

Review Article

Chemocatalytic Conversion of Cellulose into Key Platform Chemicals

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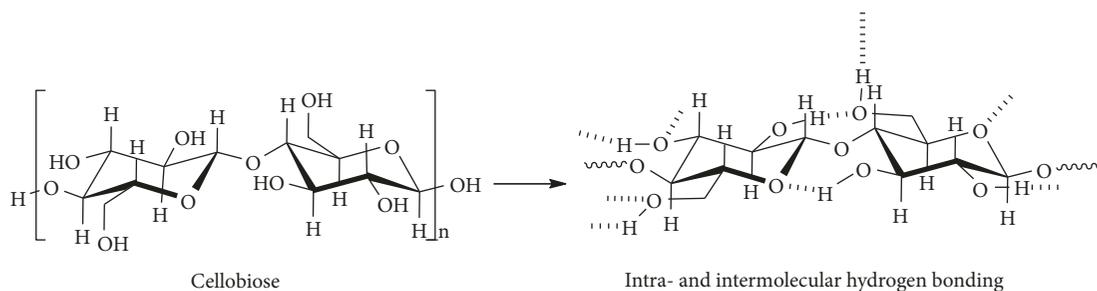
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Chemocatalytic transformation of lignocellulosic biomass to value-added chemicals has attracted global interest in order to build up sustainable societies. Cellulose, the first most abundant constituent of lignocellulosic biomass, has received extensive attention for its comprehensive utilization of resource, such as its catalytic conversion into high value-added chemicals and fuels (e.g., HMF, DMF, and isosorbide). However, the low reactivity of cellulose has prevented its use in chemical industry due to stable chemical structure and poor solubility in common solvents over the cellulose. Recently, homogeneous or heterogeneous catalysis for the conversion of cellulose has been expected to overcome this issue, because various types of pretreatment and homogeneous or heterogeneous catalysts can be designed and applied in a wide range of reaction conditions. In this review, we show the present situation and perspective of homogeneous or heterogeneous catalysis for the direct conversion of cellulose into useful platform chemicals.

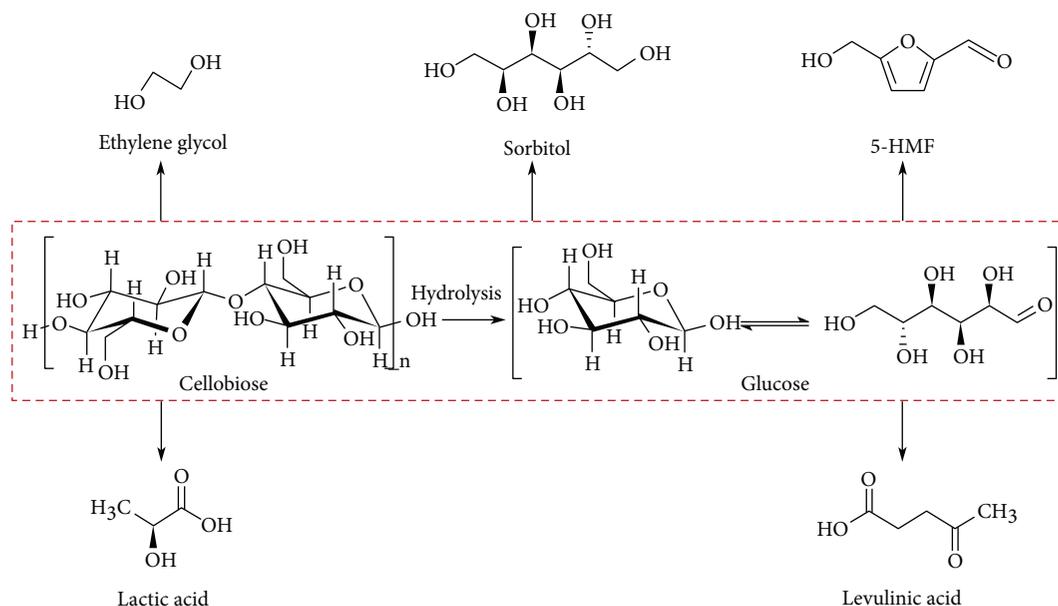
1. Introduction

With the increasing global demand for renewable and valuable chemicals and fuels, social reliance on biomass materials and sustainable technologies is imminent [1–3]. These technologies are booming and will be able to effectively use renewable resources to decrease their dependence on nonrenewable resources in order to promote social progress and development [4–7]. Currently, a promising strategy for alleviating the depletion of energy is to convert lignocellulosic biomass into high-value chemicals and fuels, which has become the current research hotspots [8–34]. As an environmentally friendly, renewable, sustainable, inexpensive, and nonfood biomass resource, lignocelluloses have gained widespread interest for the production of valuable fuels and chemicals with a variety of designed processing technologies [8, 9, 35–44]. Lignocelluloses are very abundant in the world; it is estimated that the annual global production is about 1.1×10^{11} metric tons [45]. Thus, researchers have

explored the use of lignocellulose as relatively low-cost carbon resource to produce key platform chemicals and fuels. It is well known that lignocellulose as an important biomass resource consists mainly of cellulose, hemicellulose, and lignin [46]. Cellulose accounts for the largest proportion (30–55% wt%) of lignocellulose compared to lignin (25–30% wt%) and hemicellulose (25–30% wt%) [47–57], and it is a linear polymer consisted of numerous glucose units covalently linked by β -1,4-glycosidic bonds and closely bound by intramolecular and intermolecular hydrogen-bond networks (Scheme 1) [58–66]. Most cellulose is locked in the form of lignocellulose in nature; hemicellulose and lignin need be removed by extensive cleaning and purification processes. For example, Sasaki et al. reported that semibatch hydrothermal treatment could remove hemicellulose and lignin and recover cellulose from sugarcane bagasse biomass without any catalyst or organic solvent [67]. An average of about 700,000 billion metric tons of cellulose is synthesized annually through photosynthesis of plants using solar energy in the



SCHEME 1: Chemical structure of cellulose with β -1,4-glycosidic bonds and intra- and intermolecular hydrogen bonding.



