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Catalytic transformation of cellulose into platform chemicals

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Abstract

Conversion of biomass to renewable and valuable chemicals has attracted global interest in order to build up sustainable societies. Cellulose is the most abundant and non-food biomass; however, the low reactivity of cellulose has prevented its use in chemical industry except for the paper manufacturing. The heterogeneous catalysis for the conversion of cellulose has been expected to overcome this issue, because various types of heterogeneous catalysts can be designed and applied in a wide range of reaction conditions. Furthermore, solid catalysts are easily recovered and reused. In this review article, we show the present situation and perspective of heterogeneous catalysis for the transformation of cellulose into useful platform

chemicals.

1. Introduction

Biorefinery, the transformation of biomass to renewable chemicals and fuels, is important under the situation of the rising cost and decreasing supply of oil [1-7]. Particularly, plant-derived biomass is a reproducible and low environmental-loading resource, produced from CO_2 and water via photosynthesis using sunlight. Bioethanol has been manufactured from corn and sugarcane in the United States and Brazil for a decade [8], but use of these crops has competed with the food supply. Hence, non-food biomass has to be utilized, and the most abundant inedible biomass is cellulose, which is an attractive feedstock for the production of chemicals.

Cellulose is a polymer composed of glucose units linked by β-1,4-glycosidic bonds. Glucose, which can be synthesized via the hydrolysis of cellulose, is a versatile precursor to valuable chemicals such as biodegradable plastics and ethanol [9-13] (Scheme 1). Sorbitol is also a promising platform chemical, which can be converted to polymers and medicines [14] (Scheme 2). Additionally, 5-hydroxymethylfurfural (5-HMF), gluconic acid, and other derivatives have been expected as feedstock in the bio-based industry. Hence, the conversion of cellulose has attracted worldwide interest; however, the effective degradation of cellulose is a challenge because the polymer has rigid, chemically-stable, and water-insoluble properties, which are induced from the inter- and intra-molecular hydrogen-bondings [15-18]. A large number of strategies have been applied in this subject [19-23]. Homogeneous catalysts such as sulfuric acid and cellulase enzymes produce glucose in high yields from cellulose [24,25], but these processes suffer from the complicated separation of products from the solution [26] and high costs. Although sub- and supercritical water converts cellulose to glucose without any additives [27,28], the low selectivity of product due to the further degradation of glucose

in harsh conditions should be improved. Heterogeneous catalysts are expected to overcome these problems as various types of the catalysts can be designed and applied in a wide range of reaction conditions. Furthermore, solid catalysts are easily recovered and reused [29-32]. Indeed, various types of the cellulose conversion by using heterogeneous catalysts have been reported, in which the number of research reports on the production of sorbitol and glucose is larger than those for the other chemicals in recent years. In this article, we focus on the recent progress in heterogeneous catalysis for the transformation of cellulose into chemicals, especially sorbitol and glucose.

Scheme 1

Scheme 2

2. Pretreatment techniques for degrading the rigid structure of cellulose

Crystalline structure of cellulose needs to be considered for the chemical transformation because the robust feature limits the contact of catalysts to cellulose [33]. Mechanical and chemical treatments decrease the degree of crystallization of cellulose, crystallinity index (*CrI*), and this value can be determined by XRD, ^{13}C NMR, and IR [34-37]. Milling methods such as ball-milling [38] are the typical mechanical techniques for disrupting the crystal structure of cellulose because hydrogen bonds in cellulose are cleaved during the treatments [39]. In our experiments, the ball-milling in the ceramic pot with ZrO_2 balls for 96 h decreased the *CrI* from 80% to 10%, calculated from the XRD patterns (Fig. 1). Additionally, we measured the median diameter for the secondary particles of ball-milled cellulose in water, which was also reduced from 67 μm to 42 μm, determined by laser diffraction. SEM images showed that the fibrous shape of cellulose particles turned into smaller spherical morphology by ball-milling (Fig. 2). Rod-milling and planetary ball-milling processes also convert the crystalline cellulose into amorphous one in shorter time (< 1 h) [40,41], whereas the *CrI* does

not decrease by jet-milling [40]. The jet-milling treatment simply reduced secondary particle size from 44 μm to 16 μm. The aqueous counter collision (ACC) method drastically diminished the length of particles from 100 μm to 100 nm and the width from 10 μm to 15 nm [42], and we observed that the crystal structure of cellulose was not decomposed by the ACC method (Fig. 1). In chemical methods, Wang et al. reported that the *CrI* and the degree of polymerization (DP) of cellulose decreased by treating it with phosphoric acid [43]. The parameters depended on the concentration of H_3PO_4 and the temperature and time of treatment. For example, the treatment in 43% H_3PO_4 at 298 K for 1 h decreased the *CrI* from 85 to 79 and the DP from 221 to 209, and the *CrI* and DP of cellulose diminished to 33 and 106 by 85% H_3PO_4 at 323 K for 40 min. Tsao et al. demonstrated that supercritical CO_2 reduced the degree of crystallization to ca. 50% for 1 h [44]. The amorphous cellulose thus prepared is expected to show higher reactivity than crystalline one [45].

Fig. 1

Fig. 2

Although cellulose is almost insoluble in water [46] except for at very high temperatures (> 593 K) [47], solvents of cellulose have been explored to handle it as a soluble substrate and to increase the reactivity [48]. Lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) is well known to dissolve cellulose, where chloride ions cleave hydrogen bonds of cellulose [49,50]. Schweizer's reagent forms a complex with cellulose [51] and dissociates hydrogen bonds to dissolve cellulose. In recent years, ionic liquids (ILs) such as 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) have received a significant attention as a new solvent of cellulose [52], because ILs are chemically and thermally stable and their physicochemical properties are tunable [53]. The dissolution mechanism of cellulose into ILs is almost the same as that into LiCl/DMAc [53]. It was indicated that the depolymerization of cellulose occurred during the dissolution in ILs because of the formation of acids from ILs such as [BMIM]Cl,

1-ethyl-3-methylimidazolium chloride ([EMIM]Cl), and 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) [54,55].

3. Catalytic transformation of cellulose to renewable chemicals

3.1. Hydrolytic hydrogenation of cellulose to sorbitol

Glucose is a versatile precursor to valuable chemicals as described above (Scheme 1), but the hydrolysis of cellulose to glucose has remained a challenge. This reaction requires harsh conditions, whereas glucose is easily decomposed owing to the aldehyde group in its linear structure. In contrast, sorbitol is one of the twelve building block chemicals produced from biomass resources [14], and it is thermally more stable than glucose and a good precursor to various chemicals (Scheme 2). Thus, the hydrolytic hydrogenation of cellulose to sorbitol (Scheme 3) has been studied using catalysts, and typical works are summarized in Table 1.

Scheme 3

Table 1

In the 1950s, Balandin et al. showed that Ru/C combined with mineral acids gave sorbitol from cellulose under 7 MPa of hydrogen [56,57] (Table 1, entry 1). In this process, mineral acids hydrolyze cellulose to glucose, and then glucose is hydrogenated to sorbitol by Ru/C. Later, Jacobs used Pt/USY for the hydrolytic hydrogenation of starch [58], which was a polymer of α-glucose soluble in hot water with significantly higher reactivity than cellulose [59]. Hence, the degradation of solid cellulose by solid catalysts has remained an issue for a long period. In 2006, we reported the first hydrolytic hydrogenation of cellulose using only solid catalysts [60], in which Pt/γ-Al_2O_3 produced sorbitol and mannitol in 25% and 6% yields, respectively (Table 1, entry 2). This reaction contains two steps: hydrolysis of cellulose to glucose via cellooligosaccharides and hydrogenation of glucose to sorbitol. Interestingly, the former reaction is also accelerated by the solid catalyst. The hydrolysis step was proposed

to be accelerated by proton produced via heterolysis of hydrogen over Pt [60-62]. The residual Cl on the catalysts derived from catalyst precursors such as H_2PtCl_6 also affected the catalytic performance. The rates of the hydrolysis of cellulose and side reactions were enhanced by HCl or Al^{3+} species [63,64]. This problem can be avoided by using Cl-free precursors and carbon supports. In contrast, Liu et al. proposed that protons from hot-compressed water promoted the hydrolysis step [65,66]. It seems that the major active species for the hydrolysis alters by catalysts and reaction conditions employed.

Later, we found that γ-Al_2O_3 support was transformed into boehmite [AlO(OH)] in hot water, and the catalytic activity reduced in repeated reactions [63]. Thus, the development of more active, selective, and durable catalysts has been a target. Carbons such as activated carbon (AC) and carbon nanotubes (CNT) are known as heat- and water-tolerant supports. For this reason, carbon supported metal catalysts have been extensively studied. Liu et al. conducted the hydrolytic hydrogenation of cellulose by Ru/C, which produced 39% yield of hexitols with 86% conversion with good reusability (entry 3) [66]. According to the results of ICP and TEM analyses, neither leaching nor sintering of Ru occurred. Wang et al. reported that the yield of sugar alcohols was improved to 73% by using Ru supported on CNT and H_3PO_4-pretreated cellulose (entry 4) [43]. The Ru/CNT catalyst also yielded sugar alcohols in 40% yield from microcrystalline cellulose (entry 5). We used a carbon black (BP2000, Cabot) as a support, and Pt/BP2000 afforded sugar alcohols in 58-65% yields in reuse experiments (entry 6) [63]. The rate-determining step of the hydrolytic hydrogenation is the hydrolysis of cellulose to glucose [63], and a mixture of Ru/C and heteropoly acid $H_4SiW_{12}O_{40}$ was used to enhance the hydrolysis rate [67]. This strategy gave 85% yield of sugar alcohols from ball-milled cellulose (entry 7) and 36% yield from crystalline cellulose (entry 8). Palkovits et al. showed that similar catalysts gave side reactions such as further transformation of sorbitol with higher concentration of acids for longer reaction time, in which C_2-C_6 polyols such as

erythritol, xylitol, sorbitan, and isosorbide were obtained as by-products [68].

