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Short Communication

Direct production of sugar alcohols from wood chips using supported platinum catalysts in water

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ABSTRACT

Softwood chips have been directly converted into sugar alcohols by supported platinum catalysts in water without any acid catalysts. The cellulose and hemicellulose in the wood chips were converted with 94% conversion and 62% yield and the lignin remained as solid after the reaction.

1. Introduction

Conversion of lignocellulosic biomass to fuels and chemicals has greatly attracted attention for establishing the sustainable society because of the renewability, abundance, and inedibility of the lignocellulose [1–3]. For the production of valuable chemicals from cellulose and hemicellulose, the use of woody biomass is desired because it can eliminate the competition against food and it grows densely per unit area of land. However, the highly crystalline cellulose is encapsulated in hemicellulose–lignin matrix in woody biomass; thus, severe reaction conditions are required for the utilization of cellulose and hemicellulose. Enzymatic saccharification or acid hydrolysis with a main aim of bioethanol production has been developed [4,5]; however, the process has not been operated on a large scale because of low reaction rate and high cost for enzymatic saccharification and low yield and complicated separation for acid hydrolysis. Recently, catalytic cellulose conversion to sorbitol by supported metal catalysts with hydrogen has been reported by some research groups [6–13]; however, the pure cellulose is generally produced from lignocellulose using a strong base and strong acid catalyst to remove the lignin and hemicellulose components completely. Then, direct catalytic conversion of cellulose and hemicellulose in woody biomass to valuable chemicals is highly desirable to open new possibility for the use of lignocellulosic biomass. Palkovits et al. reported that sorbitol, sorbitan, and isosorbide could be obtained from spruce chips using supported metal catalysts and sulfuric acid or phosphoric acid with 55% yield of sugar alcohols based on cellulose unit [14]. The use of mineral acid could not avoid problems of corrosion of reactor wall or neutralization processes for the removal of hazardous acid; thus, environmentally benign techniques should be applied for the biomass transformation, in which no hazardous materials are used or produced. Sels et al. also reported that several lignocellulosic biomass could be converted into sorbitan and isosorbide using a combination of a supported ruthenium catalyst and heteropoly acids and that the total yield of sorbitan and isosorbide was at most 15% based on carbon atom of lignocellulose [15]. So far, the acid catalysts were required for the direct conversion of lignocellulosic biomass to sugar alcohols and the yield was low without strong mineral acids. It was reported that arabitol could be obtained from sugar beet fiber with 83% yield based on hemicellulose unit [16]; however, the direct catalytic transformation of cellulose in lignocellulosic biomass remains a challenge. In this work, we have succeeded in direct conversion of cellulose and hemicellulose in wood chips to six-carbon (C6) and five-carbon (C5) sugar alcohols

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by supported platinum catalysts in water without any acid catalysts (Scheme 1). Without a delignification pretreatment by inorganic acid, the cellulose and hemicellulose in the wood chips were mostly converted to sugar alcohols (conversion 94%, yield 62%) and lignin could be obtained as solid after the reaction. This technique will open up an opportunity to convert hemicellulose, cellulose, and lignin into useful chemicals using supported metal catalysts in a step-by-step procedure. The conversion of lignin into useful chemicals such as aromatics is still challenging.

2. Experimental

Catalyst preparation and characterization are described in the Supporting Information. The wood chips were made of Japanese cedar, which was a typical softwood in Japan. The chips were used as a reactant with a size less than 2 mm (Fig. S1), which were obtained by a crushing apparatus (Kitagawa Iron Works Co., Ltd., KDS Micronex KSS-2), and denoted as untreated wood chips. A part of the untreated wood chips were pulverized with a ball mill at 60 rpm for 48 h (Fig. S1) and denoted as milled wood chips.

The conversion of wood chips was carried out in a batch reactor, which we described in exact detail in the Supporting Information [6,7]. The milled or untreated wood chips (0.324 g), Pt/C catalyst (0.1–0.3 g, typically 0.2 g), and water (40 g) were loaded in the reactor, then hydrogen gas (5 MPa) was loaded in the reactor. The reactor was heated to 463 K. The quantitative analysis of water-soluble products in the liquid fraction was conducted by high-performance liquid chromatography. The other water-soluble (WS) products defined in this manuscript were calculated from the amount of total organic carbon in the liquid fraction other than the amount of total carbon in sugar alcohols. The conversion of wood chips was evaluated from the weight of recovered solid materials after the reaction.

