on the leaching species from the catalyst.

## 6. Outlook: Catalytic Fractionation of Hemicellulose in Raw Biomass

Oligosaccharide hydrolysis by acid heterogeneous catalysis appears as a promising perspective for pentose valorization in biorefineries. Some pioneering papers show that it is also possible to selectively hydrolyze hemicelluloses during the fractionation of lignocellulosic biomass in liquid water using solid acid catalysts.

Sugarcane bagasse was converted over zeolites (H-USY, H-beta, and H-mordenite) and clays (K-10) at 170 °C, leading to oligosaccharides, xylose, and arabinose, the lignin and cellulose remaining in the solid state;[74] at 250 °C, furfural and HMF were selectively produced in the presence of $TiO_2$, $ZrO_2$, or $ZrO_2$–$SO_4$ catalysts,[75] indicating that cellulose is partially attacked and releases glucose. Studies on bamboo conversion over a sulfonated allophane (amorphous aluminosilicate) catalyst[79] and on various biomasses over H-USY zeolites[44] confirm that a lower temperature favors the selective hydrolysis of hemicelluloses into xylose. Xylose and glucose were also produced from rice straw at 180 °C over a sulfonated silicate SBA-15 catalyst.[80]

This kind of reaction could be attractive in the future to separate and valorize the pentose part of lignocellulose in a one pot reaction. However, several issues appear when performing a solid–solid catalytic reaction: the catalyst recovery remains a challenge, and the diffusion and adsorption of the solid reactant on the catalyst surface is difficult to control. Despite that, solid acid catalysts represent a promising alternative to mineral acids for hemicellulose valorization.

## 7. Conclusions

The hydrolysis of poly/oligosaccharides using heterogeneous catalysts has been studied since the 1970s. However, most of the papers refer to the hydrolysis of disaccharides either for food industry (in the case of sucrose hydrolysis) or as model compounds for bigger poly/oligosaccharides (in the case of maltose and cellobiose). Many catalysts are described for these reactions. Some general trends can be identified: in order to be active, a hydrolysis catalyst has to be acidic, water resistant, and must bear strong Brønsted acid sites. Microporous materials are not suitable due to diffusion issues; thus, zeolites are not the best candidates for poly/oligosaccharides hydrolysis. Mesoporous materials are preferred. Highly hydrophilic surfaces with –OH species, allowing for a good adsorption of the carbohydrate reactants, are also interesting here.

Moreover, a careful literature review underlines the need to move into studies on oligosaccharide liquors in natura instead of focusing only on studies on model compounds. Biomass hydrolysates contain not only long saccharides with complex structures and compositions, more difficult to hydrolyze than model disaccharides, but also many impurities such as phenolic compounds, carboxylic acids, or proteins, which can interact with the catalyst surface and eventually poison it. This issue must be fully addressed and clarified.

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[1] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044 – 4098.
[2] F. M. Gírio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques, R. Bogel-Lukasik, *Bioresour. Technol.* **2010**, *101*, 4775 – 4800.
[3] A. D. McNaught, *Pure Appl. Chem.* **1996**, *68*, 1919 – 2008.
[4] a) A. Moure, P. Gullón, H. Domínguez, J. C. Parajó, *Process Biochem.* **2006**, *41*, 1913 – 1923; b) M. J. Vázquez, J. L. Alonso, H. Domıʹnguez, J. C. Parajó, *Trends Food Sci. Technol.* **2000**, *11*, 387 – 393.
[5] P. Kaparaju, M. Serrano, A. B. Thomsen, P. Kongjan, I. Angelidaki, *Bioresour. Technol.* **2009**, *100*, 2562 – 2568.
[6] a) X. Tong, Y. Ma, Y. Li, *Appl. Catal. A* **2010**, *385*, 1 – 13; b) D. W. Rackemann, W. O. S. Doherty, *Biofuels Bioprod. Biorefin.* **2011**, *5*, 198 – 214; c) J. J. Verendel, T. L. Church, P. G. Andersson, *Synthesis* **2011**, 1649 – 1677; d) S. Dutta, S. De, B. Saha, M. I. Alam, *Catal. Sci. Technol.* **2012**, *2*, 2025 – 2036.
[7] F. Guo, Z. Fang, C. C. Xu, R. L. Smith, Jr., *Prog. Energy Combust. Sci.* **2012**, *38*, 672 – 690.
[8] Y. Kim, R. Hendrickson, N. Mosier, M. R. Ladisch, *Energy Fuels* **2005**, *19*, 2189 – 2200.
[9] a) A. Cabiac, E. Guillon, F. Chambon, C. Pinel, F. Rataboul, N. Essayem, *Appl. Catal. A* **2011**, *402*, 1 – 10; b) R. Rinaldi, F. Schuth, *Energy Environ. Sci.* **2009**, *2*, 610 – 626; c) P. L. Dhepe, A. Fukuoka, *ChemSusChem* **2008**, *1*, 969 – 975; d) S. Dutta, *RSC Adv.* **2012**, *2*, 12575 – 12593; e) Y.-B. Huang, Y. Fu, *Green Chem.* **2013**, *15*, 1095 – 1111.
[10] B. Hahn-hägerdal, K. Skoog, B. O. Mattiasson, *Ann. N. Y. Acad. Sci.* **1984**, *434*, 161 – 163.