Recently, Ni catalysts have been studied instead of precious metals. Nickel phosphides have both acidic and metallic sites, and they can promote not only the hydrolysis of cellulose but also the hydrogenation of glucose. Microcrystalline cellulose was converted to sorbitol (48% yield) and mannitol (5%) by a Ni_2P catalyst supported on AC (entry 9) [69]. We also reported that $Ni_{12}P_5$/AC produced sorbitol (62%) and mannitol (5%) from ball-milled cellulose (entry 10), and the high catalytic performance was attributed to an amorphous nickel phosphide phase generated during the reaction [70]. Although the nickel phosphide catalysts were active, they were not durable in hot water due to phosphorus leaching and Ni sintering. In contrast, it was reported that Ni species on carbon nanofibers (CNF) was stable for 24 h at 483 K (entries 11,12), and Ni/CNF catalyst kept its activity up to 3 runs [71]. Ni/CNF was prepared by chemical vapor deposition (CVD) of carbon on Ni/γ-Al_2O_3 using methane. The method of catalyst preparation was modified by post-treatment for a better balance of hydrolysis and hydrogenation activities [72]. Ni/CNF was treated in concentrated HNO_3 at 383 K to oxidize CNF and to remove Ni species, and then Ni was again impregnated on the CNF. The preparation scheme was complicated compared to the previous one, but the dispersion of Ni on the oxidized CNF increased thanks to more oxygenated functional groups on the CNF. Ni supported on the oxidized CNF showed higher activity than the original Ni/CNF catalyst and gave sorbitol (64%) and mannitol (7%) with 93% conversion of cellulose (entry 13). Bimetallic catalysts containing Ni were also effective for the hydrolytic hydrogenation of cellulose to hexitols, and Ir-Ni supported on mesoporous carbon (MC) afforded 58% yield of sugar alcohols in 4 repeated reactions (entry 14) [73]. Ir improved the thermal stability and catalytic activity, and MC enhanced the dispersion of metals and the adsorption of substrates onto the catalyst surface. According to a recent report about adsorption of substrates onto MC by Katz et al., the longer the chain length of glucan

becomes, the easier the glucan adsorbs onto the surface of MC [74]. The adsorption occurred by the CH-π interaction between hydrogens on the glucan molecule and aromatic rings of the MC surface.

All the catalytic reactions described above need H_2 pressure higher than 2 MPa. We found that $RuO_2 \cdot 2H_2O$/AC (vide infra) afforded sorbitol (30%) and mannitol (8%) under H_2 as low as 0.8 MPa (entry 15) [75]. It was reported that the hydrolytic hydrogenation of cellulose was promoted under low H_2 pressure (0.7 MPa) using a high Pt loading (24 mol% to cellulose) and a concentrated $H_4SiW_{12}O_{40}$ solution (0.70 M) (entry 16) [76]. Moreover, the hydrolytic transfer-hydrogenation of cellulose to sorbitol (Scheme 4) was also promoted by $RuO_2 \cdot 2H_2O$ catalyst supported on carbon (entries 17,18) [75]. In contrast, Ru/TiO_2, Ru/ZrO_2, Ru/Al_2O_3, and various metals (Rh, Ir, Pd, Pt, and Au) supported on AC were inactive for the hydrolytic transfer-hydrogenation. This reaction proceeds via the production of active hydrogen species from 2-propanol, in which the addition of H_2 gas is not necessary.

Scheme 4

3.2. Hydrolysis of cellulose to glucose

The selective and high-yielding production of glucose from cellulose is more difficult than that of sorbitol as previously described, but recently the use of solid catalysts for this process has been coming up to a promising methodology (Table 2).

Table 2

As mentioned above, cellulose is dissolved in ILs and shows higher reactivity than that in water. Zhao et al. demonstrated that cellulose dissolved in [BMIM]Cl was hydrolyzed by sulfuric acid at 373 K [77]. Schüth and co-workers showed that a sulfonated polystyrene resin (Amberlyst 15DRY) hydrolyzed cellulose in [BMIM]Cl (entry 19) [78]. Later it was found that H^+ species was released from SO_3H by ion-exchange with $[BMIM]^+$ to become a

hydrolysis catalyst [79]. This was the reason for the deactivation of Amberlyst 15DRY catalyst after the reaction in ILs; however, the catalytic activity of the resin was regenerated by washing with H_2SO_4. Furthermore, immobilized ILs and sulfonic groups on char was easily separated from the products (entry 20) [80]. However, ILs are toxic and a decisive advantage is necessary to use ILs as a solvent instead of water.

Although heteropoly acids (HPAs) work as homogeneous catalysts in water, they can be separated by extraction using organic solvents such as 2-propanol and diethylether. In some cases, the acidity of HPAs is higher than that of mineral acids. For example, the Hammet acidity function (H_0) of $H_5BW_{12}O_{40}$ (0.7 M at 298 K, vide infra) is -2.1 lower than those (ca. 0) of H_2SO_4 and HCl (0.7 M) [76]. Hence, HPAs have been expected to be active and reusable catalysts for the hydrolysis. Shimizu et al. showed that the hydrolysis of cellobiose and cellulose in water was promoted by HPAs such as $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $Sn_{0.75}PW_{12}O_{40}$ [81]. The total yield of reducing sugars was ca. 40% by $Sn_{0.75}PW_{12}O_{40}$ at 423 K for 16 h (entry 21). The authors also conducted the screening of counter cations of $PW_{12}O_{40}^{3-}$ for the hydrolysis of cellobiose and found that there was a volcano-type correlation between TOFs for glucose formation and the Lewis acidities. Thus, both Brønsted and Lewis acidities were important for the catalytic activity of HPAs, although the Lewis acidity was not checked in water. Mizuno et al. found that $H_5BW_{12}O_{40}$ showed a good performance for the conversion of crystalline cellulose to give glucose in 77% yield (entry 22) [76], and that various types of HPAs such as $H_3PW_{12}O_{40}$ (glucose yield 8%) and $H_4SiW_{12}O_{40}$ (37%) were less active than $H_5BW_{12}O_{40}$. They remarked that the acidity and the function of decreasing *CrI* were the important factors for the catalytic activity of HPAs. In fact, the order of the H_0 function was $H_3PW_{12}O_{40} < H_4SiW_{12}O_{40} < H_5BW_{12}O_{40}$ in the same order of catalytic activity. The H_0 functions were correlated with the concentration of acids and the number of negative charge of anions. Hence, HPAs containing highly negatively charged anions were preferable.

The anions also dissociated hydrogen-bonding between cellulose molecules to decrease the *CrI*. Furthermore, protons of HPAs also weakened the hydrogen bonds of cellulose, and higher concentration of proton was effective for this purpose. Thus, $H_5BW_{12}O_{40}$ worked as a highly active catalyst for the hydrolysis of cellulose. $H_5BW_{12}O_{40}$ was recovered by the extraction and recycled for 10 times.

Heterogeneous catalysts working under aqueous conditions have also been developed in recent years. Hara et al. applied a sulfonated carbon to the hydrolysis of cellulose in water at 373 K and obtained glucose (4% yield) and water-soluble oligosaccharides (64%) (entry 23) [82-84]. Sulfonic groups on large graphene sheets are usually decomposed in hot-compressed water [85], but they are stabilized by electron-withdrawing groups such as carboxylic acids on graphene with a small size (ca. 1 nm). The sulfonated carbon showed no decline in catalytic activity in reuse runs more than 25 times. The authors proposed that neutral or weakly acidic OH groups such as phenolic groups on carbon adsorbed 1,4-β-glucans by forming hydrogen bonds, and then glycosidic bonds were cleaved by the sulfonic groups [86,87]. Nevertheless, we suppose that some mechanocatalytic process might be involved in this catalytic system.

Onda et al. demonstrated that a sulfonated carbon prepared from commercial activated carbon (AC-SO_3H) gave 41% yield of glucose at 423 K for 24 h (entry 24) [88,89]. After the hydrolysis of cellulose by AC-SO_3H, they added fresh cellulose into the filtrated solution, and then the 2nd reaction was tested without the solid catalyst. However, glucose yield was as low as that in the blank reaction, indicating that the hydrolysis was not enhanced by soluble species derived from the catalyst. Furthermore, AC-SO_3H showed similar catalytic activity in the repeated reactions. Hence, they concluded that AC-SO_3H worked as a durable solid acid catalyst under the reaction conditions. It is noteworthy that they conducted pre-treatment of AC-SO_3H in hot-compressed water at 473 K before the reaction at 423 K to remove weakly bonded sulfonic groups, and remaining sulfonic groups on AC were stable and reusable under

the reaction conditions at 423 K. In our test, only a small amount of sulfate ions [35 μM (1.2% of sulfonic groups in the catalyst), detected by ion chromatography] leached from the pre-treated AC-SO_3H, and the reported performance was reproduced. In contrast, the catalyst was degraded without the pre-treatment at 473 K.

