

# Heterogeneous Strategies For Selective Conversion of Lignocellulosic Polysaccharides

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## Research Article

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# Heterogeneous strategies for selective conversion of lignocellulosic polysaccharides

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## Abstract

Lignocellulosic biomass is the most abundant renewable carbon resource on earth, for which many efforts have been made to convert it using various chemocatalytic processes. Heterogeneously chemocatalytic conversion conducted based on reusable solid catalysts is the process with the greatest potential studied presently. This *review* provides insights into the representative achievements in the research area of heterogeneous chemical catalysis technologies for the production of value-added chemicals from lignocellulosic polysaccharides (cellulose and hemicellulose). Popular approaches for the conversion of lignocellulosic polysaccharides into chemicals, including hydrolyzation (glucose, xylose

24 and arabinose), dehydration (5-hydroxymethylfurfuran, furfural and  
25 levulinic acid), hydrogenation/hydrogenolysis (sorbitol, mannitol, xylitol,  
26 1,2-propylene glycol, ethylene glycol and ethanol), selective oxidation  
27 (gluconic acid and lactic acid), have been comprehensively reviewed.  
28 However, technological barriers still exist, which have to be overcome to  
29 further integrate hydrolysis with the refinery processes based on  
30 multifunctional solid catalysts, and convert lignocellulosic polysaccharides  
31 into value-added fine chemicals. In general, the approaches and  
32 technologies are discussed and critically evaluated in terms of the  
33 possibilities and potential for further industrial implementation.

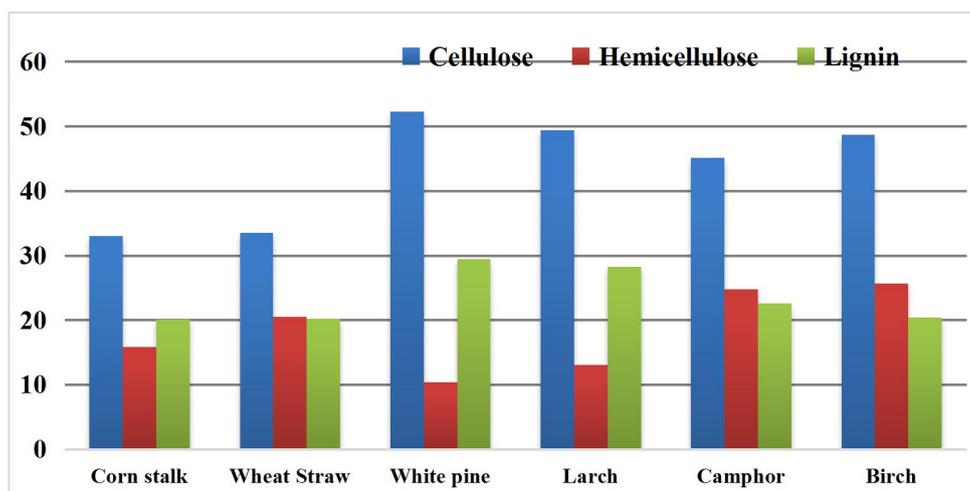
34       Keywords:       Lignocellulose;       Cellulose;       Hemicellulose;  
35 Heterogeneous catalysis; Solid catalyst; Chemicals

## 36 **1. Introduction**

37       The depletion of fossil resources and growing concern about  
38 environmental issues have accelerated the development of a series of  
39 novel chemical processes based on non-fossil sustainable resources, in  
40 particular, the biomass and biomass-derived chemicals (Alonso et al.  
41 2017; Mika et al. 2018; Sun et al. 2018b). Lignocellulosic biomass  
42 originated from biological photosynthesis is a renewable and green  
43 feedstock in abundance with easy availability for the production of fine  
44 chemicals and fuels without extra carbon emission. In addition, the  
45 production of chemicals and fuels derived from lignocellulose has great

46 potential to reduce our dependence on fossil fuel resources, promote  
47 national economic growth, and combat global climate change (Alper et al.  
48 2020; Robertson et al. 2017; Staples et al. 2017; Wittwer et al. 2021;  
49 Woolf et al. 2016). Over the past decades, the research on the  
50 lignocellulose conversion has attracted significant attention from the  
51 industry and academia (Ma et al. 2012; Serrano-Ruiz & Dumesic, 2011;  
52 Wang et al. 2020b).

53 Biochemically, lignocellulosic biomass is a series of material which  
54 is rich in cellulose (35-50%), hemicellulose (15-30%), and lignin  
55 (15-30%) (Questell-Santiago et al. 2020; Ragauskas et al. 2006). For  
56 example, various species, such as grass (*e.g.* corn stalk and wheat straw),  
57 softwood (white pine and larch) and hardwood (Camphor and Birch) are  
58 typical sources of lignocellulosic biomass (Liu et al. 2015; Xia et al.  
59 2016). Each of the main components in lignocellulose can be converted  
60 into value-added chemicals and platform molecules (Han et al. 2019;  
61 Zhang et al. 2017). Therefore, in terms of the availability from renewable  
62 bioresources and the security of food supply, lignocellulosic biomass is  
63 more practicable and sustainable, which can be utilized as the ideal  
64 feedstocks for the production of valuable platform chemicals and biofuels  
65 (Alonso et al. 2010; Wang et al. 2020a).



66  
67 Fig. 1. The weight percentage of cellulose, hemicellulose and lignin in some  
68 typical biological sources such as grass (Corn stalk and Wheat straw), softwood  
69 (White pine and Larch) and hardwood (Camphor and Birch) (Liu et al. 2015; Xia et al.  
70 2016)

71 At present, the development of the processes for one-step conversion  
72 of lignocellulose into value-added chemicals remains a huge challenge  
73 (Gallezot, 2008). In particular, the complex structural constituent of  
74 lignocellulose makes it difficult to obtain target chemicals with high yield  
75 and quality. As the major component of lignocellulose, cellulose is  
76 constructed by repeating anhydrous glucose units, which is covalently  
77 linked by  $\beta$ -1,4 -glycosidic bonds with a generic chemical formula  
78  $(C_6H_{10}O_5)_n$ . The linear-chain structure is further tightly confined by the  
79 extensive intramolecular and intermolecular bonding networks.  
80 Consequently, cellulose has the most ordered and imparted rigid  
81 crystallinity. In contrast, as a kind of branched-chain polymer,  
82 hemicellulose consists of many different sugar monomers arranged in a  
83 random and amorphous structure. Lignin is a three-dimensional  
84 amorphous biopolymer composed of phenylpropanoid units which are

85 connected by carbon-carbon and ether bonds, showing relative  
86 hydrophobic and aromatic properties (Foston & Ragauskas, 2012;  
87 Himmel et al. 2007). Those differences in terms of chemical composition  
88 and structure of cellulose, hemicellulose and lignin lead to apparent  
89 disparities in their reactivity. Therefore, the efficient chemical conversion  
90 of lignocellulose into platform chemicals requires a pretreatment process.  
91 Therefore, to obtain high yield monomers or platform chemicals, the  
92 corresponding components of lignocellulose have to be released by using  
93 a feasible pretreatment (Liheng et al. 2017; Ling et al. 2019; Vanneste et  
94 al. 2017).

95 Over past few decades, many researchers have endeavored to  
96 explore the efficient production of value-added chemicals and fuels by  
97 means of catalytic conversion of lignocellulose through homogeneous  
98 and heterogeneous processes (Jing et al. 2019; Zhang et al. 2019). Among  
99 them, heterogeneous catalytic process has received considerable  
100 attentions due to the advantages of easy recovery and reusability of solid  
101 catalysts (Scarsella et al. 2020; Sudarsanam et al. 2018). In recent years,  
102 researchers have made increasing efforts to design multifunctional  
103 catalysts to consolidate the two- or multi-step batch processes into a  
104 one-step cascade catalytic reaction system. In this manner, lignocellulosic  
105 biomass can be directly converted into various essential chemicals in an  
106 efficient and environmentally friendly way. As shown in Table 1, some

107 typical essential chemicals and fuels are refined from platform chemicals  
 108 which can be derived by chemocatalytic transformation of lignocellulose  
 109 fractions by using different chemical processes (Chatterjee et al. 2015;  
 110 Zhang et al. 2016). It is worth nothing that the strategy of “platform  
 111 chemicals” firstly considers the selective conversion of three components  
 112 in lignocellulosic biomass (cellulose, hemicellulose and lignin) to  
 113 platform chemicals via hydrolysis, dehydration,  
 114 hydrogenation/hydrogenolysis and selective oxidation processes;  
 115 secondly, the products can be further upgraded from the above platform  
 116 chemicals (Delidovich et al. 2016; Gérardy et al. 2020; Sun et al. 2018c).  
 117 Clearly in table 1, a wide range of chemicals, such as monosaccharides,  
 118 lignin monomers, alcohols, bioorganic acids, furfurals *etc.* can be  
 119 obtained through catalytic transformations of lignocellulosic biomass.

