



Catalytic production of sugar alcohols from lignocellulosic biomass



Aritomo Yamaguchi^{a,b,*}, Osamu Sato^a, Naoki Mimura^a, Masayuki Shirai^{a,c}

^a Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

^b JST, PRESTO, 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan

^c Department of Chemistry and Bioengineering, Faculty of Engineering, Iwate University, Ueda 4-3-5, Morioka, Iwate 020-8551, Japan

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ABSTRACT

Lignocellulosic biomass of Japanese cedar, eucalyptus, bagasse, empty fruit bunch, and rice straw, has been directly converted into sugar alcohols such as sorbitol, mannitol, galactitol, xylitol, and arabitol, by supported platinum catalysts with hydrogen in water without any acid catalysts. Ball-milling pulverization of the lignocellulosic biomass increased the amount of total sugar alcohols from the direct conversion. The supported ruthenium and platinum bimetallic catalysts showed higher activity for the conversion of the lignocellulosic biomass. The amount of total sugar alcohols was increased up to 0.551 g from 1 g of milled bagasse by using the supported ruthenium and platinum bimetallic catalyst.

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1. Introduction

Conversion of lignocellulosic biomass to chemicals has greatly attracted attention for establishing the sustainable society [1,2]. The use of lignocellulose in woody biomass is desirable because it can eliminate the competition against food. Not only woody biomass but also agricultural wastes such as bagasse, empty fruit bunch (EFB), and rice straw are abundant and renewable lignocellulosic resources. These bagasse, EFB, and rice straw, which are nonedible fractions of sugar cane, oil palm tree, and rice plant, respectively, are generally burned as energy or left mulching on the ground. As a lignocellulosic biomass, these agricultural wastes should be feedstocks for the chemicals production.

Catalytic conversion of pure cellulose into sorbitol using supported metal catalysts with hydrogen by hydrogenolysis reaction has been reported by some research groups [3–10]. Direct catalytic conversion of cellulose and hemicellulose in the lignocellulosic biomass into sugar alcohols has also been reported with acid catalysts [11,12]. Hemicellulose in sugar beet fiber could be converted into arabitol with 83% yield without acid catalysts [13]. We previously reported that direct conversion of cellulose and

hemicellulose in wood chips of Japanese cedar, which was a kind of softwood, to six-carbon and five-carbon sugar alcohols using supported platinum catalysts in water without any acid catalysts by hydrogenolysis reaction [14]. In this study, we applied the catalyst system in water without any acid catalysts to direct conversion of chips of hardwood eucalyptus, bagasse, EFB, and rice straw into sugar alcohols. We also developed the supported metal catalyst for the biomass conversion using bimetal of ruthenium and platinum.

2. Experimental

2.1. Catalyst preparation

The carbon supported platinum catalyst (Pt/C) was prepared by an impregnation method using a carbon black BP2000 (Cabot Corporation) and an nitric acid aqueous solution of *cis*-[Pt(NH₃)₂(NO₂)₂] (Furuya Metal Co., Ltd.) as follows [14]. The aqueous solution of platinum and the carbon black were stirred for 12 h at ambient temperature and evaporated to dryness at 323 K under reduced pressure by a rotary evaporator, where the amount of platinum in the catalyst was 4 wt% (4%Pt/C). Then the samples were dried for 10 h at 373 K in an oven, followed by treatment at 673 K for 2 h under flowing hydrogen.

The carbon supported ruthenium and carbon supported bimetal of ruthenium and platinum catalysts were prepared by the same method as Pt/C. The ruthenium precursors for aqueous solutions

* Corresponding author at: Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan.

E-mail address: a.yamaguchi@aist.go.jp (A. Yamaguchi).

were Ru(NO)(NO₃)₃ and RuCl₃. The mixed aqueous solution of platinum and ruthenium precursors was used for the bimetallic catalyst. The catalysts were denoted by the metal loading and ruthenium precursor ((N): Ru(NO)(NO₃)₃ and (Cl): RuCl₃) such as 2%Ru(Cl)2%Pt/C and 3%Ru(N)1%Pt/C.

2.2. Characterization

The component analysis such as cellulose, hemicellulose, and lignin in the biomass was carried out according to the literature [15]. Briefly, the amount of cellulose and hemicellulose was defined as the insoluble in NaClO₂ aqueous solution with dilute acetic acid at 348 K. Cellulose was defined as the insoluble of the cellulose and hemicellulose in NaOH aqueous solution at 293 K. Lignin was defined as the insoluble of the biomass in H₂SO₄ aqueous solution at 293 K.

The analysis of sugar content in the biomass was carried out according to the literature [16]. Briefly, the cellulose and hemicellulose in the biomass was hydrolyzed to sugars by the H₂SO₄ aqueous solution. The hydrolyzed solution was neutralized and analyzed by high-performance liquid chromatography (HPLC) equipped with a refractive index detector and an Aminex HPX-87P column.

2.3. Reaction

Japanese cedar, eucalyptus, bagasse, EFB, and rice straw were used as reactants. Chips of the lignocellulosic biomass were used as a reactant with a size less than 2 mm, which were obtained by a cutting or crushing apparatus, which were denoted as unmilled chips. A part of the unmilled chips were pulverized with a ball mill at 60 rpm for 48 h, which were denoted as milled chips.