These reports motivated other researchers to develop sulfonic acid catalysts. A silica/carbon nanocomposite and a mesoporous carbon CMK-3, treated by sulfonic acid, yielded glucose in 50% (entry 25) [90] and 75% (entry 26) [91], respectively. Magnetic catalysts with sulfonic groups, e.g. a composite of mesoporous silica SBA-15 and Fe_3O_4 treated by sulfonic acid [92,93] and sulfonated $CoFe_2O_4$-embedded silica [94], were also used for the hydrolysis of cellulose (entries 27-29). They were easily separable by a magnet after the catalytic reactions. Fe_3O_4-SBA-SO_3H catalyst afforded glucose in 26% yield from microcrystalline cellulose at 423 K for 3 h, whereas levulinic acid became a major product (42% yield) by prolonging the reaction time to 12 h [92]. Recently, Pan et al. synthesized a sulfonated chloromethyl polystyrene resin (CP-SO_3H) to expect promoted adsorption of cellulose onto CP-SO_3H by hydrogen bonding via Cl and subsequent hydrolysis of glycosidic bonds by SO_3H [95]. They reported that CP-SO_3H converted microcrystalline cellulose into glucose in 93% yield at 393 K for 10 h (entry 30). Unfortunately, this high yield was not obtained in our tests and the degradation of the catalyst was observed. Hence, we should take care of the possibility of leaching of SO_3H and Cl in using sulfonated or chlorinated materials as catalysts in water at high temperatures. We note that the reactions by these types of catalysts are typically conducted at S/C [substrate/catalyst (wt/wt)] ratios lower than 1. Higher S/C ratios would be favorable to improve the efficiency.

Supported metal catalysts have also been used for the hydrolysis of cellulose. We found that 2 wt% Ru/CMK-3 hydrolyzed cellulose (conversion 56%) to glucose (24% yield, 43% selectivity) in water (entry 31), and the TOF for the production of glucose was 18 h^{-1} per the

number of bulk Ru atoms [96,97]. The yield of glucose was raised up to 31% by increasing the Ru loading to 10 wt%. This catalyst was reusable up to 5 times without loss of the activity or Ru leaching, checked by ICP-AES. The Ru species on CMK-3 was highly dispersed $RuO_2 \cdot 2H_2O$ determined by XAFS and XRD, and the high valent Ru has been proposed to work as a catalyst for hydrolysis.

Intriguingly, mesoporous carbons also catalyzed the hydrolysis of cellulose to glucose even in the absence of strong acidity (entries 32,33) [73,96,97]. Katz et al. reported that even silanols with very weak acidity (pK_a = 7) were able to hydrolyze cellulose by inducing stressful conformations by forming ether bonds between silica and cellulose [98]. They proposed that the proximity of surface silanols was important to hydrolyze the biomass-derived polymer [99]. Silanols captured the polymer by forming ether bonds with hydroxyl groups, which kept neighboring other silanols close to the immobilized polymer. Then, the silanols had the enhanced chances to activate glycosidic bonds.

Recently, mechanocatalytic depolymerization of cellulose without solvents has been reported. Cellulose and kaolinite ($Al_2Si_2O_7 \cdot 2H_2O$) were milled together at 350 rpm for 3 h, and 84% of cellulose was depolymerized into water-soluble products during the milling process [100]. Rinaldi et al. conducted the planetary milling of acid-impregnated cellulose at 350 rpm for 2 h, and cellulose was almost completely hydrolyzed into water-soluble oligosaccharides [101]. After that, these oligomers were converted to glucose by the acid in water at 403 K for 1 h. Although the scalability and energy consumption in milling process might be concerned for the practical use, they estimated that 6 tons of ethanol can be produced from 12 tons of cellulose by the milling in a large vessel (112 m^3) used in cement industry and a fermentation process. Their calculation indicates that this milling process consumes 5160 kWh, which is obviously lower than the energy content in the product (45000 kWh). Although milling-free process is ideal, this method might be applicable to practical

production of chemicals from real biomass.

3.3. Conversion of cellulose to other valuable chemicals

Other valuable chemicals such as methyl glucosides, 5-HMF, gluconic acid, ethylene glycol (EG), and propylene glycol (PG) have also been synthesized from cellulose (Scheme 5).

Scheme 5

Although glucose is unstable in hot-compressed water as noted above, methyl glucosides, which are raw materials for surfactants, detergents, and cosmetics [102,103], are stable even under harsh conditions owing to the protection of a hemiacetal group [104]. For this reason, the methanolysis of cellulose to methyl glucosides has been studied. Saka et al. conducted the conversion of cellulose in supercritical methanol, and methyl glucosides were obtained in ca. 30% yield at 623 K and 43 MPa [104]. They also showed that the substitution reactions also proceeded at reducing terminal glucose residue of cellulose to form methylated oligosaccharides under the reaction conditions. Wang et al. reported that a sulfonated carbon prepared from lignin afforded 62% yield of methyl glucosides with 90% conversion of crystalline cellulose [105]. A bio-char treated by fuming sulfuric acid converted microcrystalline cellulose to methyl glucosides in 92% yield at 548 K, but the activity decreased during recycle tests [106].

The production of 5-HMF from cellulose has been a target in the biorefinery, since 5-HMF is a versatile platform chemical to fuels and plastics [107]. Antal et al. reported the formation of 5-HMF from fructose and sucrose in water at 523 K with and without mineral acids [108]. Zhang et al. demonstrated that $CrCl_2$ catalyzed the conversion of fructose and glucose to 5-HMF in [EMIM]Cl [107]. The production of 5-HMF from glucose includes four steps: isomerization of glucose to fructose and stepwise dehydration of three water molecules

from fructose [109]. The rate-determining step is the first isomerization. In [EMIM]Cl, $[EMIM]^+CrCl_3^-$ was possibly formed, and $CrCl_3^-$ anion enhanced the isomerization by forming hydrogen bonds with hydroxyl groups of glucose to promote hydride transfer. Then, the dehydration of fructose to 5-HMF rapidly occurred in the presence of the catalysts. Notably, they also succeeded in the direct synthesis of 5-HMF from cellulose in 58% yield by using $CuCl_2$-$CrCl_2$ catalyst in [EMIM]Cl [110]. Ionic liquid facilitated the reaction by dissolving cellulose. Similarly, $CrCl_2$-HCl gave 54% yield of 5-HMF from cellulose in a mixture of 10 wt% LiCl/DMAc and [EMIM]Cl, and $CrCl_3$-HCl afforded 5-HMF in 48% yield from corn stover [111].

Conversion of biomass to gluconic acid, which is used in food industry and pharmaceuticals [112], is also a challenge. The selective oxidation of glucose to gluconic acid was catalyzed by various mono- and multimetallic catalysts under basic conditions [113-116]. Au nanoparticles, active for CO oxidation [117,118], promoted the selective oxidation of glucose to gluconic acid [119]. Rossi et al. reported that Au/C gave ca. 6 times higher TOF than Pd-Bi/C and Pt-Pd-Bi/C at pH 9.5 [120]. Furthermore, Au/C catalyzed the selective oxidation even at pH 7, but the reaction was not promoted by Pd-Bi/C and Pt-Pd-Bi/C under the same conditions. They also showed that the Au particles catalyzed the reaction only when the particle size was smaller than 10 nm [121,122]. Wang et al. applied Au/CNT catalyst to the conversion of cellobiose to gluconic acid without bases and obtained gluconic acid in 70% yield at 418 K under O_2 pressure of 1.0 MPa [123]. Similarly, Onda et al. reported that Pt/sulfonated carbon afforded ca. 60% yield of gluconic acid at 393 K under 0.1 MPa of air without pH control [124]. The direct synthesis of gluconic acid from cellulose has been achieved by Au/$Cs_{1.2}H_{1.8}PW_{12}O_{40}$ catalyst, giving ca. 60% yield of gluconic acid at 418 K under 1.0 MPa of O_2 [125]. This reaction consists of two steps: the first is the hydrolysis of cellulose to oligosaccharides and glucose promoted by $Cs_{1.2}H_{1.8}PW_{12}O_{40}$ and the second is the

oxidation of reducing terminal of glucans by the small Au nanoparticles. Although $Au/Cs_{1.2}H_{1.8}PW_{12}O_{40}$ decreased its catalytic performance after the second reaction, a combined catalyst, $H_3PW_{12}O_{40}$ and $Au/Cs_{1.2}H_{1.8}PW_{12}O_{40}$, was reusable at least 6 times.

Zhang et al. demonstrated the one-pot synthesis of EG from cellulose in 61% yield by supported Ni and tungsten carbide (WC) catalyst at 518 K under 6 MPa of H_2 for 30 min [126]. They indicated that Ni promoted the hydrogenation via the activation of H_2, and that W catalyzed the C-C bond cleavage such as retro-aldol reaction [127]. WC activated H_2 without Ni [128], and WC supported on mesoporous carbon produced 73% yield of EG with 100% conversion of cellulose [129]. The WC catalyst was reusable for 3 times.

Liu et al. showed that the synthesis of EG and PG was promoted by Ru/C and WO_3 [130,131]. They used C_6 sugar substrates such as glucose and fructose to clarify the reaction mechanism for the production of EG and PG on Ru/C. The mixture of sorbitol and mannitol was obtained from both of the substrates without WO_3. In the presence of WO_3, glucose and fructose were transformed into EG and PG, respectively, in higher selectivity than sorbitol and mannitol. Mannose produced from cellulose was also converted to EG; however, relatively large amount of mannitol was produced. Hence, the main precursors to EG and PG were glucose and fructose, respectively, and WO_3 catalyzed the cleavage of C-C bonds in the sugar compounds. Moreover, the results of the model reactions using 2-deoxyglucose and 2-deoxyribose suggested that the C-C bond cleavage did not take place via the retro-aldol reaction on WO_3 catalyst, and that the hydroxyl group at C2 position of sugar molecules played an important role in the reaction. Therefore, the authors proposed that WO_3 catalyst formed a complex with a substrate by interacting with hydroxyl groups to result in the C-C bond cleavage.