120 **Table 1** A summary of platform chemicals produced by chemical conversion of  
 121 lignocellulosic biomass.

Fractions	Platform chemicals	Secondary chemicals	End use products
<b>Polysaccharides (Cellulose and hemicellulose)</b>	C <sub>6</sub> ,C <sub>5</sub> Sugar alcohols (xylitol, arabitol, sorbitol, <i>etc</i> )	Ethylene glycol, propylene glycol, hydroxyfuran, Sugar acids	Green solvent, plastic, cosmetics, detergent, pharmaceuticals
	C <sub>3</sub> Acids (propionic, malonic)	Propionyl acrylate, pharmaceutical intermediates and reagents	Water purification, dust control, gas purification, cleaners and detergents, coating, insulation, preservatives, fertilizers, pesticides
	3-Hydroxy propionate	Acrylates, acryl amides	Specialty lubricants, flocculants, chelators, paint, vamish and coating materials, insulation, packaging
	Levulinic acid	3-amino levulinate, succinates 2-methyltetrahydrofuran, 1,4-diols, $\gamma$ -valerolactone	Molded plastics, packaging, fuels, oxygenates, resin, adhesive, insulator agents, coatings

	Furfural	Furan derivatives	Fuels, oxygenates, textiles, resin, adhesive, insulator agents, coatings
	Gluconic acid	Gluconolactones, esters	Cosmetics, pharmaceuticals
<b>Lignin</b>	Lignin monomers	Benzene, toluene, xylenes, polyols, phenols	Dyestuff, plastic, fuel, solvent, drug, paint, material applications, phenol-formaldehyde resins, polyurethane foams, vanillin

122 Heterogeneous catalysis is a key and sustainable technology in  
123 modern chemical industry for the green chemical conversion of  
124 lignocellulosic biomass, which plays an essential role in meeting the  
125 theoretical, technical, and economic challenges for biomass updating  
126 (Sudarsanam et al. 2019; Sudarsanam et al. 2018). Many researchers have  
127 reviewed the most representative examples and the recent achievements  
128 in the field of catalytic conversion of lignocellulosic biomass for the  
129 production of valuable products (Cao et al. 2019; Chio et al. 2019;  
130 Shivhare et al. 2021; Wong et al. 2020). Similarly, this paper attempts to  
131 summarize and review the recent research progress in different  
132 heterogeneous catalytic processes for the conversion of lignocellulosic  
133 polysaccharides (cellulose and hemicellulose) into a vast majority of  
134 commodity chemicals and potential fuels.

## 135 **2. Isolation of the lignocellulosic fractions**

136 Lignocellulose, as the major constituent of plant cell walls, is a  
137 complex composite which consists of cellulose, hemicellulose and lignin.  
138 These biopolymers are bound together in a very unique architecture by  
139 long evolutionary process which brings huge biodiversity from the  
140 molecular to the macroscopic level. As shown in Fig.2, these biopolymers

141 are hierarchically organized. Specifically, cellulose and hemicellulose are  
142 macromolecular polymers linked by sugar units through glycosidic bonds,  
143 while lignin is a three-dimensional biological macromolecule composed  
144 of a large number of benzene rings. Hemicellulose and lignin are  
145 covalently linked to form a complex matrix structure in which cellulose is  
146 embedded (Imman et al. 2021). Although lignocellulosic biomass is  
147 attractive due to its inexpensiveness and abundance as a raw material, it  
148 has to be decomposed into individual components in order that it can be  
149 effectively treated by specific refining strategies (Zhang et al. 2021a).  
150 Isolation of the lignocellulosic biomass fractions is a difficult process  
151 started with pretreatment which is intended as a means of isolating the  
152 three components from depolymerization in subsequent heterogeneous  
153 catalytic steps. In general, this objective is achieved by the deconstruction  
154 of the complex matrix composed of lignin and hemicellulose in  
155 lignocellulose (Jusner et al. 2021; Rajak et al. 2021). Compared with  
156 one-pot deconstruction of whole lignocellulose (Sun et al. 2018b; Tian et  
157 al. 2022; Xia et al. 2016; Liao et al. 2020), emerging strategies are  
158 introduced to directly isolate components from lignocellulose to obtain  
159 tailor-made fractions through and for catalysis, thereby capitalizing on the  
160 full potential of catalysis in the refinement of lignocellulosic fractions  
161 into chemicals and fuels (Renders et al. 2018).

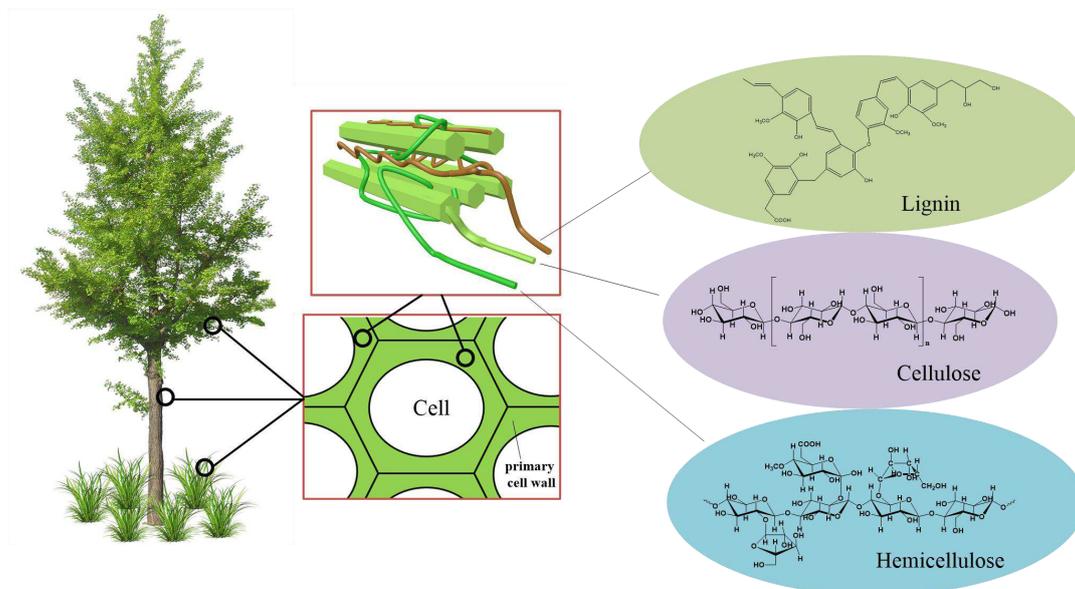


Fig. 2. Interaction of cellulose, hemicellulose and lignin in the cell wall of lignocellulosic biomass

Several technologies for isolating the three components of lignocellulose from each other were reported (Renders et al. 2018; Schutyser et al. 2018; Yang et al. 2017). For example, Schüth's group developed a solvent-free process using mechanocatalysis as a powerful methodology for the deep depolymerization of lignocellulose. This process acts as a platform for the fractionation of lignocellulose through the saccharification of the oligosaccharides (Käldström et al. 2014b). More than 90% yield of cellulose and hemicellulose can be obtained in the form of sugars (glucose and xylose) from beechwood, pinewood and sugarcane bagasse, meanwhile the sulfur-free lignin precipitates were also obtained (Käldström et al. 2014a). In addition, Leitner's group reported a one-step fractionation method to extricate the cellulose pulp, soluble hemicellulose monosaccharides and lignin from lignocellulosic material in a biphasic system. In the so-called "organocat process", lignin is

179 selectively solvolyzed and hemicellulose is catalyzed by oxalic acid at  
180 mild temperatures (80–140 °C). As this process is performed in a biphasic  
181 system (water and 2-methyltetrahydrofuran), lignin fragments extracted  
182 by the organic solvent is directly separated from water-soluble  
183 hemicellulose sugars in the aqueous phase and cellulose solid (vom Stein  
184 et al. 2011).