SCHEME 2: Direct catalytic conversion of cellulose into key platform chemicals.

world, but only 0.1 billion metric tons of cellulose is being used as feedstock in paper, food, pharmaceuticals, and textiles [68–73]. Therefore, a large amount of underutilized cellulose is wasted every year, and new technologies need to be developed to make better use of cellulose resources. In order to reduce excessive dependence on fossil fuels, it is very important to convert cellulosic biomass into renewable and valuable chemicals and fuels. As the most abundant biorenewable materials on earth, the conversion of cellulose to renewable chemicals and fuels to satisfy the growing global energy demand will attract widespread attention of academia and industrial fields [18, 74–97]. However, apart from papermaking and materials industry, a low reactivity of cellulose has seriously hindered its application in the chemical industry. Recently, researchers have designed and screened various heterogeneous or homogeneous catalysts under a variety of reaction conditions; heterogeneous or homogeneous catalysis for the transformation of cellulose into key platform molecules is expected to overcome this problem [98–102].

In this review, we focus on the recent advances in homogeneous or heterogeneous catalysis for direct conversion of

cellulose into key platform chemicals, particularly glucose, polyols, and furans, except for the production of biofuels. The thermochemical such as pyrolysis and gasification, or enzymatic process, is beyond the scope of this review. We review the recent process of direct chemocatalytic conversion of cellulose to key platform chemicals (Scheme 2), which is helpful for researchers to build a deeper understanding of existing chemical processes on the value-added utilization of cellulose and rationally design a more efficient chemical catalytic conversion system for cellulose.

2. Pretreatment Technologies for Decreasing Rigid Structure of Cellulose

Due to tight van der Waals interactions and intramolecular and intermolecular hydrogen-bonding networks, cellulose is chemically stable, structurally rigid, and insoluble in water or common organic solvents [103–111]. The recalcitrance of cellulose is a bottleneck that affects its sustainability and cost-effective utilization for the conversion of cellulosic biomass into key platform chemicals. Thus, efficient pretreatment of cellulose plays an important role in the

TABLE 1: Pretreatment technologies for the cellulose species.

| Entry | Substrate | Pretreatment | Method | Ref. |
|-------|-----------|--------------------------------|------------|-------|
| 1 | MCC | Mixed ball-milling | Mechanical | [136] |
| 2 | CNFs | ACC | Mechanical | [138] |
| 3 | CNFs | TSE | Mechanical | [139] |
| 4 | Cellulose | H ₃ PO ₄ | Chemical | [140] |
| 5 | Cellulose | [C ₄ mim]Cl | Chemical | [159] |
| 6 | Cellulose | [EMIM]Cl | Chemical | [51] |

conversion of cellulose into value-added chemicals. In recent years, various pretreatment strategies were explored for cellulose [72, 112–115]. Among these pretreatment techniques for dissolving the robust structure of cellulose, milling methods as typical mechanical techniques have been widely used, such as ball-milling [116–118]. This can disrupt the crystal structure of native cellulose by cleaving hydrogen bonds in cellulose during processing and reduce the degree of polymerization and decrease the particle size and crystallinity of cellulose, thereby increasing the glucose yield [53, 119–136]. Kobayashi et al. found that the glucose yield was 88% obtained by mixed ball-milling (60 rpm for 2 days) of catalyst (K26, the purified carbon) and microcrystalline cellulose (MCC), which was much higher than that obtained by single ball-milling (30.0%, 60 rpm for 2 days), indicating that mixed ball-milling was more efficient than single ball-milling for the pretreatment of MCC under the same conditions (180°C and 20 min) (Table 1, entry 1) [136]. This is due to the fact that mixed ball-milling improves the contact between MCC and catalyst and also promotes the collision of catalyst and MCC at the solid-solid interface. Suzuki et al. reported that jet-milling treatment only reduced particle size without decreasing the crystallinity index, whereas ball-milling and rob-milling processes converted the crystalline of cellulose into amorphous within one hour [127, 137]. Kafy et al. demonstrated that aqueous counter collision (ACC) equipment mechanically isolated the cellulose nanofiber (CNF) and broke CNFs from pulp fibers using 200.0 MPa water jets colliding each other and decreased the widths of cellulose nanofiber (CNF) within 15–22 nm and the length of CNF within 700–1000 nm (Table 1, entry 2) [138]. Rol and coworkers studied twin screw extrusion (TSE) and reported that this method diminished the width of cellulose nanofibers (CNFs) within 20–30 nm and increased energy efficiency and solid content, and the crystallinity and degree of polymerization (DP) of cellulose fibers were degraded by this mechanical treatment technology (Table 1, entry 3) [139].

In addition, chemical methods are also used to pretreat cellulose and its derivatives. Deng et al. reported that after commercial cellulose was treated by different concentrations of phosphoric acid (H₃PO₄), its crystallinity decreased from 85% to 79–35%, and the DP of cellulose reduced from 221 to 209–106, and the decreases in DP and crystallinity of cellulose raised the conversion of treated cellulose to sorbitol over the Ru/CNT catalyst (Table 1, entry 4) [140]. The authors demonstrated that the concentration of H₃PO₄, treatment temperature, and treatment time had important

effects on the crystallinity and DP of cellulose. Cellulose is hardly soluble in water, and it can only be dissolved at relatively high temperatures [141, 142]. In order to improve the utilization of cellulose, it is particularly important to explore solvents of cellulose to deal with it as soluble substrates, which could increase the reactivity of cellulose and enhance the conversion of cellulose into high-value chemicals [143]. Burchard et al. demonstrated that a complex was formed between Schweizer’s reagent and cellulose, and the reagent dissociated the hydrogen bonding of cellulose and dissolved cellulose [144]. The researchers reported that the mixtures of N,N-dimethylacetamide (DMAC) and lithium chloride (LiCl) could dissolve cellulose owing to cleaving hydrogen bonds of cellulose with the chloride ion [145–147]. Recently, ionic liquids (ILs) as cellulose-dissolved green solvents have attracted extensive attention [72, 148–153]; this is because ILs have many excellent properties as compared to other traditional solvents, such as controllable adjustment of physico-chemical properties, low vapor pressure, wide liquid range, high chemical and thermal stability, high solvation ability, and wide electrochemical window [154–156]. Swatloski and coworkers demonstrated that ILs 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) could dissolve cellulose without derivatization [157]. The dissolution mechanism of cellulose in ILs is largely believed to be formation of hydrogen bonds between hydroxyl groups of cellulose and anions of ILs [158]. Li and Zhao demonstrated that the glucose yield reached 43% at 100°C for 540 min in the homogeneous hydrolysis of cellulose using IL 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) as a solvent to completely dissolve the cellulose and dilute sulfuric acid (H₂SO₄, mass ratio of acid/cellulose = 0.11) as a catalyst without pretreatment (Table 1, entry 5) [159]. The glucose yield was higher than just water as a solvent (dilute H₂SO₄ as a catalyst, mass ratio of acid/cellulose = 0.92) or concentrated sulfuric acid (65 wt% and higher) as a catalyst. Binder and Raines observed that the yield of cellulose hydrolysis to glucose was increased to nearly 90% in 120–240 min by adding water gradually to IL-HCl solution [ILs 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as a solvent and HCl (20 wt%, mass ratio of HCl/cellulose) as a catalyst] (Table 1, entry 6) [51]. Li and coworkers showed that ILs with unsaturated heterocyclic cations generally dissolved cellulose better [160]. Li et al. reviewed in detail various structures and properties of ILs that dissolved cellulose in recent years [161]. With the rapid development of science and technology, it is believed that more efficient pretreatment technologies will be applied for the pretreatment and conversion of cellulose.