In addition, Ni/ZnO and Ni-Cu/ZnO converted cellulose into 1,2-alkanediols such as EG, PG, 1,2-butanediol, and 1,2-hexanediol with good conversion ($\geq$ 89%) in the reuse

experiments more than 4 times [132,133]. The catalytic performance of Ni-Cu/ZnO depended on the ratio of Ni and Cu, and the conversion of cellulose increased with increasing the Ni/Cu ratio. On the contrary, the selectivity of 1,2-alkanediols decreased by increasing Ni content because Ni species promote the cleavage of C-C bonds. When the ratio was 2/3, the selectivity improved to 73% with 74% conversion.

4. Conclusions

The transformation of biomass resources to renewable and valuable chemicals has progressed by using heterogeneous catalysis. The hydrolytic hydrogenation of cellulose to sorbitol and the hydrolysis of cellulose to glucose are the essential upstream steps to synthesize useful chemicals from biomass, and various catalysts have been developed to overcome this challenge. Furthermore, the direct synthesis of methyl glucosides, 5-HMF, gluconic acid, EG, and PG has been achieved in recent years. Although these processes still need to be improved for the practical use, we believe that the further progress will realize the biorefinery by heterogeneous catalysis to ensure the sustainable development.

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References

[1] Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982-985.
[2] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. 46 (2007) 7164-7183.
[3] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411-2502.
[4] M.E. Himmel, S.-Y. Ding, D.K. Johnson, W.S. Adney, M.R. Nimlos, J.W. Brady, T.D. Foust, Science 315 (2007) 804-807.

[5] P. Gallezot, ChemSusChem 1 (2008) 734-737.
[6] A. Fukuoka, P.L. Dhepe, Chem. Rec. 9 (2009) 224-235.
[7] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, Science 337 (2012) 695-699.
[8] J. Goldemberg, Science 315 (2007) 808-810.
[9] W.H. Zartman, H. Adkins, J. Am. Chem. Soc. 55 (1933) 4559-4563.
[10] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Catal. Commun. 9 (2008) 2244-2249.
[11] H. Yan, Y. Yang, D. Tong, X. Xiang, C. Hu, Catal. Commun. 10 (2009) 1558-1563.
[12] J.C. Serrano-Ruiz, R.M. West, J.A. Dumesic, Annu. Rev. Chem. Biomol. Eng. 1 (2010) 79-100.
[13] K. Matsumoto, H. Kobayashi, K. Ikeda, T. Komanoya, A. Fukuoka, S. Taguchi, Bioresour. Technol. 102 (2011) 3564-3567.
[14] T. Werpy, G. Petersen, A. Aden, J. Bozell, J. Holladay, J. White, A. Manheim, D. Elliot, L. Lasure, S. Jones, M. Gerber, K. Ibsen, L. Lumberg, S. Kelley (US Department of Energy), Top Value Added Chemicals From Biomass Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas (2004) http://eereweb.ee.doe.gov/biomass/pdfs/35523.pdf.
[15] O. Bobleter, Prog. Polym. Sci. 19 (1994) 797-841.
[16] Y.-H.P. Zhang, S.-Y. Ding, J.R. Mielenz, J.-B. Cui, R.T. Elander, M. Laser, M.E. Himmel, J.R. McMillan, L.R. Lynd, Biotechnol. Bioeng. 97 (2007) 214-223.
[17] P.L. Dhepe, A. Fukuoka, Catal. Surv. Asia 11 (2007) 186-191.
[18] P. Zugenmaier, in: T.E. Timell, R. Wimmer (Eds.), Crystalline Cellulose and Derivatives: Characterization and Structures. Springer Series in Wood Science, Springer-Verlag, Berlin, Heidelberg, 2007, pp. 101-174.
[19] B. Kamm, Angew. Chem. Int. Ed. 46 (2007) 5056-5058.
[20] R. Rinaldi, F. Schüth, ChemSusChem 2 (2009) 1096-1107.
[21] P. Gallezot, Top. Catal. 53 (2010) 1209-1213.
[22] H. Kobayashi, T. Komanoya, S.K. Guha, K. Hara, A. Fukuoka, Appl. Catal. A: Gen. 409-410 (2011) 13-20.
[23] H. Kobayashi, H. Ohta, A. Fukuoka, Catal. Sci. Technol. 2 (2012) 869-883.
[24] J.F. Saeman, Ind. Eng. Chem. 37 (1945) 43-52.
[25] E.T. Reese, Appl. Microbiol. 4 (1956) 39-45.
[26] L.P. Ramos, C. Breuil, J.N. Saddler, Enzyme Microb. Technol. 15 (1993) 19-25.

[27] M. Sasaki, B. Kabyemela, R. Malaluan, S. Hirose, N. Takeda, T. Adschri, K. Arai, J. Supercrit. Fluids 13 (1998) 261-268.
[28] M. Sasaki, M. Furukawa, K. Minami, T. Adschiri, K. Arai, Ind. Eng. Chem. Res. 41 (2002) 6642-6649.
[29] M.D. Serio, R. Tesser, L. Pengmei, E. Santacesaria, Energy Fuels 22 (2008) 207-217.
[30] A. Takagaki, C. Tagusagawa, K. Domen, Chem. Commun. (2008) 5363-5365.
[31] M.J. Climent, A. Corma, S. Iborra, Chem. Rev. 111 (2011) 1072-1133.
[32] S. Van de Vyver, J. Geboers, P.A. Jacobs, B.F. Sels, ChemCatChem 3 (2011) 82-94.
[33] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, Energy Fuels 20 (2006) 807-811.
[34] L. Segal, J.J. Creely, A.E. Martin Jr., C.M. Conrad, Text. Res. J. 29 (1959) 786-794.
[35] Y.-H.P. Zhang, L.R. Lynd, Biotechnol. Bioeng. 88 (2004) 797-824.
[36] H. Wikberg, S.L. Maunu, Carbohydr. Polym. 58 (2004) 461-466.
[37] M.L. Nelson, R.T. O'Connor, J. Appl. Polym. Sci. 8 (1964) 1325-1341.
[38] L.T. Fan, Y.-H. Lee, D.R. Beardmore, Biotechnol. Bioeng. 23 (1981) 419-424.
[39] K. Mazeau, L. Heux, J. Phys. Chem. B 107 (2003) 2394-2403.
[40] T. Suzuki, H. Nakagami, Eur. J. Pharm. Biopharm. 47 (1999) 225-230.
[41] R. Avolio, I. Bonadies, D. Capitani, M.E. Errico, G. Gentile, M. Avella, Carbohydr. Polym. 87 (2012) 265-273.
[42] T. Kondo, M. Morita, K. Hayakawa, Y. Onda, US Patent No. 7,357,339 B2 (2008).
[43] W. Deng, X. Tan, W. Fang, Q. Zhang, Y. Wang, Catal. Lett. 133 (2009) 167-174.
[44] Y. Zhen, H.-M. Lin, G.T. Tsao, Biotechnol. Prog. 14 (1998) 890-896.
[45] V.S. Chang, M.T. Holtzapple, Appl. Biochem. Biotechnol. 84-86 (2000) 5-37.
[46] J. Strachan, Nature 141 (1938) 332-333.
[47] Z. Fang, J.A. Koziński, Proc. Combust. Inst. 28 (2000) 2717-2725.
[48] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, Carbohydr. Polym. 67 (2007) 97-103.
[49] C.L. McCormick, P.A. Callais, B.H. Hutchinson Jr., Macromolecules 18 (1985) 2394-2401.
[50] T. Röder, B. Morgenstern, N. Schelosky, O. Glatter, Polymer 42 (2001) 6765-6773.
[51] W. Burchard, N. Habermann, P. Klüfers, B. Seger, U. Wilhelm, Angew. Chem. Int. Ed. 33 (1994) 884-887.

[52] R.P. Swatloski, S.K. Spear, J.D. Holbrey, R.D. Rogers, J. Am. Chem. Soc. 124 (2002) 4974-4975.
[53] J.F. Brennecke, E.J. Maginn, AIChE J. 47 (2001) 2384-2389.
[54] T. Heinze, K. Schwikal, S. Barthel, Macromol. Biosci. 5 (2005) 520-525.
[55] O.M. Gazit, A. Katz, ChemSusChem 5 (2012) 1542-1548.
[56] A.A. Balandin, N.A. Vasyunina, G.S. Barysheva, S.V. Chepigo, Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.) 6 (1957) 403.
[57] A.A. Balandin, N.A. Vasyunina, S.V. Chepigo, G.S. Barysheva, Dokl. Akad. Nauk SSSR 128 (1959) 941-944.
[58] P. Jacobs, H. Hinnekens, EP Patent 0 329 923 (1989).
[59] S. Deguchi, K. Tsujii, K. Horikoshi, Chem. Commun. (2006) 3293-3295.
[60] A. Fukuoka, P.L. Dhepe, Angew. Chem. Int. Ed. 45 (2006) 5161-5163.
[61] V. Jollet, F. Chambon, F. Rataboul, A. Cabiac, C. Pinel, E. Guillon, N. Essayem, Green Chem. 11 (2009) 2052-2060.
[62] V. Jollet, F. Chambon, F. Rataboul, A. Cabiac, C. Pinel, E. Guillon, N. Essayem, Top. Catal. 53 (2010) 1254-1257.
[63] H. Kobayashi, Y. Ito, T. Komanoya, Y. Hosaka, P.L. Dhepe, K. Kasai, K. Hara, A. Fukuoka, Green Chem. 13 (2011) 326-333.
[64] R.M. Ravenelle, F.Z. Diallo, J.C. Crittenden, C. Sievers, ChemCatChem 4 (2012) 492-494.
[65] N. Yan, C. Zhao, C. Luo, P.J. Dyson, H. Liu, Y. Kou, J. Am. Chem. Soc. 128 (2006) 8714-8715.
[66] C. Luo, S. Wang, H. Liu, Angew. Chem. Int. Ed. 46 (2007) 7636-7639.
[67] J. Geboers, S. Van de Vyver, K. Carpentier, K. de Blochouse, P. Jacobs, B.F. Sels, Chem. Commun. 46 (2010) 3577-3579.
[68] R. Palkovits, K. Tajvidi, A.M. Ruppert, J. Procelewska, Chem. Commun. 47 (2011) 576-578.
[69] L.-N. Ding, A.-Q. Wang, M.-Y. Zheng, T. Zhang, ChemSusChem 3 (2010) 818-821.
[70] P. Yang, H. Kobayashi, K. Hara, A. Fukuoka, ChemSusChem 5 (2012) 920-926.
[71] S. Van de Vyver, J. Geboers, M. Dusselier, H. Schepers, T. Vosch, L. Zhang, G. Van Tendeloo, P.A. Jacobs, B.F. Sels, ChemSusChem 3 (2010) 698-701.
[72] S. Van de Vyver, J. Geboers, W. Schutyser, M. Dusselier, P. Eloy, E. Domez, J.W. Seo, C.M. Courtin, E.M. Gaigneaux, P.A. Jacobs, B.F. Sels, ChemSusChem 5 (2012) 1549-1558.