185 Welton and co-workers have introduced protic ionic liquid (IL)  
186 1-butylimidazolium hydrogen sulfate for the removal of the lignin and  
187 hemicellulose from the lignocellulosic matrix. IL, characterized by the  
188 properties of good solubility and acid sites, shows the ability to  
189 decompose and dissolve lignin and hemicellulose. Cellulose- rich pulp is  
190 left behind as residue. Importantly, the addition of water to the IL liquor  
191 leads to the precipitation of lignin (Verdía et al. 2014). During the  
192 isolation process, the utilization of acid and high temperatures generally  
193 results in severe and nonreversible condensation between lignin  
194 fragments and soluble hemicellulose sugars, which dramatically limits the  
195 further upgradation of lignocellulose. To solve such problems,  
196 Luterbacher's group presented a strategy to restrict the formation of  
197 interunit carbon-carbon bonds via the addition of formaldehyde during  
198 lignin extraction process. In this process, the formaldehyde prevented the  
199 condensation of lignin fragments by the formation of 1,3-dioxane  
200 structures with lignin side-chain hydroxyl groups. Moreover, cellulose,

201 hemicellulose, and lignin were effectively separated for consequent  
202 refinery (Shuai et al. 2016).

### 203 **3. Transformation of lignocellulosic polysaccharides**

#### 204 **3.1 Cellulose transformation**

205 As a kind of supermolecule, cellulose is formed by anhydroglucose  
206 units with  $\beta$ -1,4-glycosidic linkages. In many cases, hydrolyzation of  
207 cellulose to glucose with glucoside bond broken is perceived as a  
208 necessary first step. Then, the glucose is further refined into various  
209 platform chemicals and value-added products on the catalytic basis  
210 (Rinaldi & Schuth, 2009; Zeng & Pan, 2020). In recent years, the direct  
211 conversion of cellulose to fine chemicals has received extensive  
212 attentions from the researchers. These fine chemicals are the precursors  
213 for the products with higher value and liquid fuels. Fig. 3 illustrates the  
214 various catalytic conversion pathway of cellulose via one-pot or multiple  
215 step models, including hydrolyzation (Glucose), selective oxidation  
216 (gluconic acid, formic acid, Levulinic acid), dehydration  
217 (5-Hydroxymethylfurfuran and Levulinic acid), and  
218 hydrogenation/hydrogenolysis (sorbitol, ethylene glycol, 1,2-propylene  
219 glycol and ethanol).

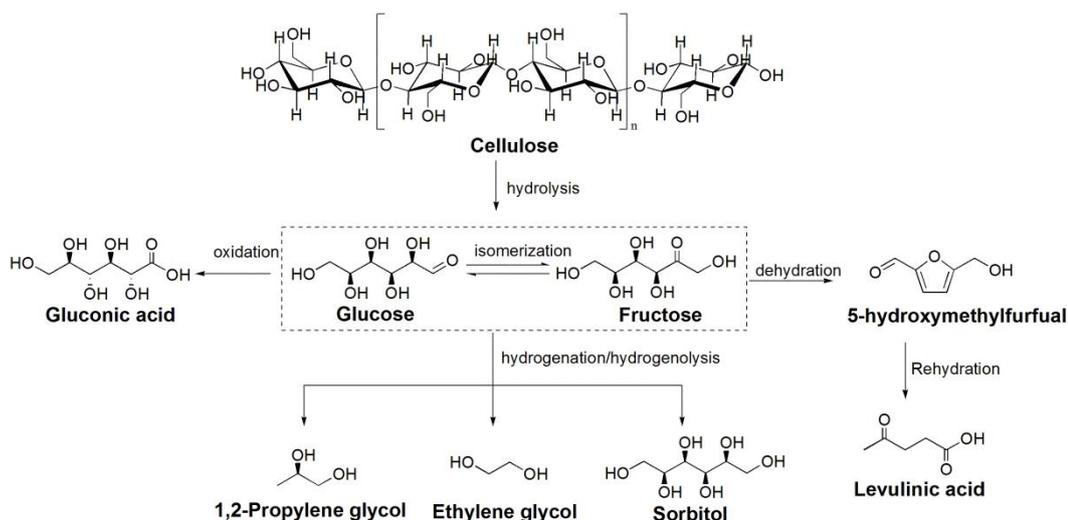


Fig. 3. The main catalytic conversion pathway of cellulose

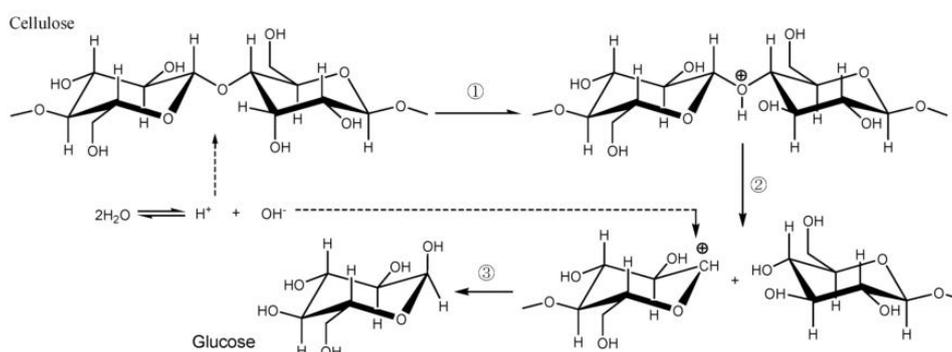
### 3.1.1 Hydrolyzation

In general, cellulose can hardly be hydrolyzed in water due to its supramolecular crystal structure. Likewise, the hydrolyzation of cellulose usually involves the utilization of Brønsted acids as catalysts or severe condition (25 MPa, 320-400 °C) without catalyst (Rinaldi & Schuth, 2009). Recent researches for acid-catalyzed hydrolysis of cellulose by cleaving glycosidic bonds are implemented through homogeneous and heterogeneous processes. Compared with homogeneous catalysts, heterogeneous solid acid catalysts for cellulose hydrolyzation have aroused increasing interest due to its inexpensiveness, reusability, controllable performance and minimization of corrosion (Tyufekchiev et al. 2018; Zeng & Pan, 2020). Therefore, the rapid development of recyclable solid acids has the potential to replace the unrecyclable liquid acid catalysts in cellulose hydrolysis process (Geboers et al. 2011b; Lin & George, 2009).

237 For decades, researchers have developed a series of heterogeneous  
238 Brønsted solid acids, such as sulfonated solid acid (nafion, amberlyst,  
239  $-\text{SO}_3\text{H}$  functionalized amorphous carbon or mesoporous silica), zeolite  
240 (H-form zeolites), metal oxide ( $\gamma\text{-Al}_2\text{O}_3$ ), heteropoly acid and other  
241 materials. In the meantime, their catalytic performances have been  
242 explored on the cellulose hydrolysis (Hu et al. 2015; Huang & Fu, 2013).  
243 With solid acid catalysts, the typical hydrolytic product, such as glucose  
244 can be produced. However, in most cases, the yields of the desired  
245 products are quite low over solid catalysts due to the lacked catalytic  
246 activity compared with liquid acid catalysts. Therefore, a longer reaction  
247 time is needed to achieve the high yield of glucose.

248 Generally, cellulose hydrolysis with the breaking of glycosylic  
249 bonds is catalyzed by the hydrogen cations ( $\text{H}^+$ ) ionized from the splitting  
250 of water molecules on the surface of solid acid catalyst. Moreover, the  
251 catalytic activity of catalysts increases with the decrease of the  
252 deprotonation enthalpy (DPE) of water (Shimizu et al. 2009). Thus, the  
253 catalyst with stronger Brønsted acidity is more beneficial to the catalytic  
254 hydrolysis of cellulose. In that case, more water molecules can be split  
255 into hydrogen cations ( $\text{H}^+$ ) and hydroxide anions ( $\text{OH}^-$ ), and the  $\text{H}^+$   
256 attacks the oxygen atom in the 1,4- $\beta$ -glycosidic linkage of cellulose.  
257 Therefore, to some extent, the amount of water in the hydrolysis system  
258 has an impact on the cleavage of  $\beta$ -1,4-glycosidic linkages and

259 intramolecular hydrogen bonds in cellulose, thereby leading to more  
 260 formation of glucose (Fig. 4). Additionally, cellulose hydrolysis over  
 261 solid acid catalysts under mild catalytic condition has been proved to be  
 262 beneficial to the production of glucose without deep degradation (Girisuta  
 263 et al. 2007).