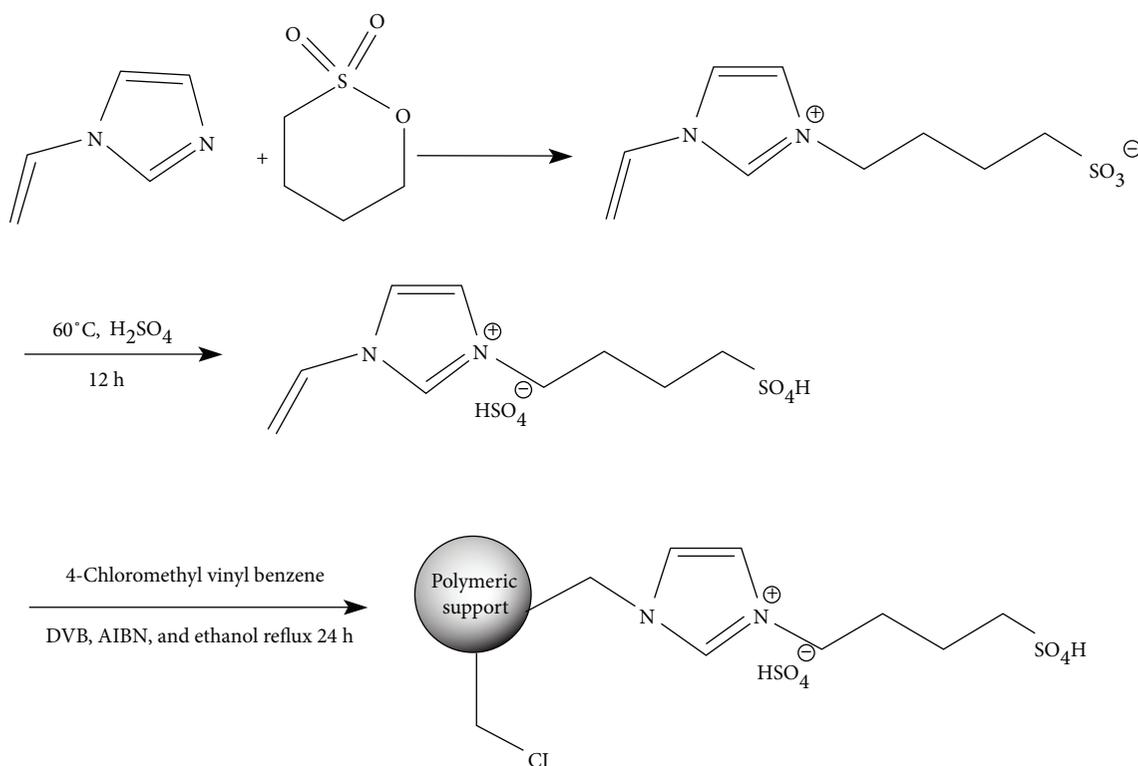
3. Direct Catalytic Conversion of Cellulose into Key Platform Molecules

3.1. Glucose. It is well known that efficient hydrolysis of cellulose as a renewable bulk and nonfood carbon source to glucose is an important challenge for the use of realization of biorefinery, which is the starting point of the overall catalytic conversion chain (Scheme 2) [162–168]. Glucose is a versatile platform chemical to value-added products such as 5-hydroxymethylfurfural (5-HMF), bioethanol,

TABLE 2: Overview of glucose yields from the hydrolysis of cellulose in the typical catalytic system.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|--------------------------------|---|----------------|--------|-------|---------|-------|
| 1 | Cellulose | [Bmim]Cl + DMF | [C ₄ SO ₃ Hmim]Cl | Stirring | 100 | 60 | 95.0 | [215] |
| 2 | MCC | H ₂ O | 40 wt% IL/CMVB | Stirring | 160 | 360 | 47.9 | [216] |
| 3 | MCC | 0.015 wt% HCl-H ₂ O | CD-C | Ball-milling | 200 | 90 | 74.0 | [220] |
| 4 | Avicel | H ₂ O | Polymer ^a | Ball-milling | 120 | 1440 | 94.9 | [229] |
| 5 | Cellulose | H ₂ O | 10-SGOC | / ^b | 160 | 300 | 17.76 | [230] |
| 6 | MCC | H ₂ O | 1 M CB | Ball-milling | 150 | 1440 | 34.6 | [233] |
| 7 | MCC | H ₂ O | GO | / | 179.85 | 60 | 61 ± 4 | [234] |
| 8 | MCC | [Emim]Cl | HY/silicalite-1 | Stirring | 110 | 480 | 50.8 | [235] |

^aBifunctional porous polymer bearing boronic and sulfonic acids as cellulase-mimetic catalyst; ^bwithout pretreatment.

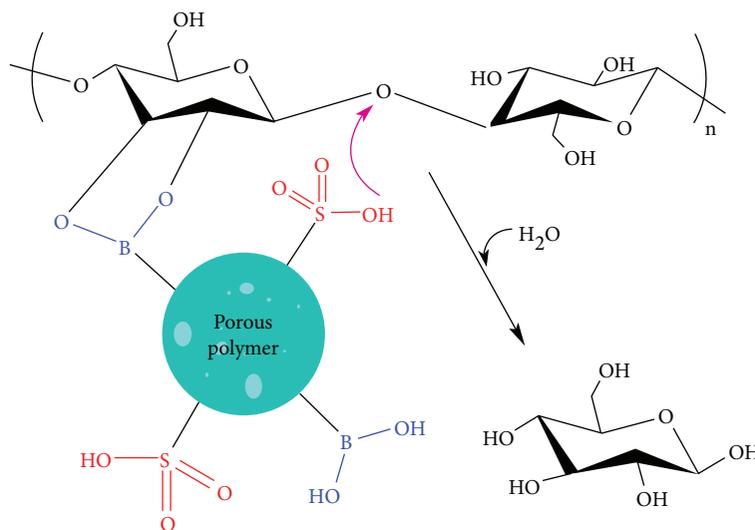


SCHEME 3: Schematic diagram of Brønsted acidic ionic liquid catalyst immobilized on 4-chloromethyl vinyl benzene (CMVB) via copolymerization. Adapted from [216].