[11] S. Van de Vyver, J. Geboers, P. A. Jacobs, B. F. Sels, *ChemCatChem* **2011**, *3*, 82–94.

[12] M. E. Zakrzewska, E. Bogel-Łukasik, R. Bogel-Łukasik, *Chem. Rev.* **2011**, *111*, 397–417.

[13] a) J. F. Saeman, *Ind. Eng. Chem.* **1945**, *37*, 43–52; b) C. Vila, G. Garrote, H. Dominguez, J. C. Parajo, *Collect. Czech. Chem. Commun.* **2002**, *67*, 509–530; c) F. Carvalheiro, G. Garrote, J. C. Parajó, H. Pereira, F. M. Gírio, *Biotechnol. Prog.* **2005**, *21*, 233–243; d) P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför, D. Y. Murzin, *Chem. Rev.* **2011**, *111*, 5638–5666.

[14] A. Abbadi, K. F. Gotlieb, H. van Bekkum, *Starch/Staerke* **1998**, *50*, 23–28.

[15] C. L. Xu, A. Pranovich, L. Vahasalo, J. Hemming, B. Holmbom, H. A. Schols, S. Willfor, *J. Agric. Food Chem.* **2008**, *56*, 2429–2435.

[16] P. Carniti, A. Gervasini, M. Marzo, *Catal. Today* **2010**, *152*, 42–47.

[17] Y. Y. Lee, P. Iyer, R. W. Torget, *Adv. Biochem. Eng./Biotechnol.* **1999**, *65*, 93–115.

[18] M. Marzo, A. Gervasini, P. Carniti, *Carbohydr. Res.* **2012**, *347*, 23–31.

[19] Y. Jiang, X. Li, Q. Cao, X. Mu, *J. Nanopart. Res.* **2011**, *13*, 463–469.

[20] J. A. Bootsma, B. H. Shanks, *Appl. Catal. A* **2007**, *327*, 44–51.

[21] N. S. Mosier, A. Sarikaya, C. M. Ladisch, M. R. Ladisch, *Biotechnol. Prog.* **2001**, *17*, 474–480.

[22] A. Charmot, A. Katz, *J. Catal.* **2010**, *276*, 1–5.

[23] C. Buttersack, D. Laketic, *J. Mol. Catal.* **1994**, *94*, L283–L290.

[24] C. Moreau, R. Durand, F. R. Alies, M. Cotillon, T. Frutz, M. A. Theoleyre, *Ind. Crops Prod.* **2000**, *11*, 237–242.

[25] D. S. Pito, I. M. Fonseca, A. M. Ramos, J. Vital, J. E. Castanheiro, *Chem. Eng. J.* **2012**, *184*, 347–351.

[26] C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, T. Tatsumi, K. Domen, *Chem. Mater.* **2010**, *22*, 3072–3078.

[27] K.-i. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, *Green Chem.* **2009**, *11*, 1627–1632.

[28] H. Kobayashi, H. Ohta, A. Fukuoka, *Catal. Sci. Technol.* **2012**, *2*, 869–883.

[29] B. T. Kusema, L. Faba, N. Kumar, P. Mäki-Arvela, E. Díaz, S. Ordóñez, T. Salmi, D. Y. Murzin, *Catal. Today* **2012**, *196*, 26–33.

[30] A. Fukuoka, P. L. Dhepe, *Angew. Chem.* **2006**, *118*, 5285–5287; *Angew. Chem. Int. Ed.* **2006**, *45*, 5161–5163.

[31] a) D. An, A. Ye, W. Deng, Q. Zhang, Y. Wang, *Chem. Eur. J.* **2012**, *18*, 2938–2947; b) W. L. Deng, R. Lobo, W. Setthapun, S. T. Christensen, J. W. Elam, C. L. Marshall, *Catal. Lett.* **2011**, *141*, 498–506.