264

265 Fig. 4. Proposal mechanism of breakage of 1,4- $\beta$ -glycosidic bonds and formation  
 266 of glucose in the hydrolysis of cellulose.

267 Among the series of solid acid catalysts, sulfonated activated carbon  
 268 (SAC) has shown excellent catalytic activity in cellulose hydrolyzation  
 269 (Konwar et al. 2019). Almost simultaneously, Onda's group and Hara's  
 270 group reported the SAC material in 2008. The former obtained a  
 271 remarkably high glucose yield of 40.5% with the selectivity higher than  
 272 90% (Onda et al. 2009; Onda et al. 2008). According to their report, the  
 273 SAC which grafted  $-\text{SO}_3\text{H}$  functional groups was characterized by the  
 274 singularly catalytic properties of strong acidity, hydrophobic planes on its  
 275 surfaces, and high hydrothermal stability. While the latter identified that  
 276 the hydrolysis of cellulose over SAC catalyst in water even showed a  
 277 much lower activity energy (110 KJ/mol) compared with that in dilute

278 H<sub>2</sub>SO<sub>4</sub> solution (170 KJ/mol). The reason is that a strong affinity between  
279 β-1,4-glycosidic bonds of cellulose and SAC surfaces accelerated the  
280 activation of cellulose molecules. (Suganuma et al. 2008)

281 Pan's group developed a novel cellulase-mimetic solid catalyst, i.e.,  
282 sulfonated chloromethyl polystyrene resin (CP-SO<sub>3</sub>H) for the hydrolysis  
283 of cellulose. CP-SO<sub>3</sub>H contained –Cl groups and -SO<sub>3</sub>H groups are taken  
284 as the cellulose-binding sites and the acidic sites, respectively, for  
285 catalytic cleavage of glycosidic bonds. With CP-SO<sub>3</sub>H as the catalyst, raw  
286 material of microcrystalline cellulose could be hydrolyzed into glucose  
287 with the yield of 93% at 120 °C within 10 hours (Shuai & Pan, 2012).

288 Hu's group proposed a new one-pot synthetic method to immobilize the  
289 phosphotungstic acid (HPW) as the acidic active sites into ordered  
290 mesoporous silica (OMS). This co-condensation technique thickened the  
291 pore wall of the HPW/OMS material while retaining its highly ordered  
292 mesoporous structure. Employing heterogeneous HPW/OMS material as  
293 the catalyst, the conversion of cellulose reached 94.1% with 61.2% yield  
294 of reducing sugars (TRS) in [BMIm]Cl at 140 °C for 4 h. In addition, the  
295 solid acid catalyst was high in hydrothermal stability and excellent in  
296 recycling performance (Yu et al. 2021). Cui's group designed the  
297 temperature-responsive HCl-releasing catalysts for the improvement of  
298 mass transfer efficiency between heterogeneous catalyst and solid  
299 cellulose particles. This kind of catalyst exhibits a unique characteristic

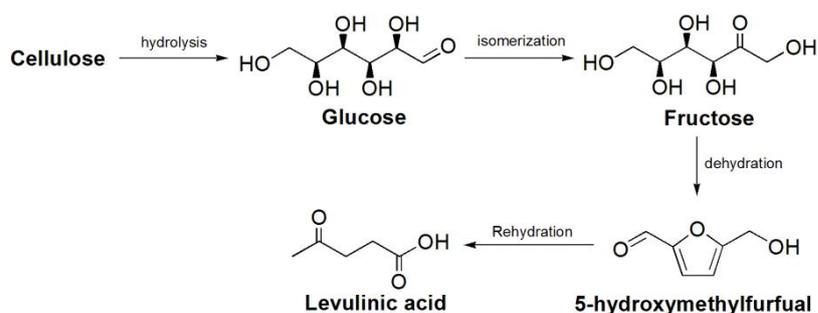
300 which can release HCl into aqueous phase for the homogeneous  
301 hydrolysis reaction of cellulose, and the released HCl can be immobilized  
302 and reused in mesoporous N-doped carbon materials via simple cooling  
303 process after reaction. The novel catalyst system provided a total TRS  
304 yield of 81.1% and 61.1% glucose yield, respectively after the reaction  
305 under 220 °C for 60 min with excellent catalytic stability (Wang et al.  
306 2020d).

307 Through the systematic evaluation of the reported synthetic catalysts,  
308 valuable information and clues can be obtained for further design and  
309 preparation of a class of effective solid acid catalysts for catalytic  
310 hydrolysis of cellulose by adjusting their physical structures, such as  
311 specific surface area and pore size, as well as the active functional groups,  
312 such as grafted acid centers and adsorption sites to meet the demands of  
313 catalytic hydrolysis and even subsequent coupling reaction.

### 314 **3.1.2 Dehydration**

315 5-Hydroxymethylfurfural (5-HMF) derived from biomass has shown  
316 the potential for applications as a versatile platform in chemical industry  
317 production process. It can be refined to access 12 important furan  
318 derivatives and nonfuranic compounds through oxidation and  
319 hydrogenation reaction (van Putten et al. 2013). Cellulose conversion for  
320 5-HMF production is currently a hotspot of both academic and  
321 commercial research. According to the researches, the chemical

322 conversion of cellulose consists of three steps: (1) an initial hydrolysis  
 323 process to convert cellulose into glucose; (2) further isomerized process  
 324 to turn glucose into fructose; (3) chemical transformation of resulted  
 325 fructose into 5-HMF (Fig. 5).



326  
 327 Fig. 5. Conversion of cellulose into 5-HMF and LA

328 Direct conversion of cellulose into HMF over heterogeneous  
 329 catalysts can be conducted in different solvent systems and with various  
 330 heterogeneous catalysts (Li et al. 2018; Wen et al. 2019). Laosiripojana's  
 331 group reported simultaneous hydrolysis/dehydration reactions of  
 332 lignocellulosic material under hot compressed water (HCW) condition  
 333 with the presence of  $\text{TiO}_2\text{-ZrO}_2$  catalyst prepared by coprecipitation  
 334 method. The yield of 5-HMF of 8.6% could be obtained at 573K and the  
 335 pressure of 34.5 MPa (Chareonlimkun et al. 2010). Wang's group  
 336 employed heterogeneous  $\text{Cr}[(\text{DS})\text{H}_2\text{PW}_{12}\text{O}_{40}]_3$ ,  
 337 Brønsted–Lewis–surfactant–combined heteropolyacid as a stable and  
 338 recyclable catalyst for 5-HMF production from cellulose. It proved that  
 339 dodecyl sulfate in the catalyst could solubilize the cellulose, and enable  
 340 better adsorption and interaction between cellulose and heteropolyacid  
 341 catalyst, with which 77% of cellulose was hydrolyzed for the yield of

342 HMF (423 K, 2h) of 52.7% (Zhao et al. 2011). Wang's group synthesized  
343 a series of water-tolerant porous niobium phosphate solid acid catalysts  
344 by tuning their surface acidity and the ratios between Brønsted and Lewis  
345 acid sites. Over the optimal NbPO-pH7 catalyst, the yield of 16.2% for  
346 5-HMF was obtained directly from cellulose in MIBK/water system at  
347 140 °C for 60 min (Zhang et al. 2015). Subsequently, they further  
348 developed a kind of mesoporous silica-alumina (AlSiO) catalysts with  
349 tunable acidity. When AlSiO-20 (Si/Al ratios=20) was used, the yield of  
350 5-HMF reached 45.2% directly from cellulose in THF/H<sub>2</sub>O system with  
351 NaCl salt at 180 °C for 1.5 h (Atanda et al. 2015). Beltramini's group  
352 used phosphate TiO<sub>2</sub> for the conversion of cellulose into 5-HMF in  
353 water-MeTHF and water-THF biphasic system containing  
354 N-methyl-2-pyrrolidone (NMP). The yield of about 33% for 5-HMF was  
355 achieved by the direct conversion of microcrystalline cellulose, but when  
356 using mechanocatalytic depolymerized cellulose as the substrate, a  
357 significant yield of 74.7%-86% for 5-HMF could be achieved (Atanda et  
358 al. 2016; Atanda et al. 2015).

