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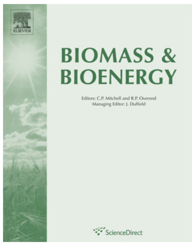

Review

Advances in hexitol and ethylene glycol production by one-pot hydrolytic hydrogenation and hydrogenolysis of cellulose

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ABSTRACT

In this review, recent advances in the one-pot hydrolytic hydrogenation and hydrogenolysis of cellulose to value-added polyols, including hexitols (sorbitol, mannitol, and isosorbide) and 1,2-alkanediols (ethylene glycol and 1,2-propylene glycol), are summarized. Methods for the generation of H^+ in the first step of cellulose hydrolysis to form intermediate sugars, such as the use of soluble acids (mineral acids and heteropoly acids) and H^+ produced *in situ* from functional supports and H_2 dissociation, are classified and analyzed, considering its combination with active metals for the subsequent hydrogenation or hydrogenolysis of sugars to polyols. The interaction of non-noble metals such as nickel, bimetals, and tungsten with support materials in the catalytic conversion of intermediate sugars to hexitols and ethylene glycol is reviewed. The corresponding reaction pathways and mechanisms are discussed, including the conversion process using basic supports and solution conditions. Major challenges and promising routes are also suggested for the future development of the chemocatalytic conversion of cellulose.

1. Introduction

Cellulose comprises a carbohydrate monomer (glucose) linked by β-1,4-glycosidic bonds. Chemocatalytic cleavage of its C–O and C–C bonds to polyols by hydrolytic hydrogenation or hydrogenolysis in a mild aqueous medium has attracted intensive scrutiny due to the abundance of cellulose (35–50% in biomass) and the wide variety of possible applications of

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Abbreviations: AC, activated carbon; BMC, ball-milled cellulose; EG, ethylene glycol; CNF, carbon nanofibers; CNT, carbon nanotube; HPA, heteropoly acid; MC, mesoporous carbon; MCC, microcrystalline cellulose; 1,2-PG, 1,2-propylene glycol; PVP, poly(N-vinyl-2-pyrrolidone).

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polyols as value-added chemicals and fuels [1–3]. In particular, sorbitol is regarded as one of the 12 important platform compounds in biomass conversion programs [4]. Additionally, 1,2-alkanediols such as ethylene glycol (EG) and 1,2-propylene glycol (1,2-PG) are used as energy platforms for the production of hydrogen and liquid alkane fuels via the aqueous reforming process or as monomers for polymerization synthesis [5–7].

The conversion of cellulose to polyols includes two consecutive reaction steps: acidic hydrolysis of cellulose to sugars and the subsequent hydrogenation or hydrogenolysis of the intermediate sugars to polyols over a supported transition metal catalyst under H_2 pressure at 4.0–12.0 MPa [8]. Each individual catalytic conversion step has been intensively studied for the efficient synthesis of sugar alcohols from mono- and polysaccharides [3,9].

Recently, one-step catalytic approaches for the conversion of cellulose to polyols have become a focal point [10]. Acid-catalytic hydrolysis, combined with *in situ* hydrolytic hydrogenation/hydrogenolysis in the same reactor, has a synergic effect due to the fast removal of unstable intermediates of cello-oligosaccharides and sugars, which reduces the side reactions [11]. When cellulose hydrolysis is coupled with glucose hydrogenation over a supported metal catalyst or with sugar hydrogenolysis over a tungsten-based catalyst, hexitol or 1,2-alkanediol (EG and 1,2-PG), respectively, will be the main product [12]. Heterogeneous catalysts, group VIII metals supported on functional materials such as active carbon (AC) and mesoporous silica, were found to be efficient for the sustainable production of polyols in the one-pot conversion of cellulose [13].

Although some publications deal with cellulose conversion, most focus on individual conversion steps, especially for glucose and fructose and their derivatives (e.g. furfural) using corrosive mineral acids [14]. This review concentrates mainly on recent progress in one-pot aqueous hydrolytic hydrogenation and hydrogenolysis of cellulose to polyols, including sorbitol, mannitol, isosorbide, EG, and 1,2-PG. Particular emphasis is placed on heterogeneous catalysts, H^+ sources for cellulose hydrolysis, the effect of functional support materials, and non-noble metals for *in situ* hydrogenation/hydrogenolysis, and their interactions under mild reaction conditions, for the one-pot conversion of cellulose and its utilization.