and biodegradable plastics [102]. Early, researchers used mineral acids such as phosphoric acid (H₃PO₄), sulfuric acid (H₂SO₄), hydrochloric acid (HCl), perchloric acid (HClO₄), hydrofluoric acid (HF), and nitric acid (HNO₃) as representative homogeneous catalysts for the hydrolysis of cellulose into glucose [162, 169–173]. These mineral acids are cheap and widely used in the early hydrolysis of cellulose to glucose. However, they have some insurmountable bottlenecks owing to their difficulties in poor recyclability, wastewater treatment, reactor corrosion, and other issues [98, 174–176]. Therefore, there is an urgent need to develop a green and sustainable hydrolysis process of cellulose into glucose.

As is well known, not only are ILs not only excellent solvents for dissolving cellulose [177–191] but also ILs modified by acidic groups can effectively catalyze the hydrolysis of

cellulose into glucose in homogeneous and heterogeneous systems [192–214]. Jiang et al. demonstrated that the acidic IL 1-butyl sulfonic acid-3-methylimidazolium chloride ([C₄SO₃Hmim]Cl) exhibited excellent activity in the hydrolysis of cellulose into glucose compared with other three acidic IL catalysts including [Bmim]Cl, [C₄SO₃Hmim]HSO₄, and [Bmim]HSO₄ at 100°C for 1 h (Table 2, entry 1) [215]. This is owing to the stronger acidity strength of the [C₄SO₃Hmim]Cl catalyst. Parveen et al. reported that the glucose yield reached 47.9% using 40% Brønsted acidic ionic liquid 1-(4-sulfobutyl)-3-vinyl-1H-imidazol-3-ium hydrogensulfate (IL) immobilized on polymer support via copolymerization with 4-chloromethyl vinyl benzene (CMVB, 40% IL/CMVB, Scheme 3) as catalyst and water as solvent, which was higher than that of 0 or 100% IL/CMVB catalyst



SCHEME 4: Proposed hydrolysis mechanism of cellulose to glucose by a bifunctional porous polymer solid acid catalyst bearing boronic and sulfonic acids. Adapted from [229].

(Table 2, entry 2) [216]. This is because 40% IL/CMVB promoted a synergistic effect for the hydrolysis of cellulose into glucose. The chlorine groups ($-\text{Cl}$) in CMVB promoted the dissolution of cellulose by breaking intermolecular and intramolecular hydrogen bonding, while the sulfonic acid groups ($-\text{SO}_3\text{H}$) in IL promoted the dissociation of β -1,4-glycosidic bonds to generate glucose units.

Recently, solid catalysts, such as carbonaceous acids, metal oxides, supported metals, H-form zeolites, acid resins, heteropoly acids, magnetic acids, and functionalized silicas, have attracted much attention as promising and appealing catalysts for the hydrolysis of cellulose into glucose due to their excellent properties, such as easy separation, recoverability and reusability from product solutions, and adjustable functional structure of catalysts [92, 98, 131, 163, 217–228]. Su et al. reported that the pretreatment of cellulose and cow dung-based carbonaceous catalyst (CD-C) via mixed ball-milling effectively enhanced the yield of glucose with 59.3% compared with unmilled catalysts (3.6% glucose yield). Moreover, the addition of trace hydrochloric acid (0.015 wt% HCl) could significantly increase the glucose yield to 74% under the same reaction conditions. The excellent performance of the hydrolysis of cellulose to glucose was attributed to the synergistic effect of the mixed ball-milling pretreatment and the addition of dilute HCl (Table 2, entry 3) [220]. Yang and Pan demonstrated an important improvement in hydrolysis of cellulose to glucose, in which a bifunctional mesoporous polymeric catalyst bearing boronic acid as cellulose-binding groups and sulfonic acid as cellulose-hydrolytic groups was prepared, resulting in an excellent hydrolysis performance (Table 2, entry 4, Scheme 4) [229]. The increase in hydrolysis performance was mainly due to the synergistic effects of more cellulose-attracting groups (boronic acid) and cellulose-hydrolyzing groups (sulfonic acid) and larger surface area of the prepared polymeric solid acids. Zhang et al. reported an effective carbonaceous solid acid catalyst (10-SGOC) for the hydrolysis of cellulose to glucose, which was prepared by

hydrothermal carbonization of cellulose using graphene oxide as a structure-directing agent and subsequent concentrated H_2SO_4 as a sulfonating agent [230]. The yield and selectivity of glucose reached 17.76% and 94.22% at 160°C for 5 h over 10-SGOC catalyst, respectively (Table 2, entry 5). 10-SGOC exhibited excellent glucose yield and selectivity in the case of low mass ratio of catalyst/cellulose compared with previously reported sulfonated solid acid catalysts [130, 217, 231, 232]. This indicated that the combination of functional groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{SO}_3\text{H}$ and layered structure with good hydrophilicity promoted a synergistic effect for the 10-SGOC catalyst, thereby better facilitating the contact of the catalyst with cellulose and effectively diffusing glucose into water. Li et al. reported a novel sulfonated carbon catalyst (1 M CB) prepared by a fast sulfonating process via a plasma technology in dilute H_2SO_4 for the hydrolysis of cellulose into glucose (Table 2, entry 6) [233]. The results demonstrated that a high yield of glucose with 34.6% and good conversion of cellulose with 40.1% were obtained at 150°C for 24 h, and the high yield and conversion were attributed to the higher $-\text{SO}_3\text{H}$ and total acidic densities of the sulfonated carbon catalyst. The combination of microwave irradiation (MW, 200 W, and 179.85°C) as a heating tool and graphene oxide (GO) as a solid catalyst were investigated by Mission et al. for the hydrolysis of MCC into glucose; the results showed that a higher yield of glucose with $61 \pm 4\%$ in 60 min was achieved compared with other solid catalysts such as phosphotungstic acid, Amberlyst 15, functionalized GO, and sulfated zirconia (Table 2, entry 7) [234]. This indicated that the combination of GO and MW promoted a synergistic effect for the hydrolysis of MCC into glucose to significantly enhance the catalytic performance, owing to the large surface area and sufficient acid density of the GO catalyst, variety of functionalities of the GO surface, and MW interaction. Yu et al. reported that silicalite-1-modified HY zeolite (HY/silicalite-1) as a catalyst could effectively enhance the selectivity of glucose, significantly reduce the