359 Various carbon materials grafted acid functional groups were  
360 introduced into the conversion of cellulose to 5-HMF. Li's group reported  
361 a carbonaceous solid acid catalyst synthesized by sucrose-derived  
362 mesoporous carbon which was functionalized with benzenesulfonic acid  
363 group as Brønsted acid sites. By the reaction in  $\gamma$ -valerolactone

364 (GVL)-H<sub>2</sub>O system at 130 °C for 20 min., the yield of 5-HMF derived  
365 from cellulose reached 22.5% (Huang et al. 2018). Gromov's group  
366 prepared Sibunit carbon material which oxidized by HNO<sub>3</sub> and sulfonated  
367 by fuming H<sub>2</sub>SO<sub>4</sub> for the hydrolysis–dehydration of cellulose under  
368 semi-flow condition. Over this oxidized–sulfonated carbon catalyst, 10%  
369 yield of 5-HMF could be produced at 200 °C under 25 MPa water  
370 pressure within 4 h (Aymonier et al. 2021). Gromov's group prepared  
371 Sibunit carbon material which was oxidized by HNO<sub>3</sub> and sulfonated by  
372 fuming H<sub>2</sub>SO<sub>4</sub> for the hydrolysis–dehydration of cellulose under  
373 semi-flow condition. Based on this oxidized–sulfonated carbon catalyst,  
374 the yield of 5-HMF of 10% could be obtained at 200 °C and under the  
375 water pressure of 25 MPa within 4 h. Cui's group further investigated the  
376 temperature-responsive HCl-releasing catalysts for 5-HMF production,  
377 with these catalysts, 96.4% of cellulose was converted into 5-HMF with  
378 the yield of 52.6% in MIBK/water biphasic system after reacting at  
379 220°C for 80 min (Wang et al. 2020c).

380       Compared with the case using glucose and fructose as feedstock, the  
381 direct conversion of cellulose into 5-HMF is more challenging because  
382 the additional hydrolyzation and isomerization steps must be  
383 implemented prior to fructose dehydration. These multistep processes  
384 often result in poor 5-HMF yields in aqueous phase system, as shown in  
385 the following aspects. Firstly, in general, glucose isomerization occurs at

386 the temperature of 100-120 °C, while the temperature required for  
387 fructose dehydration is above 120 °C. This significant temperature  
388 variation may lead to the production of humins as byproducts synthesized  
389 from the products of catalytic sugar transformations, such as furfural,  
390 formaldehyde, formic acid, and levulinic acid. Secondly, 5-HMF shows  
391 poor stability, especially in the aqueous phase system due to the fact that  
392 it can be easily hydrolyzed and condensed into byproducts. Therefore, the  
393 improvement of efficiency in HMF production from cellulose drives the  
394 quest for more active catalysts and the regulation of the reaction  
395 conditions for by-products reduction.

396 Over decades of study, the researchers have endeavored to develop  
397 the efficient heterogeneous catalysts for the synthesis of levulinic acid  
398 from cellulose (Boonyakarn et al. 2019; Weingarten et al. 2012; Zunita et  
399 al. 2020). Fu's group synthesized a novel heterogeneous catalyst of  
400 sulfonated chloromethyl polystyrene (CP) resin (CP-SO<sub>3</sub>H-1.69) with  
401 sulfonic-acid groups and chlorine groups (-Cl) as the acid centers and  
402 cellulose-binding sites, respectively. With this catalyst, the yield of 65.5%  
403 for levulinic acid was obtained by in the conversion of microcrystalline  
404 cellulose (Zuo et al. 2014). Wu's group designed a hierarchically porous  
405 titanium-silica zeolite (ETS-10) loaded with highly dispersed Ni catalyst  
406 with moderate Lewis acidic centers and hierarchical pores, which was  
407 revealed to be beneficial to the activation of the reaction substrates and

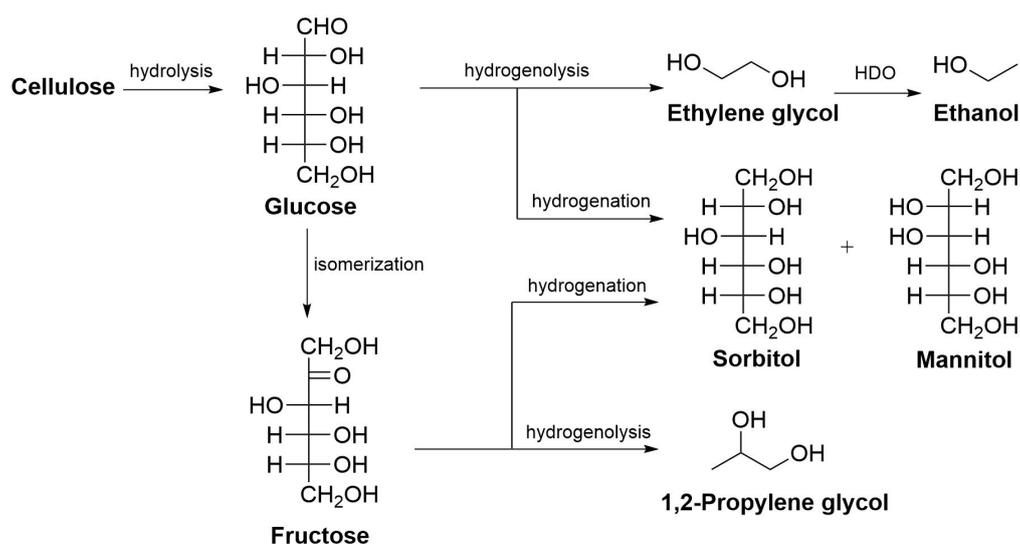
408 mass transfer process. The significantly high yield (91.0%) of levulinic  
409 acid was achieved with full conversion of cellulose over the impressive  
410 Ni-HMETS-10 catalyst under mild reaction condition (Xiang et al. 2017).  
411 In recent years, researchers are constantly developing new heterogeneous  
412 catalytic technologies to produce levulinic acid from cellulose by  
413 introducing suitable solvent system to improve the interaction between  
414 cellulose and the solid acid catalyst, and tuning pore structure and acid  
415 sites (Ma et al. 2021; Sun et al. 2018a).

### 416 **3.1.3 Hydrogenation/Hydrogenolysis**

417 The direct conversion of cellulose through hydrogenation and  
418 hydrogenolysis processes provides access to a diverse range of chemical  
419 platforms, i.e., C<sub>6</sub> polyols (sorbitol and mannitol), C<sub>3</sub> polyol  
420 (1,2-Propylene glycol), and C<sub>2</sub> alcohols (ethylene glycol and ethanol).  
421 Among them, sorbitol is listed as one of the 12 most important platform  
422 compounds derived from biomass by the U.S. Department of Energy  
423 (Luo et al. 2020; Tindall et al. 2021). With the rapid development of  
424 chemical industry, biomass derived alcohols become more important  
425 gradually, which has a wide range of applications in pharmaceutical, food,  
426 energy, chemical, agrochemical and other fields, as well as in the  
427 scientific research (Kumar et al. 2020; Lee, 2015).

428 As shown in Fig. 6, the conventional route of the heterogeneous  
429 synthesis of hexitols (sorbitol/mannitol) from cellulose consists of two

430 steps: (1) cellulose is firstly hydrolyzed into glucose by  $\text{H}_3\text{O}^+$  ions, which  
 431 are formed by  $\text{H}^+$  (from acid ionization with high temperature water and  
 432  $\text{H}_2$  overflow) combined with water molecules; (2) glucose is subsequently  
 433 hydrogenated into sorbitol over the hydrogenation catalyst, and fructose,  
 434 derived from glucose isomerization, into mannitol.



435

436 Fig. 6. Reaction pathway of one-pot cellulose conversion to polyols over  
 437 biofunctional catalysts

438 The reactions coupling hydrolyzation with hydrogenation to produce  
 439 sorbitol and mannitol have been widely studied (Rey-Raap et al. 2019;  
 440 Ribeiro et al. 2017; Ruppert et al. 2012). These reactions are preceded by  
 441 a hydrolysis process to depolymerize cellulose into glucose and fructose,  
 442 and followed by hydrogenation to obtain the corresponding C6 polyols. It  
 443 is known that liquid water is available to form  $\text{H}^+$  ions capable of  
 444 conducting acid-catalyzed reaction at elevated temperature (above 473 K).  
 445 Therefore, Liu's group reported an efficient method combing hydrolysis  
 446 using  $\text{H}^+$  ions which were reversibly formed *in situ* in hot water with

447 instantaneous hydrogenation on Ru/C for the conversion of cellulose into  
448 hexitols (Luo et al. 2007). Ma's group used amorphous zirconium  
449 phosphate catalyst as hydrolyst and commercial Ru/C as hydrogenation  
450 catalyst for hexitols production. With this catalyst, the yield of 63.5% for  
451 C<sub>6</sub> alditols was obtained from microcrystalline cellulose at 488 K for 1.5  
452 h. Moreover, they investigated the ball-milled cellulose as the feedstocks,  
453 and the yield of sugar alcohols can be reached as high as 90.3% at 463 K  
454 for 2.5 h (Liao et al. 2014a; Liao et al. 2014b).