[32] C. Marcilly, *Acido-Basic Catalysis: Application to Refining and Petrochemistry, Vol. 1–2*, Technip, Paris, **2006**.

[33] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.

[34] T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641–3666.

[35] B. K. Adnadjevic, J. D. Jovanovic, *J. Mol. Catal. A* **2012**, *356*, 70–77.

[36] I. Plazl, S. Leskovsek, T. Koloini, *Chem. Eng. J.* **1995**, *59*, 253–257.

[37] K. Zajsek, A. Gorsek, *React. Kinet. Mech. Catal.* **2010**, *100*, 265–276.

[38] S. Suganuma, K. Nakajima, M. Kitano, S. Hayashi, M. Hara, *ChemSusChem* **2012**, *5*, 1841–1846.

[39] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, *Langmuir* **2009**, *25*, 5068–5075.

[40] A. Takagaki, C. Tagusagawa, K. Domen, *Chem. Commun.* **2008**, 5363–5365.

[41] P. L. Dhepe, M. Ohashi, S. Inagaki, M. Ichikawa, A. Fukuoka, *Catal. Lett.* **2005**, *102*, 163–169.

[42] R. M. Ravenelle, F. Schuessler, A. D'Amico, N. Danilina, J. A. van Bokhoven, J. A. Lercher, C. W. Jones, C. Sievers, *J. Phys. Chem. C* **2010**, *114*, 19582–19595.

[43] R. Dimitrijevic, W. Lutz, A. Ritzmann, *J. Phys. Chem. Solids* **2006**, *67*, 1741–1748.

[44] L. Zhou, M. Shi, Q. Cai, L. Wu, X. Hu, X. Yang, C. Chen, J. Xu, *Microporous Mesoporous Mater.* **2013**, *169*, 54–59.

[45] A. Chakrabarti, M. M. Sharma, *React. Polym.* **1993**, *20*, 1–45.

[46] E. R. Gilliland, H. J. Bixler, J. E. O'Connell, *Ind. Eng. Chem. Fundam.* **1971**, *10*, 185–191.

[47] C. Tagusagawa, A. Takagaki, A. Iguchi, K. Takanabe, J. N. Kondo, K. Ebitani, S. Hayashi, T. Tatsumi, K. Domen, *Angew. Chem.* **2010**, *122*, 1146–1150; *Angew. Chem. Int. Ed.* **2010**, *49*, 1128–1132.

[48] a) T. J. Schwartz, M. Lawoko, *Bioresources* **2010**, *5*, 2337–2347; b) F. Carvalheiro, L. C. Duarte, S. Lopes, J. C. Parajo, H. Pereira, F. M. Girio, *Process Biochem.* **2005**, *40*, 1215–1223.

[49] M. M. Nasef, H. Saidi, M. M. Senna, *Chem. Eng. J.* **2005**, *108*, 13–17.

[50] H. Jüntgen, *Fuel* **1986**, *65*, 1436–1446.

[51] R. Ormsby, J. R. Kastner, J. Miller, *Catal. Today* **2012**, *190*, 89–97.

[52] M. O. Guerrero-Pérez, J. M. Rosas, R. López-Medina, M. A. Bañares, J. Rodríguez-Mirasol, T. Cordero, *Catal. Commun.* **2011**, *12*, 989–992.

[53] M. O. Guerrero-Pérez, M. J. Valero-Romero, S. Hernández, J. M. L. Nieto, J. Rodríguez-Mirasol, T. Cordero, *Catal. Today* **2012**, *195*, 155–161.

[54] J. M. Rosas, J. Bedia, J. Rodriguez-Mirasol, T. Cordero, *Ind. Eng. Chem. Res.* **2008**, *47*, 1288–1296.

[55] M. Hara, *Energy Environ. Sci.* **2010**, *3*, 601–607.

[56] a) A. Onda, T. Ochi, K. Yanagisawa, *Green Chem.* **2008**, *10*, 1033–1037; b) S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, *J. Am. Chem. Soc.* **2008**, *130*, 12787–12793.

[57] K. T. Klasson, M. Uchimiya, I. M. Lima, L. L. Boihem, Jr., *Bioresources* **2011**, *6*, 3242–3251.

[58] D.-m. Lai, L. Deng, J. Li, B. Liao, Q.-x. Guo, Y. Fu, *ChemSusChem* **2011**, *4*, 55–58.

[59] D.-m. Lai, L. Deng, Q.-x. Guo, Y. Fu, *Energy Environ. Sci.* **2011**, *4*, 3552–3557.