[73] J. Pang, A. Wang, M. Zheng, Y. Zhang, Y. Huang, X. Chen, T. Zhang, Green Chem. 14 (2012) 614-617.
[74] P.-W. Chung, A. Charmot, O.M. Gazit, A. Katz, Langmuir 28 (2012) 15222-15232.
[75] H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, Chem. Commun. 47 (2011) 2366-2368.
[76] Y. Ogasawara, S. Itagaki, K. Yamaguchi, N. Mizuno, ChemSusChem 4 (2011) 519-525.
[77] C. Li, Z.K. Zhao, Adv. Synth. Catal. 349 (2007) 1847-1850.
[78] R. Rinaldi, R. Palkovits, F. Schüth, Angew. Chem. Int. Ed. 47 (2008) 8047-8050.
[79] R. Rinaldi, N. Meine, J. vom Stein, R. Palkovits, F. Schüth, ChemSusChem 3 (2010) 266-276.
[80] C. Zhang, Z. Fu, Y. Liu, B. Dai, Y. Zou, X. Gong, Y. Wang, X. Deng, H. Wu, Q. Xu, R.K. Steven, D. Yin, Green Chem. 14 (2012) 1928-1934.
[81] K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itaya, A. Satsuma, Green Chem. 11 (2009) 1627-1632.
[82] S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, J. Am. Chem. Soc. 130 (2008) 12787-12793.
[83] D. Yamaguchi, M. Kitano, S. Suganuma, K. Nakajima, H. Kato, M. Hara, J. Phys. Chem. C 113 (2009) 3181-3188.
[84] K. Fukuhara, K. Nakajima, M. Kitano, H. Kato, S. Hayashi, M. Hara, ChemSusChem 4 (2011) 778-784.
[85] X. Mo, D.E. López, K. Suwannakarn, Y. Liu, E. Lotero, J.G. Goodwin Jr., C. Lu, J. Catal. 254 (2008) 332-338.
[86] M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, Langmuir 25 (2009) 5068-5075.
[87] K. Nakajima, M. Hara, ACS Catal. 2 (2012) 1296-1304.
[88] A. Onda, T. Ochi, K. Yanagisawa, Green Chem. 10 (2008) 1033-1037.
[89] A. Onda, T. Ochi, K. Yanagisawa, Top. Catal. 52 (2009) 801-807.
[90] S. Van de Vyver, L. Peng, J. Geboers, H. Schepers, F. de Clippel, C.J. Gommes, B. Goderis, P.A. Jabobs, B.F. Sels, Green Chem. 12 (2010) 1560-1563.
[91] J. Pang, A. Wang, M. Zheng, T. Zhang, Chem. Commun. 46 (2010) 6935-6937.
[92] D.-M. Lai, L. Deng, J. Li, B. Liao, Q.-X. Guo, Y. Fu, ChemSusChem 4 (2011) 55-58.
[93] D.-M. Lai, L. Deng, Q.-X. Guo, Y. Fu, Energy Environ. Sci. 4 (2011) 3552-3557.
[94] A. Takagaki, M. Nishimura, S. Nishimura, K. Ebitani, Chem. Lett. 40 (2011) 1195-1197.

[95] L. Shuai, X. Pan, Energy Environ. Sci. 5 (2012) 6889-6894.
[96] H. Kobayashi, T. Komanoya, K. Hara, A. Fukuoka, ChemSusChem 3 (2010) 440-443.
[97] T. Komanoya, H. Kobayashi, K. Hara, W.-J. Chun, A. Fukuoka, Appl. Catal. A: Gen. 407 (2011) 188-194.
[98] O.M. Gazit, A. Charmot, A. Katz, Chem. Commun. 47 (2011) 376-378.
[99] O.M. Gazit, A. Katz, Langmuir 28 (2012) 431-437.
[100] S.M. Hick, C. Griebel, D.T. Restrepo, J.H. Truitt, E.J. Buker, C. Bylda, R.G. Blair, Green Chem. 12 (2010) 468-474.
[101] N. Meine, R. Rinaldi, F. Schüth, ChemSusChem 5 (2012) 1449-1454.
[102] M.A. Grolitzer, US Patent No. 4,528,106 (1985).
[103] L.N. Mutua, C.C. Akoh, J. Am. Oil. Chem. Soc. 70 (1993) 43-46.
[104] Y. Ishikawa, S. Saka, Cellulose 8 (2001) 189-195.
[105] W. Deng, M. Liu, Q. Zhang, X. Tan, Y. Wang, Chem. Commun. 46 (2010) 2668-2670.
[106] S. Dora, T. Bhaskar, R. Singh, D.V. Naik, D.K. Adhikari, Bioresour. Technol. 120 (2012) 318-321.
[107] H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316 (2007) 1597-1600.
[108] M.J. Antal Jr., W.S.L. Mok, G.N. Richards, Carbohydr. Res. 199 (1990) 91-109.
[109] G.R. Akien, L. Qi, I.T. Horváth, Chem. Commun. 48 (2012) 5850-5852.
[110] Y. Su, H.M. Brown, X. Huang, X.-D. Zhou, J.E. Amonette, Z.C. Zhang, Appl. Catal. A: Gen. 361 (2009) 117-122.
[111] J.B. Binder, R.T. Raines, J. Am. Chem. Soc. 131 (2009) 1979-1985.
[112] S. Ramachandran, P. Fontanille, A. Pandey, C. Larroche, Food Technol. Biotechnol. 44 (2006) 185-195.
[113] K. Deller, H. Krause, E. Peldszus, B. Despeyroux, US Patent No. 5,132,452 (1992).
[114] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes, G. Fleche, J. Catal. 152 (1995) 116-121.
[115] M. Wenkin, R. Touillaux, P. Ruiz, B. Delmon, M. Devillers, Appl. Catal. A: Gen. 148 (1996) 181-199.
[116] A. Onda, T. Ochi, K. Kajiyoshi, K. Yanagisawa, Appl. Catal. A: Gen. 343 (2008) 49-54.
[117] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. 16 (1987) 405-408.
[118] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301-309.
[119] Y. Önal, S. Schimpf, P. Claus, J. Catal. 223 (2004) 122-133.
[120] S. Biella, L. Prati, M. Rossi, J. Catal. 206 (2002) 242-247.

[121] M. Comotti, C.D. Pina, R. Matarrese, M. Rossi, Angew. Chem. Int. Ed. 43 (2004) 5812-5815.
[122] T. Ishida, N. Kinoshita, H. Okatsu, T. Akita, T. Takei, M. Haruta, Angew. Chem. Int. Ed. 120 (2008) 9405-9408.
[123] X. Tan, W. Deng, M. Liu, Q. Zhang, Y. Wang, Chem. Commun. (2009) 7179-7181.
[124] A. Onda, T. Ochi, K. Yanagisawa, Catal. Commun. 12 (2011) 421-425.
[125] D. An, A. Ye, W. Deng, Q. Zhang, Y. Wang, Chem. Eur. J. 18 (2012) 2938-2947.
[126] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Angew. Chem. Int. Ed. 47 (2008) 8510-8513.
[127] C. Li, M. Zheng, A. Wang, T. Zhang, Energy Environ. Sci. 5 (2012) 6383-6390.
[128] H. Böhm, F.A. Pohl, Wiss. Ber. AEG-Telefunken 41 (1968) 46-50.
[129] Y. Zhang, A. Wang, T. Zhang, Chem. Commun. 46 (2010) 862-864.
[130] T.Y. Deng, J.Y. Sun, H. Liu, Sci. China Chem. 53 (2010) 1476-1480.
[131] Y. Liu, C. Luo, H. Liu, Angew. Chem. Int. Ed. 51 (2012) 3249-3253.
[132] X. Wang, L. Meng, F. Wu, Y. Jiang, L. Wang, X. Mu, Green Chem. 14 (2012) 758-765.
[133] X. Wang, F. Wu, S. Yao, Y. Jiang, J. Guan, X. Mu, Chem. Lett. 41 (2012) 476-478.

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Table 1. Conversion of cellulose to sugar alcohols.

Table 2. Hydrolysis of cellulose to glucose.

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Scheme 1. Derived chemicals from glucose.

Scheme 2. Derived chemicals from sorbitol.

Scheme 3. Hydrolytic hydrogenation of cellulose to sorbitol via glucose.

Scheme 4. Hydrolytic transfer-hydrogenation of cellulose to sorbitol with 2-propanol.

Scheme 5. Conversion of cellulose to valuable chemicals.

List of Figures

Fig. 1. XRD patterns of celluloses.