455 For coupling method, it's worth noting that the optimized balance  
456 between two catalytic functions of hydrolyzation with hydrogenation is  
457 essential for an effective and selective catalytic hydrolytic hydrogenation  
458 system. Cellulose can be hydrolyzed by using the acid catalyst, which is  
459 followed by a fast metal-catalyzed hydrogenation of the resulted glucose  
460 to hexitols. However, the coupling reaction mixed with different catalysts  
461 usually brings inevitable issues of separation. A one-pot combined  
462 approach has been developed for the direct conversion of cellulose into  
463 sorbitol and mannitol based on bifunctional catalysts. The "bifunctional"  
464 catalysts are generally composed of metal ingredients (Ru, Pt, Ni)  
465 supported by Brønsted acidic zeolites (H-USY, H-ZSM-5, H mordenite)  
466 and carbon materials (Deng et al. 2014; Yabushita et al. 2014), on which  
467 the glucose and fructose are generated *in situ* by acidic hydrolysis of  
468 cellulose and then converted into polyols by hydrogenation catalyst.

469 Since 2006, Fukuoka's group had firstly reported the independent  
470 utilization of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in hydrolytic hydrogenation of the  
471 cellulose for hexitols production. Cellulose was firstly catalyzed by the  
472 acidic sites into glucose, and the C=O group in glucose was promptly  
473 reduced by Pt to form sorbitol. The hydrolysis of cellulose to glucose is a  
474 rate-determining step because the reduction of glucose gave an almost  
475 stoichiometric amount of sorbitol over the Pt catalyst. Accordingly, a total  
476 yield of 31% for C6 polyols (sorbitol: 25%, mannitol: 6%) was achieved  
477 over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Fukuoka & Dhepe, 2006).

478 Sels' group proposed a nickel catalyst supported by carbon nanofiber  
479 (Ni-CNF) for transforming 93% of cellulose with sorbitol and mannitol  
480 with the yields of 69% and 7%, respectively. The reason of high hexitol  
481 yield is considered to be based on the pear-shaped Ni nanoclusters on the  
482 tips of the carbon nanofibers, which effectively restrains the undesired  
483 C-C and C-O bond breaking (Van de Vyver et al. 2010; Van de Vyver et al.  
484 2012). However, cellulose and cello-oligomers are unable to be  
485 effectively depolymerized into glucose before hydrogenation by the metal  
486 sites during the reaction process, resulting in a finite hexitols yield. After  
487 that, they provided Ru-loaded zeolites (Ru/H-USY) catalyst accompanied  
488 by with trace amounts of mineral acid (PH=3) for hydrolytic  
489 hydrogenation of cellulose. A much lower soluble acid concentration is  
490 sufficient for the completion of cellulose conversion, leading to an

491 excellent yield (>90%) of hexitols (Geboers et al. 2011a). The research  
492 emphasized the advantages of the multifunctional activity for the direct  
493 conversion of cellulose into hexitols. However, physicochemical and  
494 catalytic data showed that the rate-determining step lies in the hydrolysis  
495 of cellulose to glucose, depending on the surface acidity of catalysts.  
496 Therefore, it is important to achieve a balance between the hydrolysis and  
497 hydrogenation step without excessive dehydration.

498 Ethylene glycol (EG) and 1,2-propylene glycol (PG) produced by  
499 industrial petrochemical route are important organic compounds and  
500 platform chemicals used in industrial processes of energy, plastics,  
501 automobiles, etc. The direct conversion of cellulose into EG and PG has  
502 been regarded as a new type high-value utilization of biomass. Zhang's  
503 group first proposed the utilization of Ni-W<sub>2</sub>C/AC catalyst for one-pot  
504 synthesis of EG from cellulose, and achieved the yield of 61% (518 K, 6  
505 MPa of H<sub>2</sub> for 30 min) (Ji et al. 2008). It was revealed that nickel  
506 components promoted the hydrogenation by activating hydrogen, and the  
507 tungsten active components are available to catalyze the substrate by  
508 selectively breaking its C–C bonds, such as retro-aldol reaction (Li et al.  
509 2012). Liu's group investigated the mixed Ru/C+WO<sub>3</sub> catalysts for  
510 cellulose hydrogenolysis, and a total yield of 56.3% for diols (EG: 48.9%,  
511 PG: 7.4%) was obtained. WO<sub>3</sub> crystallite played two roles in this reaction,  
512 namely, the acceleration of the hydrolysis of cellulose into sugars and the

513 selective cleavage of the C-C bonds in these sugars. Ru/C catalyst  
514 promoted the hydrogenation of intermediates by activating hydrogen,  
515 leading to the controllable synthesis of diols from cellulose (Liu et al.  
516 2012). They further explored the product distribution in the hydrolytic  
517 hydrogenolysis of cellulose using Pt-SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. A significant  
518 change in the distribution of polyols occurred with the Sn/Pt atomic ratio  
519 ranging largely from 0.1-3.8 on Pt-SnO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. When the Sn/Pt  
520 ratio exceeding 1.5, higher selectivity to idols (e.g. EG, PG) could be  
521 obtained compared with Pt/Al<sub>2</sub>O<sub>3</sub>, which explained that the formation of  
522 crystalline Pt-Sn alloy led to the preferential conversion of cellulose into  
523 idols (Deng & Liu, 2013). A two-step thermochemical catalytic process  
524 was adopted by Zhang's group to convert cellulose into EG, in which  
525 methyle glycolate (MG) was firstly produced by using a physical mixture  
526 of WO<sub>x</sub> and CMK-3 as the catalyst, and then nearly and quantitatively  
527 converted into EG over Cu/SiO<sub>2</sub> catalyst. The two-step method is able to  
528 effectively suppress the coking of the intermediates, and improve the  
529 yield of EG. However, cellulose depolymerization requires high  
530 temperature and multi-step reaction conditions, resulting in a complex  
531 and uneconomic process (Xu et al. 2017).

532 In the previous researches, tungsten oxide is mainly used as the  
533 catalyst support, and noble metal or base metal Ni is taken the active  
534 species (Lv et al. 2020). On the one hand, the conversion efficiency is not

535 high over such catalyst (for example, only about 80% conversion), on the  
536 other hand, considering the cost and catalyst stability, the catalysts of  
537 metal oxide supported by metal require the properties of low cost, high  
538 catalytic stability and conversion efficiency. Therefore, Zhang's group  
539 designed a simple and efficient process using weakly alkaline Co/CeO<sub>x</sub>  
540 catalyst for one-pot conversion of cellulose into diols. The base metal Co  
541 catalysts supported by non-tungsten oxides as hydrogenation metals are  
542 characterized by simple structure, stable performance and high catalytic  
543 efficiency. Notably, a total yield of 89.1% for diols (EG: 55.2%, PG:  
544 33.9%) was achieved in aqueous catalytic system over 10% Co/CeO<sub>x</sub>  
545 catalyst under relatively mild condition (245 °C, 3 MPa H<sub>2</sub>, 6 h) (Li et al.  
546 2019a). Accordingly, one-pot catalytic conversion of cellulose into diols  
547 is a complex reaction network, which consists of hydrolysis,  
548 isomerization, retro-aldol-type fragmentation, hydrogenation,  
549 dehydrogenation, and thermal side reactions. The key factor for obtaining  
550 high yield of cellulosic diols lies in the balance among various catalytic  
551 steps to match the reaction rates (Zheng et al. 2017).

552 Ethanol (EtOH) is regarded as an ideal fuel substitute for the  
553 reduction of the consumption of petroleum in the future. As a traditional  
554 technology, biological fermentation processes have been employed to  
555 produce ethanol, in which enzymes depolymerize cellulose into simple  
556 sugars, such as glucose, which is followed by fermentation and

557 distillation. Nevertheless, the fermentation process suffers many  
558 problems, such as high cellulase price, long production cycle and many  
559 inhibiting factors in the reaction process. Chemical conversion method  
560 has the advantages of wide adaptability of raw materials, high production  
561 intensity and easy amplification, which is expected to break the  
562 bottleneck of the limit yield and concentration of EtOH produced by  
563 traditional biological fermentation. Consequently, one-pot production of  
564 EtOH directly from cellulose by chemical method provides an important  
565 direction for the development in recent year (Chu et al. 2021).