TABLE 3: Overview of EG yields from the conversion of cellulose in the typical catalytic system.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|------------------|--|--------------|--------|-------|---------|-------|
| 1 | Cellulose | H ₂ O | 3Al-15W-3Ni | Stirring | 229.85 | 90 | 76.0 | [273] |
| 2 | MCC | H ₂ O | 0.8%Ru-30%W/CNT | Ball-milling | 205 | 180 | 40.0 | [274] |
| 3 | MCC | H ₂ O | 15%Ni-20%W/SiO ₂ -EEG | Stirring | 240 | 120 | 63.3 | [275] |
| 4 | Cellulose | H ₂ O | Ni _{0.3} -W _{0.3} /CNF | Stirring | 245 | 120 | 33.6 | [276] |
| 5 | Cellulose | H ₂ O | 1%Ru/WO ₃ | Stirring | 240 | 120 | 76.3 | [277] |

hydrolysis temperature, and greatly increase the yield of glucose to 50.8% within 8 h in the ionic liquid [Emim]Cl under the same reaction conditions as compared to the non-modified HY catalyst (Table 2, entry 8) [235]. This might be due to a decrease in Lewis acidity of the modified HY catalyst and a decrease in contact probability of Lewis acid sites with sugar caused by the outer silicalite-1 layer.

3.2. Polyols. The conversion of resource-abundant, renewable, and nonedible cellulosic biomass to high-value chemicals is beneficial to the development of a sustainable society. In particular, the direct catalytic conversion of cellulose to polyols is an important part of biorefinery, which has attracted extensive interest to meet the world's energy needs [236–242]. In this section, we focus on the recent developments in the chemical catalytic conversion of cellulosic biomass into ethylene glycol (EG) and sorbitol, which are widely used in the food industry, pharmaceutical production, cosmetics, and so on.

3.2.1. Ethylene Glycol (EG). With the increase of the market demand of renewable products from biomass, it is highly desirable to design a series of effective catalysts which can control the selectivity of polyols [169, 243–263]. The direct conversion of cellulose to value-added polyols in biorefinery is an attractive and promising approach. Although significant advances have been made in the transformation of cellulose to polyols, the production of quite valuable EG is still challenging [88, 264–272].

Hamdy et al. reported a novel 3Al-15W-3Ni catalyst prepared by one-pot hydrothermal sol-gel process for selective hydrogenolysis of cellulose into EG. The catalyst showed the multiple active sites and exhibited a high cellulose conversion (100%) and an excellent yield of EG with 76.0% at 229.85°C for 90 min under 4.0 MPa of H₂ pressure (Table 3, entry 1) [273]. Ribeiro and coworkers synthesized a carbon nanotube (CNT-) supported bimetallic 0.8%Ru-30%W/CNT catalyst prepared via a sequential incipient wetness impregnation method (first loaded with W and then with Ru component) for the hydrolytic hydrogenation of cellulose to EG, leading to 100% cellulose conversion and about 40% EG yield in aqueous solution at 205°C for 3 h of reaction under 5.0 MPa of H₂ pressure, which was demonstrated to be an improved catalytic performance compared with monometallic Ru/CNT or W/CNT catalyst under the same reaction conditions (Table 3, entry 2) [274]. This was because the combination of W and Ru components promoted a synergistic effect for the bimetallic catalyst, thereby increasing the yield of EG. A novel SiO₂-OH nanosphere-supported 15%Ni-20%W/SiO₂-

EEG catalyst was prepared by Xiao et al. via the incipient wetness impregnation method [275]. When this catalyst was employed for the selective hydrogenolysis of cellulose into EG in aqueous solution, 63.3% yield of EG was obtained at 240°C for 2 h under 5.0 MPa of H₂ pressure (Table 3, entry 3). A good EG yield of the bimetallic catalyst for the conversion of cellulose to EG was attributed to the synergistic effect between W and Ni active sites. Yang et al. prepared a carbon nanofiber- (CNF-) supported bimetallic Ni_{0.3}-W_{0.3}/CNF catalyst, resulting in 95.0% conversion of cellulose and 33.6% EG yield in aqueous solution at 245°C for 2 h under 6.0 MPa of H₂ pressure. The improved performance of the bimetallic catalyst was attributed to excellent accessibility and uniform dispersion of metal species (Table 3, entry 4) [276]. Li et al. found that the WO₃-supported 1% Ru/WO₃ catalyst prepared by homogeneous deposition-precipitation (HDP) technique was effective for the selective hydrogenolysis of cellulose to EG, leading to 76.0% EG yield with 100% cellulose conversion in aqueous solution at 240°C for 2 h under 4.0 MPa of H₂ pressure (Table 3, entry 5) [277]. The addition of Ru species significantly increased the active site of W⁵⁺, thereby promoting the retro-aldol condensation reaction of glucose and enhancing the etching of H⁺ in aqueous solution for the hydrogenolysis of cellulose to EG, thus obtaining a high yield of EG from cellulose.

3.2.2. Sorbitol. With the gradual depletion of nonrenewable resources, such as fossil fuels and coal, cellulosic biomass, as a large-scale renewable and sustainable carbon source on earth, has attracted wide attention for its catalytic conversion to value-added chemicals, such as the hydrolytic hydrogenation of cellulose to produce sorbitol [140, 278–287].

Zhang et al. prepared a magnetic catalyst (Ni_{4.63}Cu₁Al_{1.82}Fe_{0.79}) for the direct transformation of cellulose to sorbitol, resulting in 68.07% sorbitol yield in 0.06% H₃PO₄-H₂O solution at 214.85°C and 4.0 MPa H₂ after 3 h, which was shown to be enhanced catalytic performance in comparison to Cu₁Al_{1.71}Fe_{0.72} with about 29% sorbitol yield under the same conditions (Table 4, entry 1) [288]. This indicated that the modification of Ni species improved the catalytic reaction activity, and a synergistic effect might be promoted between active Ni/Cu and Cu sites.