The amounts of cellulose, hemicellulose, and lignin in the wood chips were determined according to the literature [17]. Briefly, the amount of holocellulose, which was sum of cellulose and hemicellulose, was defined as the insoluble in $NaClO_2$ aqueous solution with dilute acetic acid at 348 K. Cellulose was defined as the insoluble of the holocellulose in NaOH aqueous solution at 293 K. The hemicellulose content was determined by subtracting the amount of cellulose from that of the holocellulose. Lignin was defined as the insoluble of the wood chips in H_2SO_4 aqueous solution at 293 K.

The sugar content in the holocellulose was analyzed according to the literature [18]. Briefly, the wood chips were hydrolyzed by the H_2SO_4 aqueous solution to dissolve sugar content in the holocellulose. The hydrolyzed solution was neutralized and analyzed by high-performance liquid chromatography (JASCO, LC-2000 Plus HPLC) equipped with a refractive index detector (JASCO, RI-2031 Plus) and an Aminex HPX-87P column (Bio-Rad).

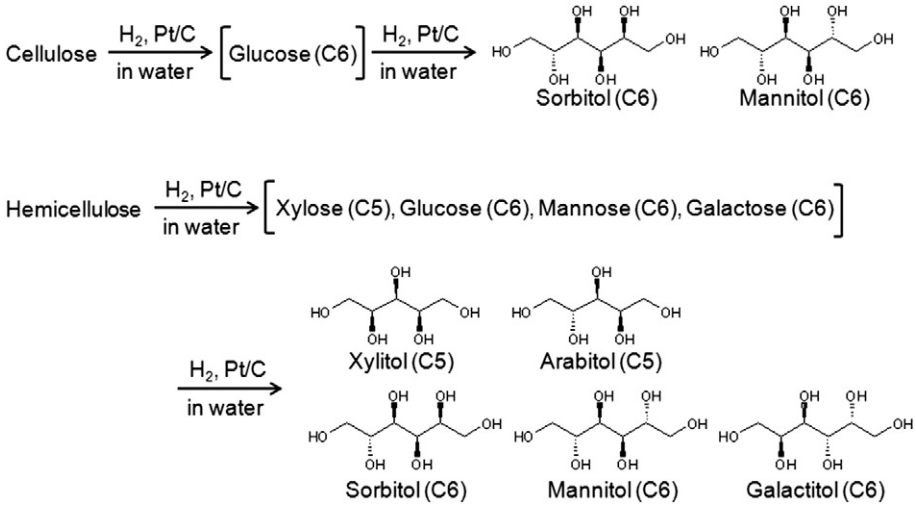
3. Results and discussion

The amounts (weight percentage) of cellulose, hemicellulose, and lignin in the wood chips were 40.9%, 24.8%, and 33.4%, respectively. The sugar content in the holocellulose (weight percentage based on the wood chips) was glucose 46.5%, mannose 8.8%, galactose 1.8%, and xylose 5.7%, respectively. Table 1 shows the product yields obtained from the conversion of Japanese cedar chips with 2 mm size at 463 K over the 2%Pt/C catalyst with 5 MPa H_2 for 8, 16, and 24 h (characterization results of the wood chips and the Pt/C catalyst are shown in the Supporting Information, Fig. S2). The conversion of wood chips was evaluated from the weight of recovered solid materials after the reaction. Carbon balance was more than 97% under the conditions of Table 1. The product yield was calculated based on sugar content in the reactant wood chips as follows:

$$\text{Yield for sugar alcohol (\%)} = (\text{each sugar alcohol in product (mol)}) / (\text{sum of sugar in introduced wood chips (mol)}) \times 100.$$

C6 sugar alcohols such as sorbitol (2.8%), mannitol (8.5%), and galactitol (1.7%), and C5 sugar alcohols such as xylitol (6.5%) and arabitol (2.4%) could be obtained at 8 h directly from the wood chips, indicating that a part of hemicellulose and/or cellulose in the wood chips were converted directly into the sugar alcohols by hydrogenolysis. The selectivity of each sugar alcohol in the product sugar alcohols was sorbitol 12.8%, mannitol 38.8%, galactitol 7.8%, xylitol 29.7%, and arabitol 10.9%. The conversion of the wood chips increased with increasing reaction time and consequently the water-soluble (WS) products increased; however, the yield of total sugar alcohols reached a maximum value in 16 h and then decreased. The product yield of C6 or C5 sugar alcohols was also calculated based on hexose or pentose in the reactant wood chips, respectively, as follows:

$$\text{Yield for C6 sugar alcohol (C6\%)} = (\text{each C6 sugar alcohol in product (mol)}) / (\text{sum of hexose in introduced wood chips (mol)}) \times 100.$$



Scheme 1. Direct catalytic conversion of cellulose and hemicellulose in woody biomass into sugar alcohols.