566 Since 2017, Zhang's group had provided a two-step  
567 cellulose-MG-EtOH route for the conversion of cellulose into ethanol.  
568 Methylene glycolate (MG), derived from cellulose in the first step, was  
569 converted into EtOH over Cu/SiO<sub>2</sub> catalyst at 280 °C with the selectivity  
570 of 50% and the total yield of 29% based on cellulose (Xu et al. 2017).  
571 Then, they improved the method into the one-pot production of cellulosic  
572 EtOH at the yield of 43.2 C% over a multifunctional Mo/Pt/WO<sub>x</sub> catalyst.  
573 It is identified that the formed <sub>x</sub>OMo–Pt–WO<sub>x</sub> interfacial structure  
574 succeeded in accelerating the speed of EG hydrogenolysis into ethanol  
575 (Yang et al. 2019). Shortly afterwards, the multi-functional catalysts of  
576 H<sub>2</sub>WO<sub>4</sub>-Pt/ZrO<sub>2</sub> and Ru-WO<sub>x</sub>/HZSM-5 had been reported by Wang's and  
577 Zhang's group, which obtain the cellulosic EtOH yield of 32% and 53.7%,  
578 respectively (Li et al. 2019b; Song et al. 2019). To efficiently hydrolyze

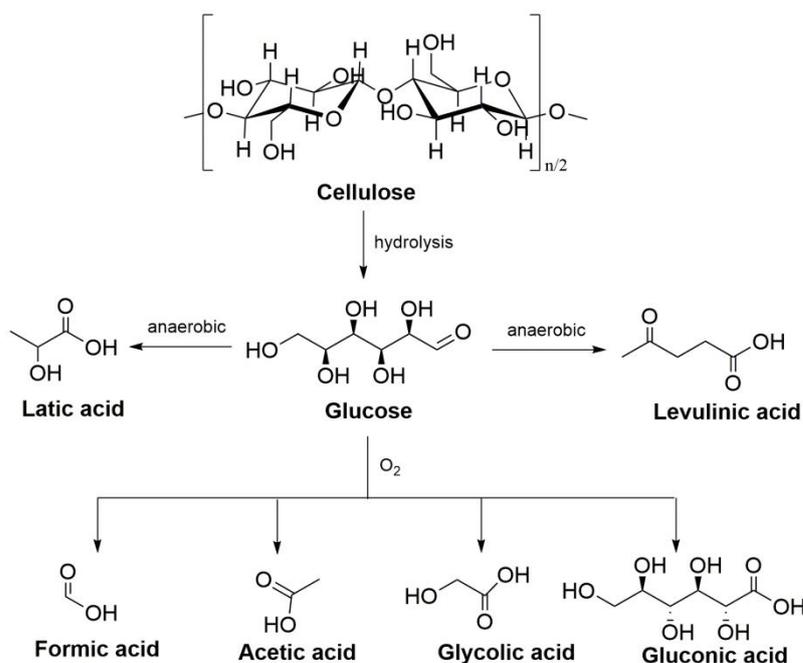
579 cellulose into glucose for the subsequent hydrogenation and  
580 hydrogenolysis reactions, Ma's group introduced phosphoric acid ( $\text{H}_3\text{PO}_4$ )  
581 to assist Ni@C in one-pot efficient conversion of cellulose to EtOH.  
582 Moreover,  $\text{H}_3\text{PO}_4$  interacts with glucose to form cyclic di-ester bonds,  
583 promoting EtOH formation under the synergistic hydrogenation of Ni@C.  
584 69.1% of EtOH yield (carbon mole basis), and reaching the concentration  
585 of 8.9 wt% in this catalytic system (Liu et al. 2019). One-pot chemical  
586 catalytic routes to EtOH from cellulose are considered as promising  
587 pathways with growing interest, although the reaction networks are very  
588 complex. The product selectivity thus plays a crucial role, and the key  
589 factor lies in the balance among the major cascade catalytic reaction  
590 steps.

591 The product distribution in hydrogenation/hydrogenolysis of  
592 cellulose is mainly controlled by the respective capacities of cellulose  
593 hydrolysis and glucose hydrogenation/hydrogenolysis. The catalysts with  
594 specific acid/metal site ratios should be developed for the regulation of  
595 the hydrolysis of cellulose and its hydrogenation/hydrogenolysis of  
596 glucose. In this manner, sugar alcohols (sorbitol and mannitol) and small  
597 molecule alcohols (EG, PG and EtOH) can be prepared in a controlled  
598 way.

#### 599 **3.1.4 Selective oxidation**

600 The direct transformation of cellulose through selective oxidation

601 pathway can provide a diverse range of organic acids, such as gluconic  
 602 acid, lactic acid, levulinic acid and formic acid (Zhang & Huber, 2018)  
 603 (Fig.7), which exhibits widespread applications in the food, detergent,  
 604 and pharmaceutical industries. Gluconic acid and lactic acid are produced  
 605 commercially by the fermentation (enzymatic oxidation) of glucose,  
 606 presenting problematic enzyme separation, waste water removal, and a  
 607 narrow window of reaction conditions. There is hence an opportunity for  
 608 the heterogeneously catalyzed routes. Selective oxidation of cellulose  
 609 can be conducted by using anaerobic and aerobic methods.



610  
 611 Fig. 7. Organic acids that can be produced form cellulose via glucose

612 For the current commercial production of gluconic acid, submerged  
 613 fermentation method was used. The chemical conversion of cellulose into  
 614 gluconic acid is a big challenge, and the reported works focused on its  
 615 aerobic selective oxidation pathway. Synthesis of gluconic acid from  
 616 cellulose has been generally achieved by using metal catalysts (Au, Pd, Pt)

617 supported by carbon materials (carbon nanotube and mesoporous carbon)  
618 and heteropolyacid catalyst. Most of the research works mainly focused  
619 on the oxidative conversion of glucose and cellobiose into gluconic acid  
620 (Guo et al. 2019; Zhang et al. 2021b; Zhang et al. 2020), and few works  
621 are known for direct conversion of cellulose. Wang's group reported an  
622  $\text{Au/Cs}_{1.2}\text{H}_{1.8}\text{PW}_{12}\text{O}_{40}$  catalyst for the transformation of cellulose into  
623 gluconic acid with the yield of 60% (418 K, 1.0 MPa  $\text{O}_2$ ). Although  
624  $\text{Au/Cs}_{1.2}\text{H}_{1.8}\text{PW}_{12}\text{O}_{40}$  showed decreased catalytic performance in the  
625 second run, a combined catalyst between  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and  
626  $\text{Au/Cs}_{1.2}\text{H}_{1.8}\text{PW}_{12}\text{O}_{40}$  was reusable at least for 6 runs (An et al. 2012).  
627 Direct conversion of cellulose as the feedstocks should be encouraged for  
628 the production of gluconic acid through hydrolytic selectively oxidation  
629 process. Basically, this reaction system requires two successive steps, that  
630 is, the acid-catalyzed hydrolysis of cellulose into glucose promoted by  
631 acidic sites and the oxidation of resulted glucose by the metal particles.