Xi and coworkers reported a novel mesoporous niobium phosphate-supported bifunctional Ru catalyst (5%Ru/NbOPO₄-pH2), which exhibited excellent performance for the selective transformation of cellulose to sorbitol [289]. When the mixture of cellulose and 5%Ru/NbOPO₄-pH2 was ball-milled for 10 h and the hydrolytic hydrogenation reaction was conducted in water, the sorbitol yield was

TABLE 4: Overview of sorbitol yields from the conversion of cellulose in the typical catalytic system.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|------------------|--|------------------|--------|-------|---------|-------|
| 1 | Cellulose | H ₂ O | Ni _{4.63} Cu ₁ Al _{1.82} Fe _{0.79} | Heating-stirring | 214.85 | 180 | 68.07 | [288] |
| 2 | MCC | H ₂ O | 5%Ru/NbOPO ₄ -pH2 | Ball-milling | 160 | 1440 | 69.1 | [289] |
| 3 | MCC | H ₂ O | 3.0%Ru/SiO ₂ -SO ₃ H | Ball-milling | 150 | 600 | 61.2 | [290] |
| 4 | MCC | H ₂ O | 0.4%Ru/AC | Ball-milling | 205 | 60 | 68.0 | [291] |
| 5 | Cellulose | H ₂ O | 0.4%Ru-3%Ni/AC | Ball-milling | 205 | 60 | 70.0 | [292] |

TABLE 5: Overview of 5-HMF yields from the conversion of cellulose in the typical catalytic system.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|-----------------------|--|--------------|------|-------|---------|-------|
| 1 | Cellulose | [EMIM]Br | SPPS | Stirring | 180 | 240 | 68.2 | [333] |
| 2 | MCC | H ₂ O/MIBK | ChH ₂ PW ₁₂ O ₄₀ | Stirring | 140 | 480 | 75.0 | [334] |
| 3 | MCC | [Emim]Cl | CrCl ₃ /[(CH ₃) ₄ N]ReO ₄ | Stirring | 150 | 30 | 49.3 | [335] |
| 4 | MCC | THF/H ₂ O | Nb/C-50 | Ball-milling | 170 | 480 | 53.3 | [336] |
| 5 | MCC | DMOE/H ₂ O | AlCl ₃ -H ₃ PO ₄ | Stirring | 180 | 120 | 49.42 | [337] |

up to 69.1% at 160°C and 4.0 MPa H₂ after 24 h, which was higher than 5%Ru/NbOPO₄-pH2 with 57.3% without ball-milled pretreatment (Table 4, entry 2). Zhu et al. synthesized a sulfonic acid-functionalized silica-supported Ru catalyst (3.0%Ru/SiO₂-SO₃H) for the hydrolytic hydrogenation of cellulose to sorbitol, leading to 61.2% sorbitol yield in aqueous solution after 10 h at 150°C and 4.0 MPa H₂, which was demonstrated to be a better yield of sorbitol than that of the mechanical mixture of Ru/SiO₂ and SiO₂-SO₃H with 43.3% sorbitol yield under the same reaction conditions (Table 4, entry 3) [290]. This indicated that the combination of Ru metal and acidic sites promoted a strong synergistic effect between the proximate Ru site and acid site for enhanced sorbitol yield of 3.0% Ru/SiO₂-SO₃H catalyst in the conversion of cellulose into sorbitol. Ribeiro and coworkers studied an activated carbon- (AC-) supported Ru catalyst (0.4%Ru/AC) for the one-pot transformation of cellulose to sorbitol and observed that the sorbitol yield reached 68.0% in H₂O after 1 h of reaction at 205°C and 5.0 MPa H₂ when 0.4%Ru/AC was ball-milled together with cellulose, whereas it was only 49.0% when the catalyst and cellulose were separately ball-milled under the same reaction conditions (Table 4, entry 4) [291]. This demonstrated that mix-milling pretreatment enhanced the reaction rates in the hydrolytic hydrogenation of cellulose to sorbitol, which was not owing to the mechanocatalytic hydrolysis in the process of treatment but was mixing. Afterward, Ribeiro et al. prepared an AC-supported Ru-Ni bimetallic catalyst (0.4%Ru-3%Ni/AC) for hydrolytic hydrogenation of cellulose to sorbitol [292]. The addition of Ni species promoted a synergic effect between Ni species and Ru species for the bimetallic Ru-Ni/AC catalyst in the one-pot conversion of cellulose to sorbitol. A sorbitol yield of 70.0% was obtained over the 0.4%Ru-3%Ni/AC catalyst in H₂O after 1 h at 205°C and 5.0 MPa H₂ when the catalyst was ball-milled with cellulose (Table 4, entry 5).

3.3. *5-Hydroxymethylfurfural (5-HMF)*. 5-HMF is a promising and versatile biomass-based platform molecule from biorefinery carbohydrates, which can be used to produce various chemicals and liquid fuels currently derived from nonrenewable fossil resources [293–296]. It is worth noting that the production of 5-HMF from renewable cellulose has become an integral part of biorefinery and attracted extensive attention in recent years [297–332].

Li et al. prepared a sulfonated poly(phenylene sulfide) (SPPS) catalyst with strong Brønsted acid sites and a sulfonation degree of 21.8 mol%; when it was used for the direct conversion of cellulose to 5-HMF in IL 1-methyl-3-ethyl imidazolium bromide ([EMIM]Br) solvent, the yield of 5-HMF with 68.2% was obtained at 180°C for 4 h (Table 5, entry 1) [333]. DFT calculations indicated that the –SO₃H groups in SPPS play an important role in catalytic conversion, and it acts as a proton donor for Brønsted acids and acts as a proton acceptor as a conjugate base. In addition, the anions and cations of ILs together with SPPS-SO₃H are conducive to stabilizing the transition states and reaction intermediates, which also leads to the easy conversion of cellulose to 5-HMF.

Zhang et al. reported a temperature-responsive heteropolyacid (ChH₂PW₁₂O₄₀) catalyst, prepared by H₃PW₁₂O₄₀ and choline chloride (ChCl) as raw materials, which was used for one-pot transformation of cellulose to 5-HMF in the biphasic solvent system including H₂O and methyl isobutyl keton (MIBK) (H₂O/MIBK), leading to 75.0% 5-HMF yield and 87.0% cellulose conversion at the volumetric ratio of H₂O/MIBK = 1 : 10 at 140°C for 8 h (Table 5, entry 2) [334]. Compared to homogeneous H₃PW₁₂O₄₀, the remarkable 5-HMF yield might be attributed to the thermoregulation property and higher Brønsted acidity.