2. Cellulose to sorbitol and mannitol via hydrolytic hydrogenation

Sorbitol and mannitol, and their dehydration product sorbitan, are important precursors of renewable chemicals and fuels.

Sorbitol is traditionally produced via the two-step chemo-catalytic process described above. Mannitol is produced along with sorbitol through the epimerization of glucose to mannose [15,16]. The use of dilute or concentrated H_2SO_4 or HCl as the H^+ source and the low efficiency of individual steps encouraged studies on the one-pot conversion of cellulose into hexitols through hexose intermediates (reducing sugars) over a homo- or heterogeneous catalyst, as shown in Fig. 1 [17].

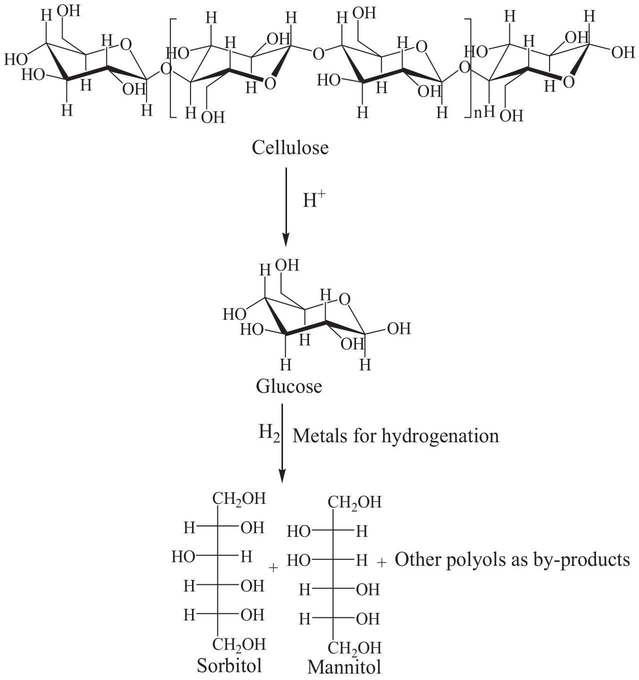

Fig. 1 – Reaction pathway of one-pot cellulose conversion to hexitols.

There are contradictory assumptions about the cleavage of glycosidic bonds (C–O–C) in cellobiose, traditionally used as the model compound for cellulose. One is the direct hydrolysis of cellubiose to glucose. The other is the hydrogenation of C–O bond on one of the glucose rings in the molecules of cellubiose, leading to the formation of cellobitol, which is further hydrolyzed to sorbitol and glucose [18]. Various reaction parameters such as temperature and the catalyst as well as the method of producing H^+ appear to affect these contradictory assumptions [19].

Here, the rate-determining step is the H^+-catalyzed hydrolysis of glycoside bonds to glucose via water-soluble oligosaccharides [11]. Depending the method used to introduce the acidic functional groups via H^+, catalysts for the one-pot hydrolytic hydrogenation of cellulose to hexitols can be categorized into two types: soluble acid/metal catalysts and *in situ*-generated H^+/metal catalysts.

2.1. *Soluble acid/metal catalysts*

Early research always used a homogeneous acid in combination with hydrogenation catalysts such as supported noble metals (Ru, Pt, and Pd). The supports have included carbon, carbon nanotubes (CNTs), and zeolites [20–22]. Until recently, much work focused on soluble mineral acids such as H_2SO_4, H_3PO_4, and HCl combined with supported Ru catalysts, and some recent advances are listed in Table 1 [23,24]. New ideas such as the formation of Ru particles with special morphology on functional supports, decreasing the cellulose crystallinity to enhance its susceptibility, and the introduction of soluble heteropoly acids (HPAs), under hydrothermal conditions, have initiated further developments of the traditional one-pot