The conversion of reactant chips to sugar alcohols by hydrogenolysis reaction was carried out in a batch reactor, of which inner volume was 100 cm³ [3,14]. The unmilled or milled chips (0.324 g), the supported metal catalyst (0.2–0.3 g), and water (40 g) were loaded in the reactor and the reactor was purged with hydrogen gas, then hydrogen gas (5 MPa) was loaded in the reactor at ambient temperature. The reactor was heated to 463 K and maintained at the temperature for the reaction time (16 h) with screw stirring. After the reaction, a mixture of liquid and solid was recovered and filtered to separate the solid materials from the liquid fraction. The quantitative analysis of water-soluble products in the liquid fraction was conducted by HPLC with a refractive index detector and a UV-Vis detector equipped with a Phenomenex SC1211 column. Amount of products and remained solid (g/biomass-g) were defined as those obtained from unit weight of dry biomass. Sugar alcohol yield was calculated based on sugar content in the reactant chips as follows:

$$\text{Sugar alcohol yield (\%)} = \frac{\text{sugar alcohol in product (mol)}}{\text{sugar in reactant chips (mol)}} \times 100.$$

3. Results and discussion

3.1. Conversion of lignocellulosic biomass using Pt/C

Table 1 shows component and sugar content for Japanese cedar, eucalyptus, bagasse, EFB, and rice straw used as reactants in this study. The weight percentages of cellulose, hemicellulose, and lignin in those lignocellulosic biomass were 26–41%, 17–39%, and 16–33%, respectively. In the case of rice straw, the total weight amount of cellulose, hemicellulose, and lignin was 64%, indicating that the rice straw also contained the other component such as SiO₂. The weight percentages of glucose were more than 37% in all the biomass used in this study. The weight percentage of xylose in

Japanese cedar was only 5.7%; on the other hand, those in eucalyptus, bagasse, EFB, and rice straw were more than 14%. Especially, bagasse and EFB contained xylose with more than 20% wt%.

We have reported direct conversion of the Japanese cedar chips into sugar alcohols using the Pt/C catalysts [14]. At first, we applied the direct conversion method to obtain sugar alcohols using Pt/C from the other lignocellulosic biomass. Table 2 shows amount of products, remained solid, and total yield of sugar alcohols from conversion of unmilled and milled lignocellulosic biomass over 4%Pt/C with 5 MPa H₂ for 16 h. All the kinds of lignocellulosic biomass such as softwood, hardwood, and herbaceous biomass could be converted into sugar alcohols. The amount of total sugar alcohols was increased by ball-milling pretreatment for all the kinds of biomass (Table 2). Interestingly, the amount of xylitol and arabitol did not change largely by the ball-milling pretreatment; on the other hand, the amount of sorbitol increased drastically. The yield of sorbitol from pure cellulose conversion by the hydrogenolysis reaction was reported to be enhanced by the ball-milling pulverization because of the decrease of cellulose crystallinity [17]. Improvement of the sorbitol yield in this study should be due to the decrease of cellulose crystallinity in the lignocellulosic biomass. Xylitol could be obtained from xylose in the hemicellulose and the xylitol yield did not change regardless of the ball-milling pulverization (Table 2), indicating that sugars of the hemicellulose in the lignocellulosic biomass could be converted to sugar alcohols effectively even without the ball-milling pretreatment. The amount of xylitol in the products (Table 2) increased with the amount of xylose in the reactant lignocellulosic biomass (Table 1). The sugar alcohol yields from milled bagasse and Japanese cedar were more than 60%; however, those from milled eucalyptus, EFB, and rice straw were less than 50%, indicating that the effectiveness of direct conversion to sugar alcohols depended on types of biomass.

3.2. Catalyst development using bimetal of Ru and Pt for lignocellulose conversion

The supported ruthenium catalysts as well as the supported platinum catalysts were also reported to be active for the cellulose hydrogenolysis to sorbitol [4,7,9,18–20]. We carried out direct conversion of the milled Japanese cedar chips to sugar alcohols using the 4%Ru(Cl)/C or 4%Ru(N)/C catalyst (Table 3). The Ru(Cl)/C catalyst showed activity for the direct conversion; however, the amount of total sugar alcohols (0.354 g/biomass-g) was less than that using 4%Pt/C (0.385 g/biomass-g). The Ru(N)/C catalyst did not show any activity for the hydrogenolysis of lignocellulosic biomass; however, the remained solid after the reaction was 0.190 g/biomass-g, indicating that hydrolysis of cellulose and hemicellulose in the chips into water-soluble sugars could proceed and that hydrogenation of sugars such as glucose and xylose into sugar alcohols did not occur. We confirmed that the water-soluble organic materials were formed in the aqueous phase after the reaction using Ru(N)/C by a total organic carbon analyzer. The remained solid after the reaction was 0.380 g/biomass-g without any catalysts (Table 3), indicating that the hydrolysis of cellulose and hemicellulose in the chips into water-soluble sugars could also proceed without any catalysts. In that case, no sugar alcohols were produced because hydrogenation of sugar did not proceed without supported metal catalysts. Sugars were not stable in high-temperature water at 463 K and degraded into other organic materials. In the case of Ru(N)/C catalyst, hydrogenation reaction of sugars would be slow and degradation of sugars preferentially proceeded. The metal dispersions of Ru in Ru(Cl)/C and Ru(N)/C were estimated from CO pulse adsorption experiments. The metal dispersions were 43.0% and 26.0% in Ru(Cl)/C and Ru(N)/C, respectively, indicating that the ruthenium species in Ru(Cl)/C were more highly dispersed than those in Ru(N)/C. That could possibly be a reason why Ru(Cl)/C was

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