



# Catalytic transformations of cellulose and cellulose-derived carbohydrates into organic acids



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## ABSTRACT

The efficient utilization of lignocellulosic biomass for the production of chemicals and fuels is of high significance from the viewpoint of establishing sustainable society. The selective transformation of cellulose, the main component of lignocellulosic biomass, into platform chemicals, which can be easily converted to various chemicals or fuels in the subsequent step, under mild conditions is a promising route. Organic acids such as levulinic acid, lactic acid, gluconic acid, and formic acid are important platform chemicals, and the conversion of carbohydrates into organic acids has attracted much attention in recent years. The present short review article highlights recent research progress in the development of new routes for the production of organic acids from cellulose or cellulose-derived carbohydrates. In particular, we will demonstrate that the bifunctional catalysts coupling the acid sites for the activation of the glycosidic bonds via hydrolysis and the metal nanoparticles for the oxidation of glucose intermediate show promising performances for the conversion of cellulose into gluconic acid in water in the presence of O<sub>2</sub>. The multifunctional catalysts or catalytic systems combining the abilities of isomerization and dehydration–rehydration or retro-aldol fragmentation can provide levulinic acid or lactic acid from cellulose under anaerobic conditions. The reaction mechanism in each case will also be discussed to gain insights into how the C–C or C–O bonds in cellulose or glucose are activated and cleaved and the roles of catalysts in these steps.

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## 1. Introduction

The limited reservoir of fossil resources, the increasing demands for energy, and the growing emissions of CO<sub>2</sub> have stimulated

research into the production of chemicals and fuels from renewable biomass resources [1–10]. The conversion of biomass cannot only provide renewable energy but also has potential to reduce the emissions of CO<sub>2</sub>, because the CO<sub>2</sub> released from the chemical processes will be captured in the growth of biomass through photosynthesis. Among various biomass resources, lignocellulosic biomass is the most abundant and is non-edible, and thus is a promising candidate for sustainable production of chemicals.

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Generally, Lignocellulosic biomass consists of 40–50% of cellulose, 25–30% of hemicellulose, and 15–30% of lignin. Therefore, the transformation of cellulose, the major component in lignocellulosic biomass, to chemicals is essential for the efficient utilization of biomass and has received much attention in recent years [3,10]. So far, the high-temperature gasification and pyrolysis of cellulose into syngas (CO and H<sub>2</sub>) and bio-oils have been established, but these processes suffer from the problems of high energy consumption and relatively low selectivity [1,2]. It is highly desirable to develop efficient catalytic systems for the direct transformation of cellulose under mild conditions.

Cellulose is a crystalline polymer of D-glucose linked by β-1,4-glycosidic bonds. The repeated glucose units define the degree of polymerization (DP) of cellulose. Depending on the origin and the pretreatment of the raw lignocellulosic biomass, the DP of cellulose may vary from 100 to 15,000. The oligosaccharides with DP from 2 to 6 are soluble in water, and those from 7 to 13 or larger are soluble in hot water at least to some extent. The structure and property of the polysaccharides with DP larger than 30 become similar to those of cellulose [11]. Meanwhile, because of the huge amounts of hydroxyl groups in cellulose, there exist extensive intra- and inter-molecular hydrogen bonding networks, which make the crystalline structure of cellulose robust [11]. Microcrystalline cellulose is insoluble in water and most typical solvents at mild temperatures. All these facts have caused difficulties in the activation of cellulose under mild conditions. Moreover, there are various kinds of C–C and C–O bonds in cellulose macromolecules, and this makes the selective production of a compound by breaking down specific C–C or C–O bonds also difficult.

The hydrolysis of cellulose to glucose is known to be catalyzed by cellulase enzymes under mild conditions [11]. However, the enzymatic hydrolysis is a high-cost process. Mineral acids, such as H<sub>2</sub>SO<sub>4</sub> and HCl, can also catalyze the hydrolysis of cellulose to glucose. During the hydrolysis, the β-1,4-glycosidic bonds in cellulose are selectively activated by the Brønsted acids in aqueous medium. Relatively high yields (30–70%) of glucose can be achieved by using concentrated H<sub>2</sub>SO<sub>4</sub>. However, the problems of corrosion, unrecyclability, and large amounts of mineral acid wastes make the hydrolysis of cellulose by mineral acids not attractive. In this context, many studies have been devoted to developing solid-acid catalysts for the hydrolysis of cellulose to glucose [7,9,12]. Among these catalysts, carbon materials bearing SO<sub>3</sub>H groups [13–18], sulfonated resins [19], and layered metal oxides [20] have attracted particular attention. Excellent performances for the formation of glucose have been obtained by using solid materials possessing SO<sub>3</sub>H groups. However, the stability of these materials may be problematic because of the leaching of SO<sub>3</sub>H groups in water medium at high temperatures used for the conversion of cellulose. On the other hand, the layered metal oxides only exhibited very low yields of glucose [20].