Bai et al. reported a novel bifunctional catalytic system, when the CrCl₃/[R₄N]ReO₄ catalyst was used for the degradation of cellulose into 5-HMF in [Emim]Cl; 5-HMF with a

TABLE 6: Overview of LA yields from the conversion of cellulose in the typical catalytic system.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|--|---|--------------|------|-------|---------|-------|
| 1 | MCC | H ₂ O/[BSMim]HSO ₄ | [BSMim]HSO ₄ | / | 120 | 120 | 39.4 | [348] |
| 2 | MCC | MIBK/H ₂ O | ChH ₄ AlW ₁₂ O ₄₀ | Stirring | 120 | 600 | 74.8 | [349] |
| 3 | Cellulose | H ₂ O | [C ₄ (Mim) ₂][2(HSO ₄)(H ₂ SO) ₂] | Stirring | 100 | 180 | 55.0 | [350] |
| 4 | CFP | H ₂ O | 0.375 wt% TiOSO ₄ | Stirring | 195 | 240 | 69.0 | [351] |
| 5 | MCC | H ₂ O | 5-Cl-SHPAOs | Ball-milling | 165 | 300 | 50.0 | [352] |
| 6 | MCC | H ₂ O | Ni-HMETS-10 | Stirring | 200 | 360 | 91.0 | [353] |

CFP: α cellulose from filter paper.

yield of 49.3% was obtained at 150°C for 30 min under the conditions of 7 mol% of CrCl₃ and 5 mol% of tetramethylammonium perrhenate. The effective catalytic activity of CrCl₃/[R₄N]ReO₄ for the production of 5-HMF from cellulose was attributed to the bifunctional catalytic system of the catalyst, which was better than the single CrCl₃ catalyst (Table 5, entry 3) [335].

Li et al. reported an efficient niobia/carbon catalyst (Nb/C-50, 50 wt% of Nb₂O₅) prepared from niobium tartrate (Nb₂O₅) and glucose as raw materials via carbonization, for the conversion of cellulose into 5-HMF, leading to 53.3% HMF yield and 77.8% total carbon yield in the THF/H₂O biphasic system at 170°C for 8 h (Table 5, entry 4) [336]. What is noteworthy is that the Nb/C-50 catalyst was agglomerated particles and contained suitable Brønsted/Lewis acid sites and weak to medium acid strength, which favored the conversion of cellulose to 5-HMF.

Zhao et al. reported an interesting bifunctional catalytic system using AlCl₃ as the Lewis acidic catalyst and H₃PO₄ as Brønsted acidic catalyst, and when the AlCl₃-H₃PO₄ catalyst was employed for the transformation of cellulose to 5-HMF, the highest yield of 5-HMF with 49.42% was achieved in a single-phase reaction system of 1,2-dimethoxyethane (DMOE) and water at 180°C for 120 min under the reaction conditions of mole ratio of 1:0.8 of AlCl₃/H₃PO₄ and volumetric ratio of 7:1 of DMOE/H₂O (Table 5, entry 5) [337].

3.4. Levulinic Acid (LA). LA is an important platform molecule, which can be prepared by many acid-catalyzed reactions of renewable biomass resources, which is a versatile raw material for resins, pharmaceuticals, pesticides, dyes, and chemical intermediates [338]. The preparation of LA from biorenewable cellulose has attracted more and more attention of researchers [47, 340–347].

Shen and coworkers reported that a high catalytic activity for the conversion of cellulose to LA with a yield of 39.4% was achieved in the presence of IL 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate ([BSMim]HSO₄) with addition of water at 120°C for 120 min (Table 6, entry 1) [348]. The ILs demonstrated a dual solvent-acid role for the direct synthesis of LA from cellulose. More recently, Sun et al. reported a good temperature-responsive heteropolyacid (HPA) catalyst (ChH₄AlW₁₂O₄₀) prepared using H₅AlW₁₂O₄₀ and choline chloride as raw materials, and when it was used for the one-pot conversion of cellulose

into LA in a green cosolvent MIBK/H₂O with a volumetric ratio of 10:1, leading to the highest LA yield with 74.8% at 98.9% cellulose conversion at 120°C for 10 h compared with other reported catalysts (Table 6, entry 2) [349]. The excellent catalytic activity of ChH₄AlW₁₂O₄₀ was due to three synergistic effects of temperature stimulus, double-acidity property (Lewis and Brønsted acidity), and biphasic solvent system including MIBK and H₂O.

Khan et al. synthesized a dicationic IL catalyst [C₄(Mim)₂][2(HSO₄)(H₂SO)₂] including 1,1-bis(3-methylimidazolium-1-yl) butylene ([C₄(Mim)₂]) cation with counter anions hydrogensulfate, dihydrogensulfate, methanesulfonate, and trifluoromethanesulfonate, which was used for the direct conversion of cellulose into LA, resulting in 55% LA yield in H₂O at 100°C for 3 h, which was demonstrated to be a better catalytic activity than other reported ILs (Table 6, entry 3) [350]. The excellent yield of [C₄(Mim)₂][2(HSO₄)(H₂SO)₂] was attributed to higher Hammett acidity of the prepared ILs including more acidic sites in the HSO₄ anion.

Most recently, Chiappe et al. reported one-pot synthesis of LA from CFP (α cellulose from filter paper) by using 0.375 wt% TiOSO₄ as a catalyst, in which the highest 69% yield of LA was obtained in H₂O at 195°C for 4 h compared with other catalysts, such as (TMGH)(HSO₄)-CrCl₃ in H₂O, (TMGH)(HSO₄)-CrCl₃ in H₂O-CO₂, and FeCl₃ in H₂O (Table 6, entry 4) [351]. The excellent performance of 0.375 wt% TiOSO₄ was mainly due to the mixed Brønsted-Lewis acid catalytic system.

Yu et al. reported an efficient sulfonated hyperbranched poly(arylene oxindole)s with 5-chloro-substituent group polymer acid catalyst (5-Cl-SHPAOs), and when it was applied for the catalytic conversion of cellulose into LA in H₂O, the LA yield was up to 50% at 165°C for 5 h, which was twice as high as unsubstituted SHPAOs (Table 6, entry 5) [352].

A novel hierarchically porous ETS-10-supported Ni catalyst (5.0 wt% Ni-HMETS-10) was prepared by Xiang et al., and when it was used for the catalytic conversion of cellulose to LA in aqueous solution, a high yield of LA with 91.0% was achieved at 200°C for 6 h under 6.0 MPa of H₂ pressure. An excellent catalytic activity of 5.0 wt% Ni-HMETS-10 for the conversion of cellulose to LA was attributed to the synergistic effect of Lewis acid sites and unique hierarchical porous structures centered at 16 nm in ETS-10 in a H₂ atmosphere (Table 6, entry 6) [353].