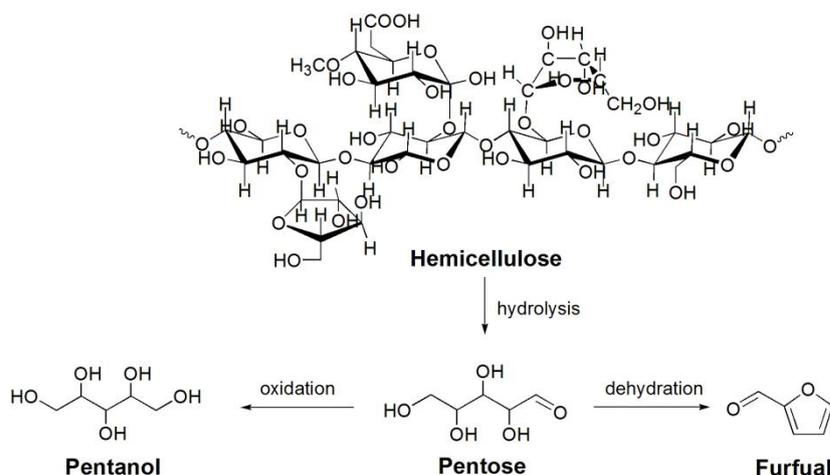
632 Heterogeneous synthesis of lactic acid from cellulose involves a set  
633 of tandem steps, i.e., the hydrolysis of cellulose to glucose, the  
634 isomerisation of glucose to fructose, the retro-aldol condensation of  
635 fructose to C3 intermediates and the subsequent conversion of the C3  
636 intermediates to lactic acid (Li et al. 2016). Wang's group designed stable  
637 solid  $\text{Yb}(\text{OTf})_2\text{-SO}_3\text{-SBA-15}$  catalysts to deal with the recycle issue of  
638 trifluoromethanesulfonic acid, and found that efficient conversion of

639 cellulose to lactic acid was achieved by regulating the amount of  
640  $\text{Yb}(\text{OTf})_3$  immobilized on sulfo-functionalized SBA-15, and the yield of  
641 71.6% for lactic acid was obtained at 493K for 2 h (Wang et al. 2018).  
642 Shi's group prepared the solid  $\text{Al}_2(\text{WO}_4)_3$  catalyst to provide Al-OH and  
643 W=O functional groups as the active sites, thereby enhancing the  
644 hydrolytic oxidation of cellulose into lactic acid. Under the optimum  
645 condition of 220 °C for 3 h, the yield of 46% for lactic acid could be  
646 produced based on the synergistic effect of the W=O species and the  
647 adjacent Al=OH species in  $\text{Al}_2(\text{WO}_4)_3$  (Shi et al. 2019) Wang's group  
648 further reported the yttrium modified siliceous Beta zeolites for highly  
649 efficient conversion of cellulose into lactic acid. It was demonstrated that  
650 the dealumination operation suppressed the by-products (e.g. 5-HMF) in  
651 the dehydration process and modification of yttrium increased Lewis  
652 acidity amount for lactic acid production. In this regard, the yield of  
653 49.2% for lactic acid was obtained at 220 °C within 30 min (Ye et al.  
654 2021).

### 655 **3.2 Hemicellulose transformation**

656 Hemicellulose is an amorphous heteropolymer composed of several  
657 different types of monosaccharides, such as xylose, arabinose, galactose,  
658 etc., which can be extracted from cell walls (Tian et al. 2022; Wang et al.  
659 2021). Although the composition of hemicellulose fraction changes with  
660 the cell types and plant species, it typically contains large amounts of

661 xylose, arabinose and pentose sugars commonly used as the starting  
662 materials for furans, polyols and their subsequent products (Fig. 8) (Sun  
663 et al. 2021).



664

665

Fig. 8. The main catalytic conversion pathway of hemicellulose

666

Direct conversion of hemicellulose over heterogeneous catalysts is  
667 rarely reported due to its poor product selectivity. Fukuoka's group  
668 reported a combined hydrolytic hydrogenation process for the conversion  
669 of hemicellulose into arabitol over Ru/C catalyst with the yield of 83%  
670 for arabitol at 155 °C for 24 h. The observed product selectivity depends  
671 on the acidity and the carbonic structure used in the Ru/C catalysts (Guha  
672 et al. 2011). Zhang's group converted hemicellulose and cellulose in  
673 woody biomass into a mixture of ethylene glycol and other diols using a  
674 Ni–W<sub>2</sub>C catalyst, and obtained the total yield of 75.6% at 235 °C for 4 h  
675 (Li et al. 2012). Lin's group demonstrated that lactic acid could be  
676 produced from xylan, represented by hemicellulose using ZrO<sub>2</sub> catalyst. It  
677 was revealed that the acid/base pairs on the surface of ZrO<sub>2</sub> played a  
678 crucial role in facilitating the retro-aldol fragmentation of xylose, and the

679 molar yield of 30% for lactic acid was obtained at 200 °C for 40 min  
680 (Yang et al. 2015). Fan's group carried out cascade reaction for the  
681 integrate conversion of hemicellulose into  $\gamma$ -Valerolactone (GVL), in  
682 which hemicellulose first underwent hydrolyzation to ensure the  
683 dehydration for furfural over ZSM-5 catalyst. Subsequently, the formed  
684 furfural was transformed to GVL over Au/ZrO<sub>2</sub> catalyst combined with  
685 ZSM-5. At last, the yield of 61.5% for GVL based on hemicellulose was  
686 obtained at 120 °C for 24 h (Zhu et al. 2016).

687 Hemicellulose is more readily hydrolyzed to sugars than cellulose  
688 mostly due to the amorphous and branched structures. Consequently, it  
689 is impossible for the optimization to maximize individual cellulosic  
690 glucose and hemicellulose sugar recovery in the same reaction system of  
691 lignocellulose. In general, the first step of the chemical conversion of  
692 hemicellulose is a depolymerization process in liquid acid media during  
693 the isolation process, as we mentioned previously in Section 2.  
694 Hemicellulose was extracted in the form of hexoses (e.g. xylose and  
695 arabinose) for further refinery to furfural, xylitol and other chemicals.  
696 The methods for converting the hexoses derived from hemicellulose to  
697 chemical platform products were reviewed in recently references (Gurbuz  
698 et al. 2013; Zhang et al. 2016) .

#### 699 **4. Future Perspectives**

700 All the current commercial chemicals are derived from

701 petrochemical feedstocks. Despite the renewed interest and extensive  
702 researches in the development of lignocellulose biorefinery, no  
703 commercialized biofuels and bulk commodity chemicals are produced  
704 from lignocellulosic polysaccharides due to the economic and  
705 environmental considerations on low overall carbon yield and separation  
706 problems (Chandel et al. 2018). However, further conversion of  
707 lignocellulosic polysaccharides has great potential to deal with some  
708 knotty global problems, such as global warming, food crisis and  
709 environmental problems. Catalytic routes for lignocellulosic  
710 polysaccharides conversion to renewable chemicals and fuels will  
711 underpin the valorization of bio-derived feedstocks. The exploitation of  
712 new strategies for value-added platform chemicals and scale-up of these  
713 processes to produce bio-derived products at commercial scale is the  
714 objective of most researchers to work in high-valued utilization of  
715 lignocellulosic biomass. The development of the designs of new  
716 heterogeneous catalytic processes for biorefinery applications still  
717 represent a significant challenge requiring more advanced research and  
718 collaboration to across the interfaces between the following aspects:

719 1. Since the chemical components in the cell wall of lignocellulosic  
720 biomass can be regulated by using biological technology, the operations  
721 are necessary to be implemented on genetic engineering to increase the  
722 homogeneity of the polymer or the proportion of easily cleavable linkages

723 in lignocellulosic biomass.

724 2. The complex nature of lignocellulosic biomass in the chemical  
725 composition and structure in cellulose, hemicellulose and lignin may  
726 result in much different reactivity, meaning that more efficient and green  
727 progress in the fractionation of lignocellulosic biomass should be  
728 conducted. Moreover, the optimal pretreatment has to be done for the  
729 reduction of the energy activity of lignocellulosic fractions, for example,  
730 destroying the crystal structure of cellulose and decreasing lignin  
731 repolymerization.

732 3. Heterogeneous catalysis is a key technology for the valorization  
733 of lignocellulosic polysaccharides (cellulose in particular) and lignin. The  
734 development of the advanced catalysis technology facilitates the rational  
735 design of robust catalysts with specific physical structures, such as  
736 surface area and pore size, as well as the active functional groups, such as  
737 grafted acid centers and adsorption sites, solvent systems and metallic  
738 sites with optimal acid/metal site ratios for selective transformation of  
739 lignocellulosic components.

740 4. Further mechanistic analysis has become increasingly  
741 important in elucidating new reaction pathways and developing  
742 associated kinetic models to guide the design process, and maintain the  
743 catalyst performance. Moreover, it will also play a significant role in  
744 understanding the distinction in product selectivity, and developing the

745 catalysts suitable for commercial applications of these processes.

746 5. To date, most of the catalytic methods used for lignocellulosic  
747 conversion belong batch reactions, while consecutive reaction is more  
748 suitable for industrial production, which is mainly because that it is  
749 almost insoluble in most solvents (cellulose in particular). In this context,  
750 effective pretreatment and catalytic techniques should be developed,  
751 which presents another focus for the production of fine chemicals in  
752 biorefineries.

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### 758 **Declarations**

759 **Conflicts of interest:** The authors confirm that this article content has no  
760 conflict of interest.

761 **Ethical approval:** This article does not contain any studies with human  
762 participants or animals performed by any of the authors.

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