Besides glucose, other important platform chemicals including polyols, alkyl glucosides, and 5-hydroxymethylfurfural (HMF), can also be formed from cellulose [5,7–10,21–24]. Bifunctional or multifunctional catalysts are required for the direct conversion of cellulose to these products. For example, Pt or Ru nanoparticles, capable of catalyzing hydrogenation reactions, loaded on acidic supports such as γ-Al<sub>2</sub>O<sub>3</sub> and acid functional group-bearing carbon nanotubes (CNTs) could catalyze the formation of hexitols (e.g., sorbitol) from cellulose via a hydrolysis–hydrogenation route [25,26]. The combination of reversibly generated H<sub>3</sub>O<sup>+</sup> in hot water (>473 K) with an activated carbon (AC)-supported Ru catalyst could produce hexitols from cellulose with a yield of about 40% [27]. Ni–W<sub>2</sub>C/AC and WO<sub>3</sub>–Ru/C catalysts with C–C cleavage ability could catalyze the direct hydrogenolysis of cellulose to ethylene glycol and propylene glycol [28,29]. Many promising multifunctional catalysts for the catalytic transformation of cellulose or

cellulose-derived carbohydrates to polyols and HMF have been developed, and there are several excellent review papers on these topics [24,30–33].

On the other hand, some recent studies have demonstrated that several important organic acids such as levulinic acid, lactic acid, gluconic acid, and formic acid can be produced from cellulose or cellulose-derived carbohydrates (Fig. 1) [34–40]. Different from the production of polyols, the formation of organic acids will not consume expensive H<sub>2</sub>. Instead, aerobic or anaerobic conditions are typically employed. For instance, several studies have demonstrated that gluconic acid can be attained by the oxidative conversion of glucose in the presence of supported gold or platinum catalysts [41–46]. Formic acid can be produced by using quantities of stoichiometric periodic acid [47]. It has been demonstrated that levulinic acid can be generated from glucose by isomerization, dehydration and rehydration. A series of tandem reactions including isomerization and retro-aldol fragmentation are mainly involved in the formation of lactic acid [34,35]. The development of multifunctional catalysts is essential for the selective production of organic acids.

This review article highlights some recent progress in the development of efficient catalysts or catalytic systems for the aerobic or anaerobic conversions of cellulose into organic acids including levulinic, lactic, gluconic, acetic, and formic acids. Key factors influencing the catalytic behaviors will be analyzed to provide information for rational design of more efficient catalytic systems for cellulose transformations. The reaction paths and the catalyst function in each step will also be discussed to provide deep understanding of the reaction mechanism.

## 2. Anaerobic conversion of cellulose and cellulose-derived carbohydrates into organic acids

### 2.1. Levulinic acid

Levulinic acid, also known as 3-acetylpropanoic acid, 4-oxovaleric acid or 4-oxopentanoic acid, is a water soluble organic compound with both a ketonic and a carboxylic group, which make it a versatile platform chemical [48]. Based on its bifunctional groups, levulinic acid can be utilized to synthesize various kinds of important chemicals such as succinic acid, γ-valerolactone, tetrahydrofuran, acrylic acid, and ethyl levulinate by hydrogenation, oxydehydrogenation, esterification, condensation, and other chemical reactions. For instance, γ-valerolactone (GVL), which could be obtained by the hydrogenation and esterification of levulinic acid, can be readily blended with petroleum products to form cleaner burning fuels that do not suffer from phase separation. GVL can also be converted to valeric biofuels by esterification to pentenoate esters [49], decarboxylation to alkenes, and oligomerization to hydrocarbon fuels [50].

The selective formation of levulinic acid from cellulose, cellulose-derived carbohydrates, or other biomasses has been extensively studied in aqueous mineral acids [34,51–55]. It is accepted that the acid-catalyzed conversion of cellulose into levulinic acid is a multi-step process, including (1) the hydrolysis of cellulose into glucose; (2) the isomerization of the formed glucose to fructose; (3) the dehydration of fructose to HMF, and (4) the rehydration of HMF with two molecules of water to levulinic acid and formic acid. During these steps, by-products can also be formed from the formed intermediates and levulinic acid (Fig. 2). Based on the reaction network in Fig. 2, many kinetic modeling studies have been performed to optimize the yield of levulinic acid from cellulose or glucose [54,56,57]. Huber and co-workers claimed that in the H<sub>2</sub>SO<sub>4</sub>-catalyzed conversion of glucose, relatively lower temperatures (413–433 K) and longer residence times (more than

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