Fig. 2. SEM images of celluloses: (a) microcrystalline cellulose; (b) ball-milled cellulose.

Table 1.

Conversion of cellulose to sugar alcohols.

Entry	Catalyst	Pretreatment of cellulose	*T* /K	Time /h	*P*(H_2) /MPa	Conv. /%	Yield /%			Ref
							Sor[a]	Man[b]	Total[c]	
1	H_2SO_4, Ru/C	Sulfite	433	2	7	nd[g]	nd[g]	nd[g]	82[h]	56
2	2.5 wt% Pt/γ-Al_2O_3	Microcrystalline	463	24	5.0	nd[g]	25	6	31	60
3	4.0 wt% Ru/C	Microcrystalline	518	0.5	6.0	86	30	10	39	66
4	1.0 wt% Ru/CNT	H_3PO_4	458	24	5.0	nd[g]	69	4	73	43
5	1.0 wt% Ru/CNT	Microcrystalline	458	24	5.0	nd[g]	36	4	40	43
6	2.0 wt% Pt/BP2000	Ball-milled	463	24	5.0	82	49	9	58	63
7	5.0 wt% Ru/C, $H_4SiW_{12}O_{40}$	Ball-milled	463	1	9.5	100	nd[g]	nd[g]	85	67
8	5.0 wt% Ru/C, $H_4SiW_{12}O_{40}$	Microcrystalline	463	1	9.5	77	nd[g]	nd[g]	36	67
9	16 wt% Ni_2P/AC	Microcrystalline	498	1.5	6.0	100	48	5	53	69
10	$Ni_{12}P_5$/AC[d]	Ball-milled	503	0.7	5.0	92	62	5	67	70
11	3.0 wt% Ni/CNF	Ball-milled	463	24	6.0	92	50	6	57	71
12	3.0 wt% Ni/CNF	Microcrystalline	483	24	6.0	87	30	5	35	71
13	7.5 wt% Ni/oxidized CNF	Ball-milled	463	24	6.0	93	64	7	71	72
14	4.0 wt% Ir-4.0 wt% Ni/MC	Microcrystalline	518	0.5	6.0	100	47	12	58	73
15	2.0 wt% Ru/AC	Ball-milled	463	18	0.8	83	30	8	38	75
16	Pt, $H_4SiW_{12}O_{40}$[e]	Mercerization, ball-milled	333	24	0.7	nd[g]	54	nd[g]	nd[g]	76
17	2.0 wt% Ru/AC	Ball-milled	463	18	0.0[f]	74	34	9	43	75
18	2.0 wt% Ru/CMK-3	Ball-milled	463	18	0.0[f]	81	36	9	45	75

[a] Sorbitol.

[b] Mannitol.

[c] Total yield of sorbitol and mannitol.

[d] Ni and P loadings were 10 wt% and 2.6 wt%, respectively.

[e] Pt amount was 24 mol% to cellulose and the concentration of $H_4SiW_{12}O_{40}$ was 0.70 M.

[f] 2-propanol was used instead of H_2.

[g] No data.

[h] Monoanhydrides of sorbitol.

Table 2.

Hydrolysis of cellulose to glucose.

Entry	Catalyst	Pretreatment of cellulose	S/C[a] (wt/wt)	*T* /K	Time /h	Conv. /%	Yield /%		Ref
							Glc[b]	Olg[c]	
19[d]	Amberlyst 15DRY	Microcrystalline	5.0	373	5	29	0.9	0.6[k]	78
20[e]	C-SO_3H-IL	Microcrystalline	2.0	363	2	nd[i]	33[j]	nd[i]	80
21	$Sn_{0.75}PW_{12}O_{40}$	Ball-milled	0.9	423	2	23	23[j]	nd[i]	81
22	$H_5BW_{12}O_{40}$	Microcrystalline[f]	0.3	333	48	nd[i]	77	5[k]	76
23	C-SO_3H	Microcrystalline	0.083	373	3	nd[i]	4	64	82
24	AC-SO_3H	Ball-milled	0.9	423	24	nd[i]	41	nd[i]	88
25	SiO_2-C-SO_3H	Ball-milled	1.0	423	24	61	50	2	90
26	CMK-3-SO_3H	Ball-milled	0.9	423	24	94	75	nd[i]	91
27	Fe_3O_4-SBA-SO_3H	[BMIM]Cl	0.7	423	3	nd[i]	50	nd[i]	92
28	Fe_3O_4-SBA-SO_3H	Microcrystalline	1.0	423	3	nd[i]	26	nd[i]	92
29	$CoFe_2O_4$/SiO_2-SO_3H	[BMIM]Cl	1.0	423	3	nd[i]	7.0	30[j]	94
30	CP-SO_3H	Microcrystalline	0.2	393	10	nd[i]	93	nd[i]	95
31	2.0 wt% Ru/CMK-3	Ball-milled	6.5	503	0.83[g]	56	24	16	96
32	CMK-3	Ball-milled	6.5	503	0.83[g]	54	16	5	96
33	MC	Ball-milled	3.3	518	0.75[h]	71	41	0.9[k]	73

[a] Ratio of substrate and catalyst based on weight.

[b] Glucose.

[c] Cellooligosaccharides.

[d] The reaction was conducted in [BMIM]Cl.

[e] Microwave (350 W) was used.

[f] Cellulose was immersed in the solution for 1 h before reaction.

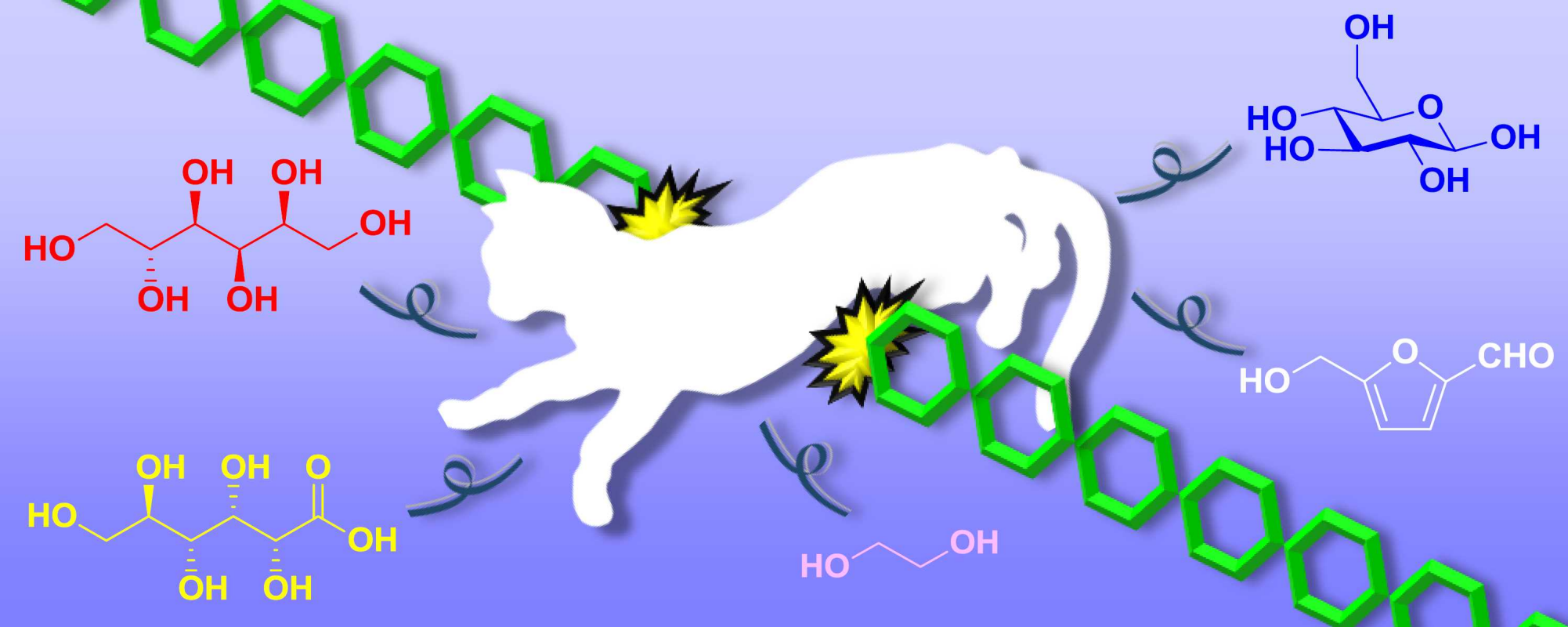
[g] Total time including heating and cooling.

[h] The reaction mixture was heated from room temperature to 518 K in 45 min and rapidly cooled down to room temperature.

[i] No data.

[j] Total yield of reducing sugars.

