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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.

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

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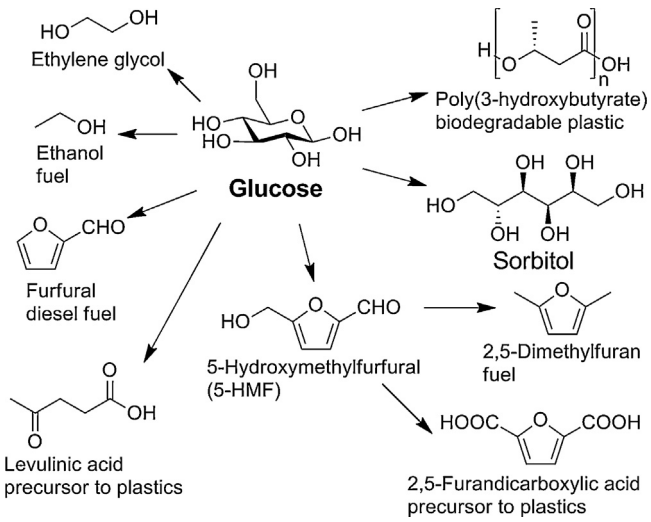


Scheme 1. Derived chemicals from glucose.

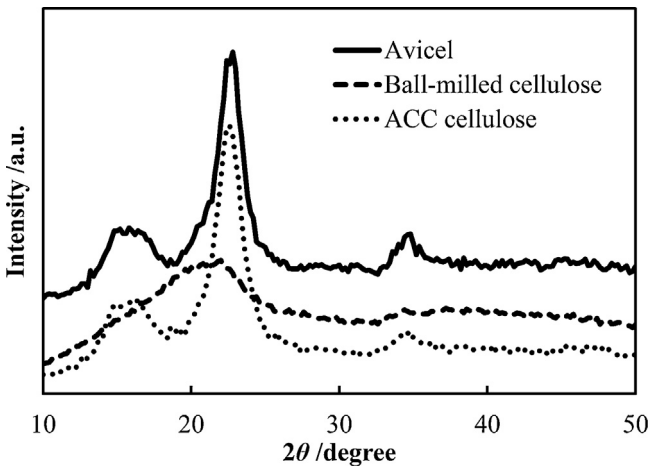
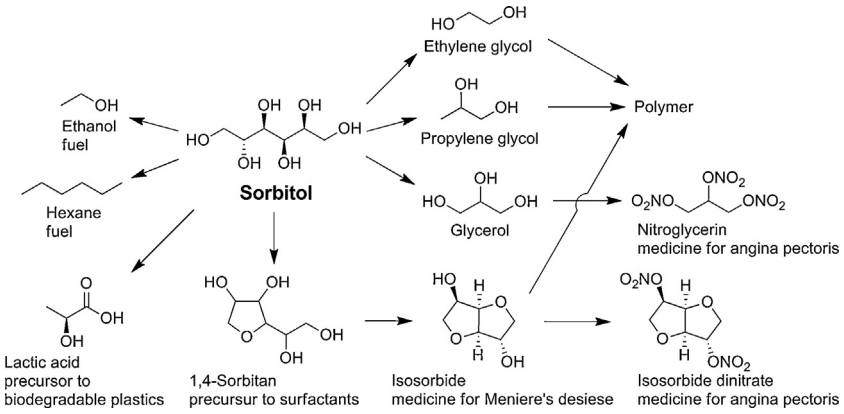


Fig. 1. XRD patterns of celluloses.

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 a 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



Scheme 2. Derived chemicals from sorbitol.

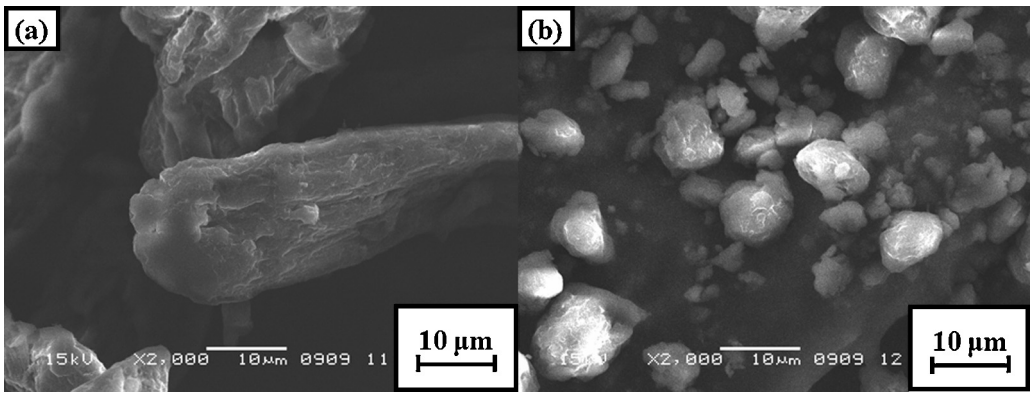


Fig. 2. SEM images of celluloses: (a) microcrystalline cellulose; (b) ball-milled cellulose.