[60] L. Peña, M. Ikenberry, B. Ware, K. L. Hohn, D. Boyle, X. S. Sun, D. Wang, *Biotechnol. Bioprocess Eng.* **2011**, *16*, 1214–1222.

[61] V. Degirmenci, D. Uner, B. Cinlar, B. H. Shanks, A. Yilmaz, R. A. van Santen, E. J. M. Hensen, *Catal. Lett.* **2011**, *141*, 33–42.

[62] A. Gervasini, P. Carniti, M. Marzo, A. Auroux, *J. Catal.* **2012**, *296*, 143–155.

[63] W.-J. Liu, K. Tian, H. Jiang, H.-Q. Yu, *Sci. Rep.* **2013**, *3*, 2419.

[64] S. Sumiya, Y. Kubota, Y. Oumi, M. Sadakane, T. Sano, *Appl. Catal. A* **2010**, *372*, 82–89.

[65] R. Kourieh, S. Bennici, M. Marzo, A. Gervasini, A. Auroux, *Catal. Commun.* **2012**, *19*, 119–126.

[66] A. Takagaki, C. Tagusagawa, K. Takanabe, J. N. Kondo, T. Tatsumi, K. Domen, *Catal. Today* **2012**, *192*, 144–148.

[67] R. Kourieh, S. Bennici, A. Auroux, *React. Kinet. Mech. Catal.* **2012**, *105*, 101–111.

[68] a) C. Tagusagawa, A. Takagaki, K. Takanabe, K. Ebitani, S. Hayashi, K. Domen, *J. Catal.* **2010**, *270*, 206–212; b) A. Takagaki, C. Tagusagawa, S. Hayashi, M. Hara, K. Domen, *Energy Environ. Sci.* **2010**, *3*, 82–93.

[69] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171–198.

[70] a) M. Cheng, T. Shi, H. Guan, S. Wang, X. Wang, Z. Jiang, *Appl. Catal. B* **2011**, *107*, 104–109; b) M. Cheng, T. Shi, S. Wang, H. Guan, C. Fan, X. Wang, *Catal. Commun.* **2011**, *12*, 1483–1487.

[71] H. Iloukhani, S. Azizian, N. Samadani, *React. Kinet. Catal. Lett.* **2001**, *72*, 239–244.

[72] B. T. Kusema, G. Hilmann, P. Maki-Arvela, S. Willfor, B. Holmbom, T. Salmi, D. Y. Murzin, *Catal. Lett.* **2011**, *141*, 408–412.

[73] P. D. Carà, M. Pagliaro, A. Elmekawy, D. R. Brown, P. Verschuren, N. R. Shiju, G. Rothenberg, *Catal. Sci. Technol.* **2013**, *3*, 2057–2061.

[74] R. Sahu, P. L. Dhepe, *ChemSusChem* **2012**, *5*, 751–761.

[75] A. Chareonlimkun, V. Champreda, A. Shotipruk, N. Laosiripojana, *Fuel* **2010**, *89*, 2873–2880.

[76] J. A. Bootsma, M. Entorf, J. Eder, B. H. Shanks, *Bioresour. Technol.* **2008**, *99*, 5226–5231.

[77] L. C. Duarte, T. Silva-Fernandes, F. Carvalheiro, F. M. Girio, *Appl. Biochem. Biotechnol.* **2009**, *153*, 116–126.

[78] S. I. Mussatto, I. C. Roberto, *Bioresour. Technol.* **2004**, *93*, 1–10.

[79] Y. Ogaki, Y. Shinozuka, M. Hatakeyama, T. Hara, N. Ichikuni, S. Shimazu, *Chem. Lett.* **2009**, *38*, 1176–1177.

[80] S. Li, E. W. Qian, T. Shibata, M. Hosomi, *J. Jpn. Pet. Inst.* **2012**, *55*, 250–260.

[81] B. T. Kusema, T. Tonnov, P. Maki-Arvela, T. Salmi, S. Willfor, B. Holmbom, D. Y. Murzin, *Catal. Sci. Technol.* **2013**, *3*, 116–122.

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**Hydrolysis of Oligosaccharides Over Solid Acid Catalysts: A Review**

**So solid catalyst:** The hydrolysis of soluble poly/oligosaccharides increases the cost-effectiveness of biomass upgrading within the biorefinery framework. Solid acid catalysts represent an advantageous green alternative to catalyze this reaction. This Review discusses the advantages and limitations of their use and identifies desirable characteristics in the design of future solid acid catalysts.