[k] Cellobiose.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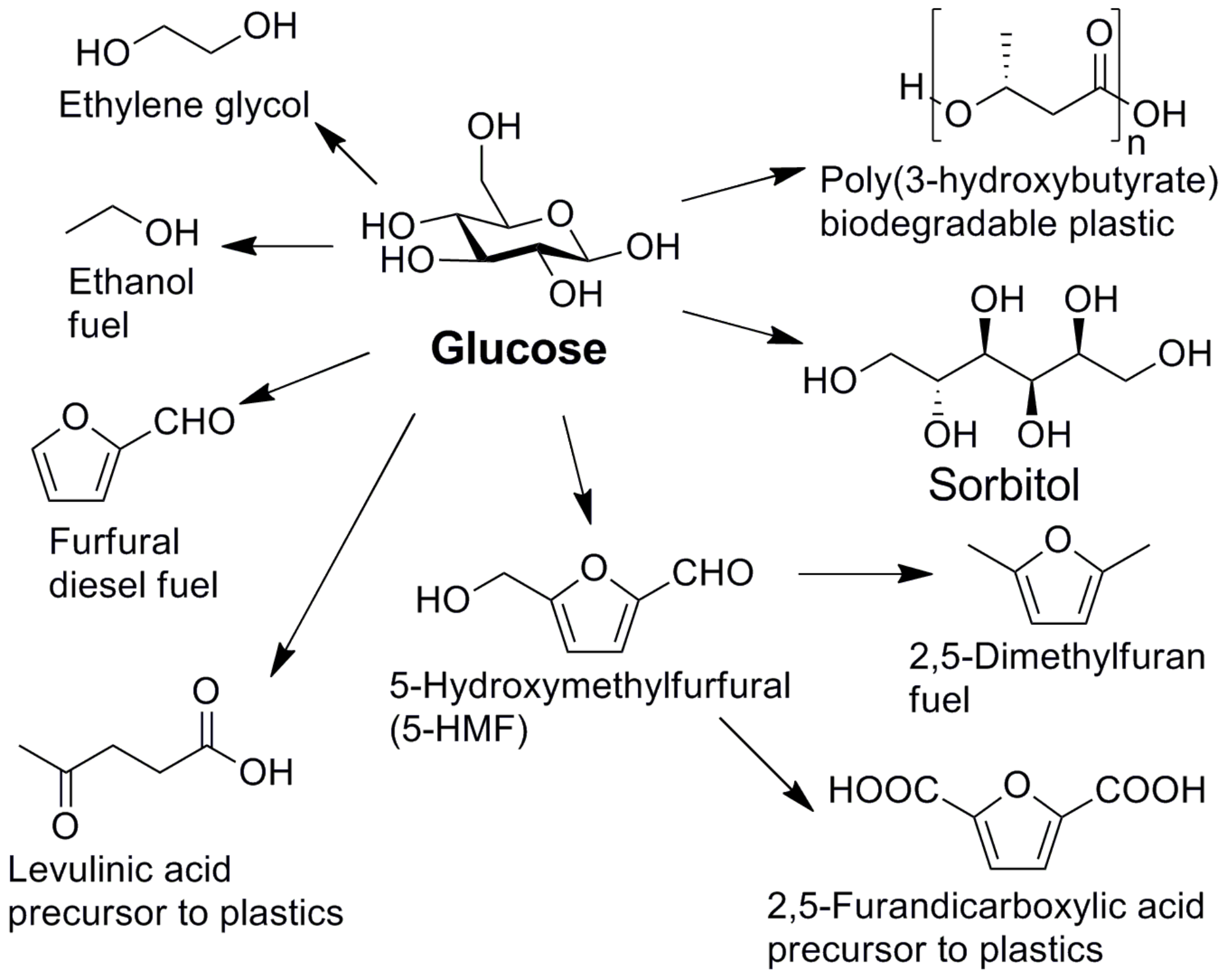
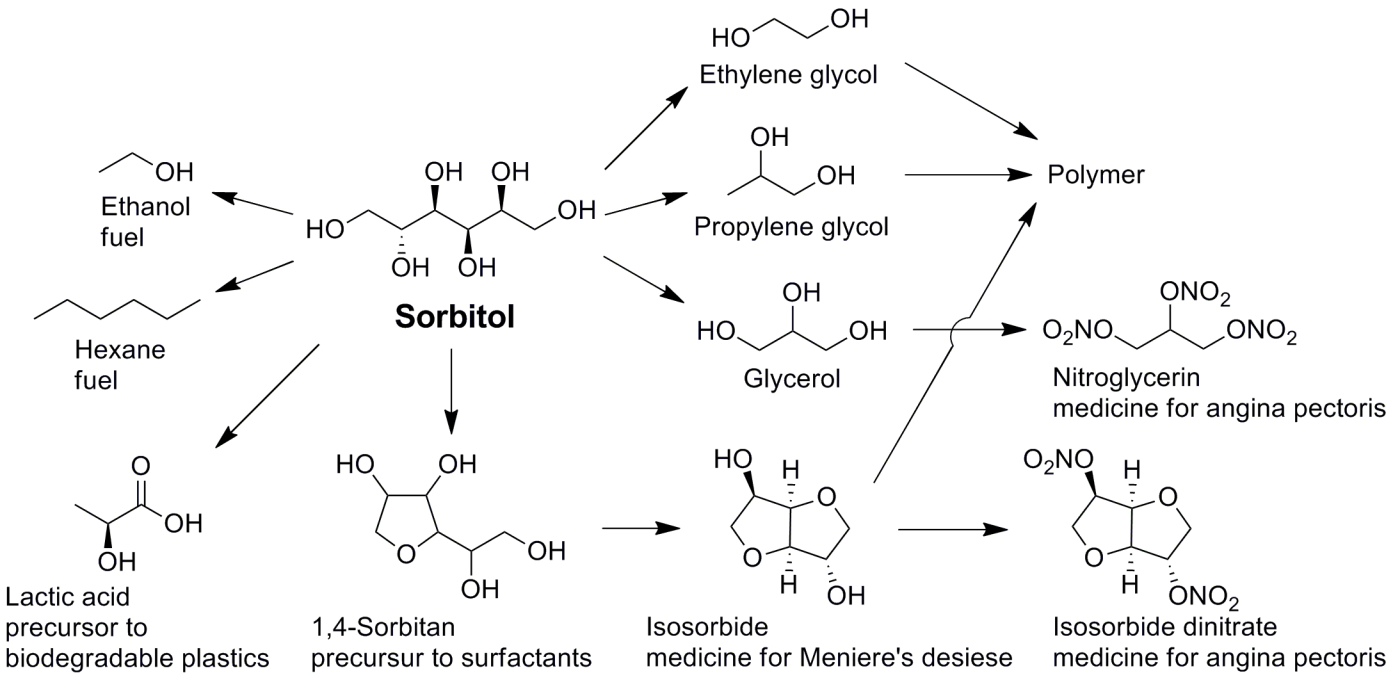
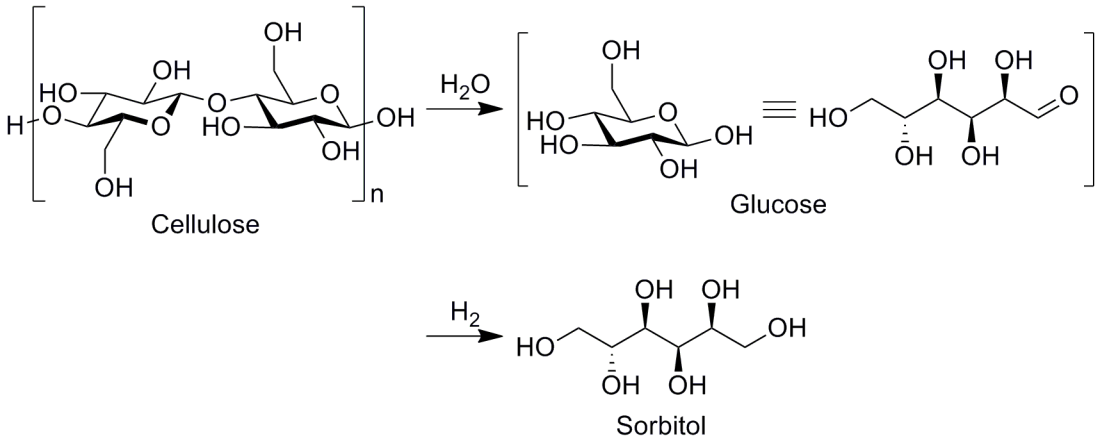
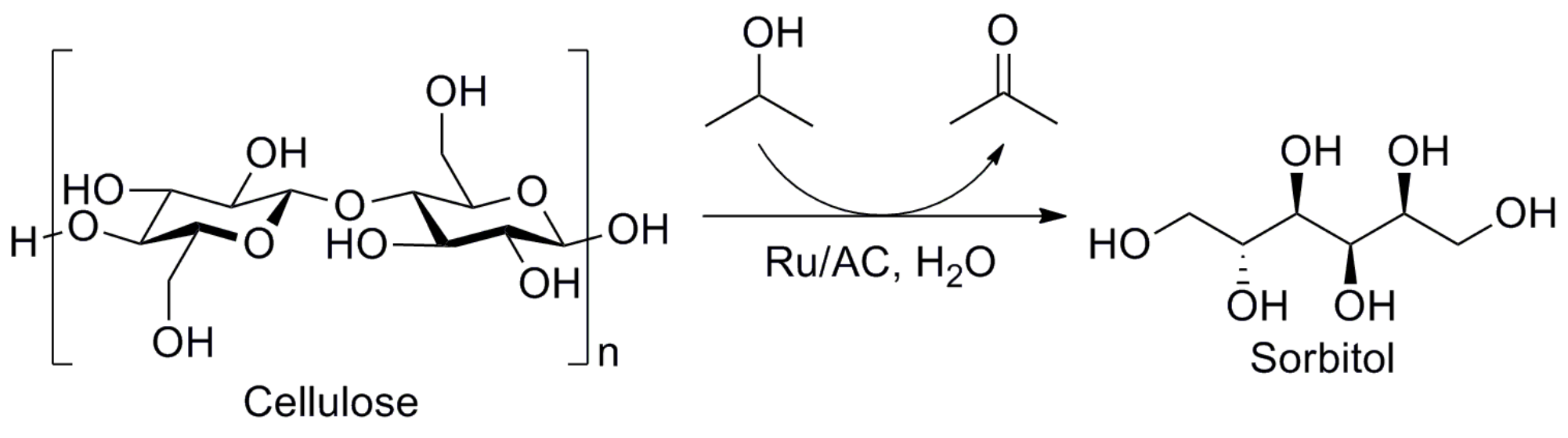