TABLE 7: Lactic acid yields obtained with various catalysts.

| Entry | Substrate | Solvent | Catalyst | Pretreatment | T/°C | t/min | Yield/% | Ref. |
|-------|-----------|------------------|---|--------------------|--------|-------|---------|-------|
| 1 | Cellulose | H ₂ O | Al(III)-Sn(II) | Ball-milling | 189.85 | 120 | 65.0 | [358] |
| 2 | MCC | H ₂ O | Er/K10(S)-3 | Mechanical stirrer | 240 | 30 | 67.6 | [359] |
| 3 | MCC | H ₂ O | Er/deAlb-2 | Mechanical stirrer | 240 | 30 | 57.9 | [360] |
| 4 | MCC | H ₂ O | ZRO-7 ZrO ₂ | Ball-milling | 199.85 | 360 | 21.2 | [361] |
| 5 | MCC | H ₂ O | 10%ZrO ₂ -Al ₂ O ₃ | Ball-milling | 199.85 | 360 | 25.3 | [362] |

3.5. *Lactic Acid.* Lactic acid is an important organic acid, which is also a key platform molecule in the biobased economy. Lactic acid and its derivatives have been used in many fields, such as food, medicine, cosmetics, and other industries. Highly selective catalytic transformation of cellulose into lactic acid has become a hot and difficult issue in recent years [354–357].

Deng et al. reported a bifunctional Al(III)-Sn(II) catalyst with a molar ratio of 1/1, which was applied for the catalytic conversion of cellulose and related carbohydrates to lactic acid, resulting in as high as 65% lactic acid yield in H₂O at 189.85°C for 2 h under 3.0 MPa of N₂ pressure (Table 7, entry 1) [358]. The bifunctional catalyst exhibited an excellent lactic acid yield because the combination of Al(III) and Sn(II) cations promoted the catalytic conversion of cellulose to lactic acid and limited the side reaction.

A series of erbium ion-exchanged montmorillonite K10 catalysts were prepared by Wang et al. and used as solid acid catalysts for the conversion of cellulose to lactic acid. Interestingly, Er/K10(S)-3 exhibited the highest yield of lactic acid with 67.6% in aqueous solution at 240°C for 30 min under 2.0 MPa of N₂ pressure (Table 7, entry 2) [359]. Following this work, Wang et al. reported a series of Er/ β -zeolite catalysts prepared using erbium species grafted on β -zeolites, which were used for one-pot hydrothermal transformation of cellulose to lactic acid [360]. 57.9% lactic acid yield was achieved over the 12.4 wt% Er/deAlb-2 catalyst (synthesized by erbium species grafted on de-aluminated β -zeolite) with a Si/Al ratio of 159 for the conversion of cellulose into lactic acid in H₂O at 240°C for 30 min under 2.0 MPa of N₂ pressure (Table 7, entry 3). The excellent activity of Er/deAlb-2 might be due to its higher erbium content, larger average pore diameter, and external surface area, which promoted contact between active erbium ions and reactant molecules.

Wattanaphawong et al. studied the effect of a large number of transition metal oxides on the catalytic activity of cellulose conversion to lactic acid. They found that ZRO-7 exhibited the highest yield of lactic acid from cellulose with 21.2% in H₂O at 199.85°C for 6 h compared with transition metal oxide catalysts, such as Al₂O₃, V₂O₅, CeO₂, Y₂O₃, Ga₂O₃, and MgO (Table 7, entry 4) [361]. The remarkable catalytic activity of ZRO-7 was due to the large amount of base and acid sites on the ZRO-7 catalyst. Following this work, the 10%ZrO₂-Al₂O₃ catalyst synthesized by Wattanaphawong et al. was used for the production of lactic acid from cellulose, leading to 25.3% lactic acid yield at 199.85°C for 6 h in aqueous solution (Table 7, entry 5), which was superior to ZRO-7 [362]. Compared to pure

ZrO₂, the ZrO₂-Al₂O₃ catalysts contained more Lewis acid sites and fewer base sites. The researchers suggested that the Lewis acid sites on ZrO₂-Al₂O₃ play a more important role than do basic sites for the production of lactic acid from cellulose.

4. Conclusions

Direct chemocatalytic conversion of lignocellulosic biomass to renewable and value-added chemicals has attracted worldwide attention in order to build up sustainable societies. Cellulose is the most abundant, renewable, and nonedible biomass resource in lignocellulosic biomass. However, the recalcitrance and low reactivity of cellulose have hampered its sustainability and cost-effective utilization for chemical industry except for papermarking. It has been expected that homogeneous or heterogeneous catalysts for the direct chemocatalytic conversion of cellulosic biomass into high-value platform chemicals can overcome this problem due to the fact that various types of pretreatment as well as homogeneous or heterogeneous catalysts can be designed and applied under a wide range of reaction conditions. In this review, we have summarized the recent pretreatment methods for decreasing the rigid structure of cellulose and catalytic conversion of cellulose into key platform chemicals, such as glucose, ethylene glycol, sorbitol, 5-hydroxymethylfurfural, levulinic acid, and lactic acid, via a variety of homogeneous or heterogeneous catalysts. This work will be helpful for researchers to build a deeper understanding of existing chemical processes on the value-added utilization of cellulosic biomass to high-value chemicals and rationally design a more efficient chemical catalytic conversion system for cellulosic biomass.

Conflicts of Interest

The authors declare no conflict of interest.

Acknowledgments

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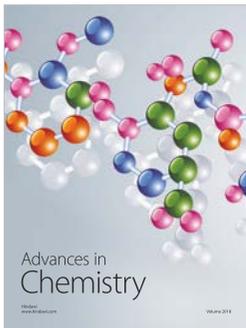
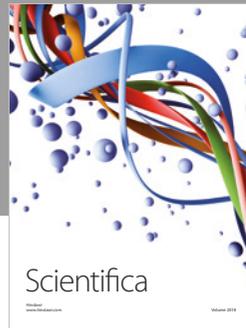
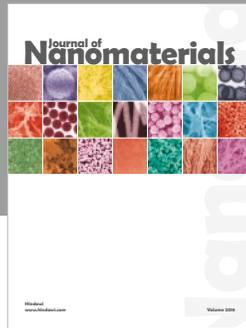
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