Ethylene glycol
Poly(3-hydroxybutyrate)
biodegradable plastic
Ethanol
fuel
Glucose
Furfural
diesel fuel
Sorbitol
5-Hydroxymethylfurfural
(5-HMF)
2,5-Dimethylfuran
fuel
Levulinic acid
precursor to plastics
2,5-Furandicarboxylic acid
precursor to plastics


Ethylene glycol
Polymer
Ethanol
fuel
Propylene glycol
Hexane
fuel
Sorbitol
Glycerol
Nitroglycerin
medicine for angina pectoris
Lactic acid
precursor to
biodegradable plastics
1,4-Sorbitan
precursur to surfactants
Isosorbide
medicine for Meniere's desiese
Isosorbide dinitrate
medicine for angina pectoris

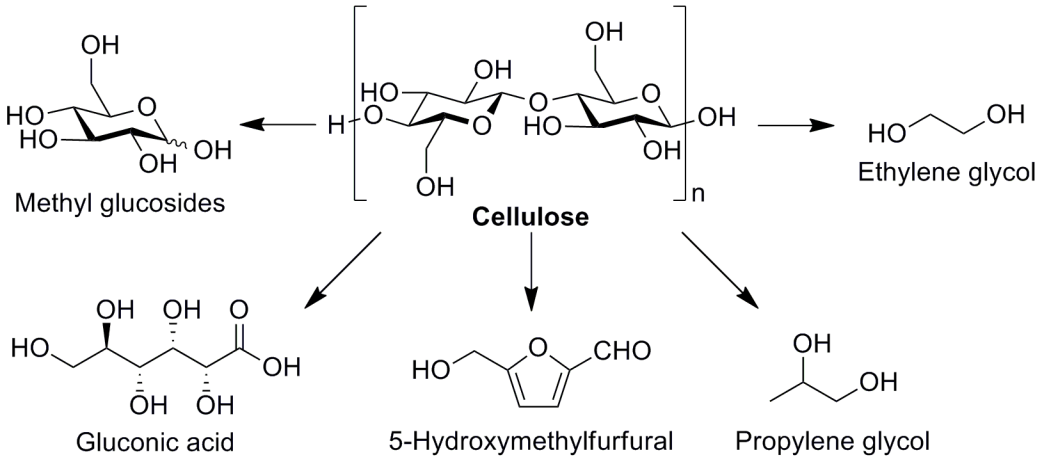


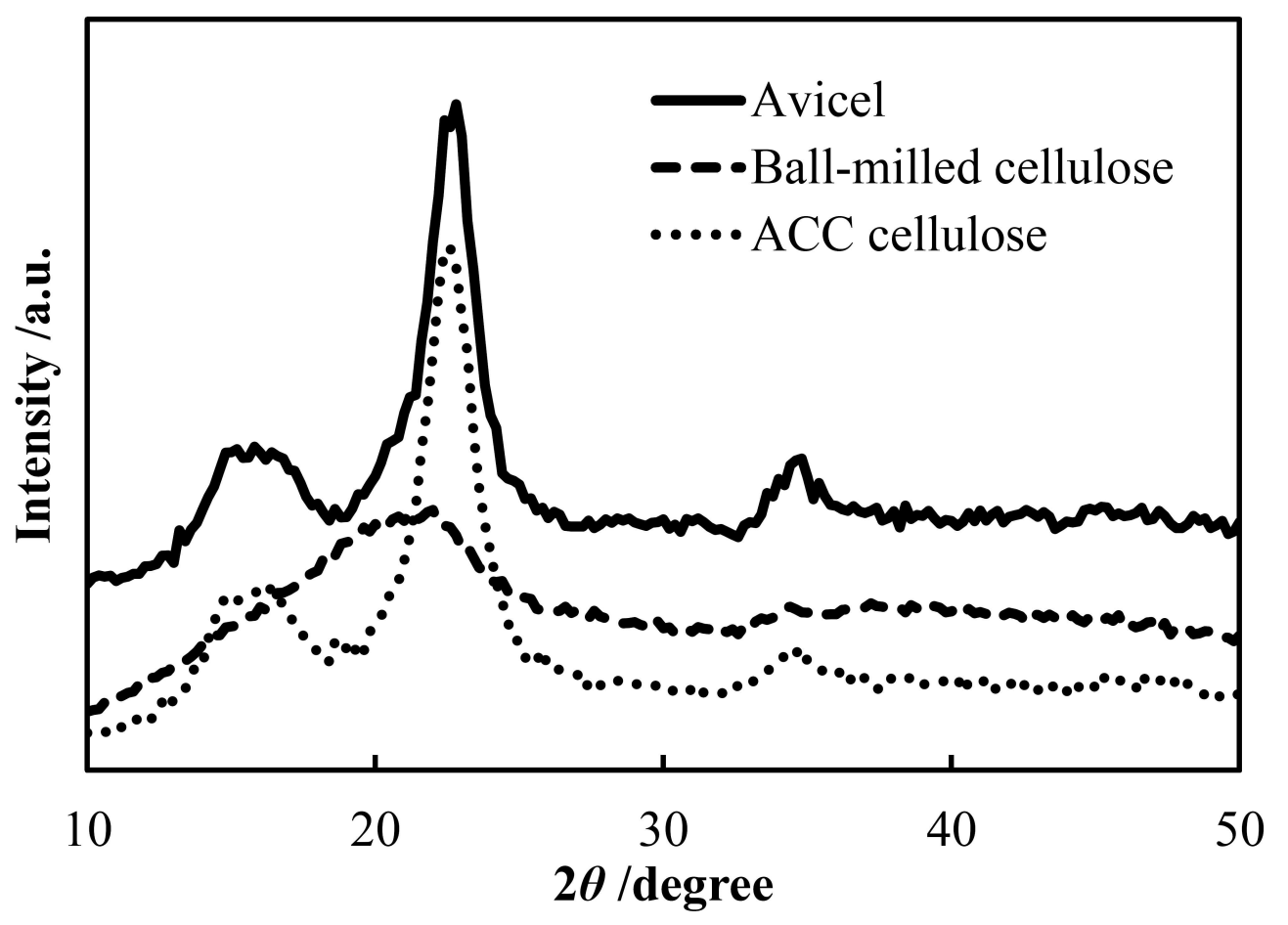
Cellulose
H_2O
Glucose
H_2
Sorbitol

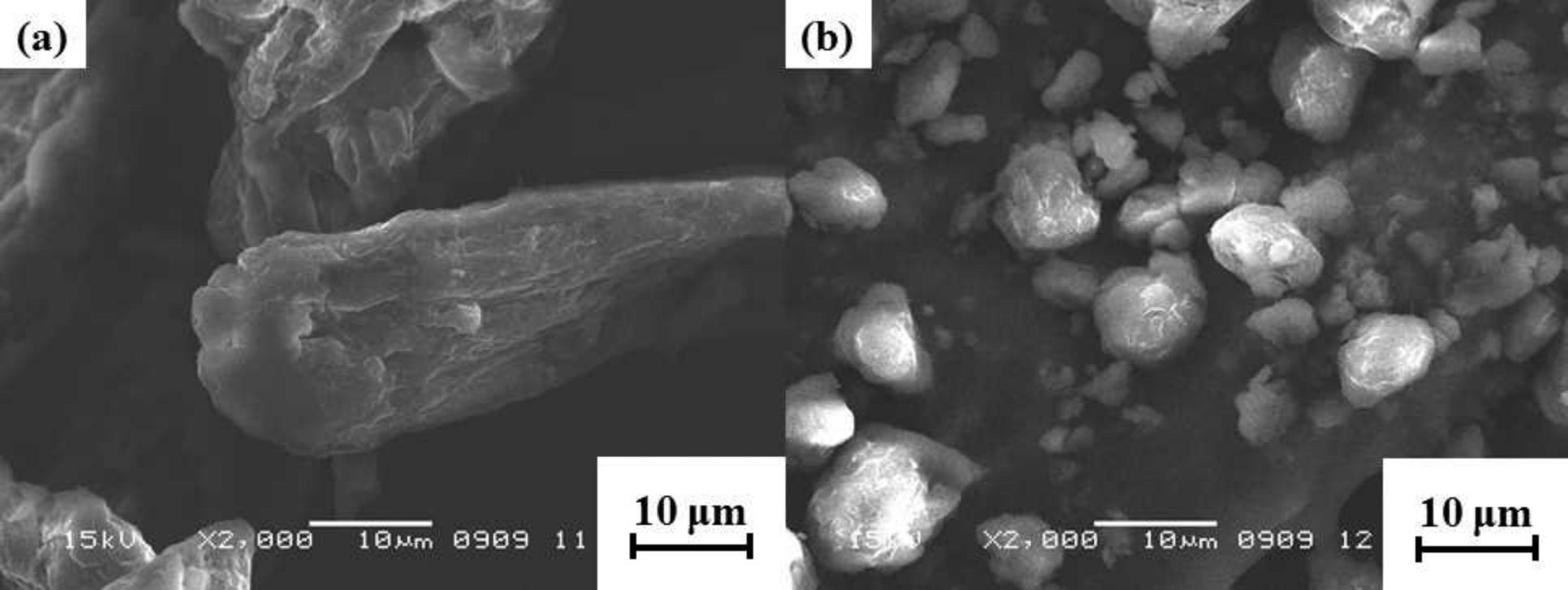


Cellulose

Sorbitol


Methyl glucosides
Cellulose
Ethylene glycol
Gluconic acid
5-Hydroxymethylfurfural
Propylene glycol


Avicel
Ball-milled cellulose
ACC cellulose
Intensity /a.u.
10
20
30
40
50
2θ /degree


(a)
15kV X2,000 10µm 0909 11
10 µm
(b)
15kV X2,000 10µm 0909 12
10 µm