Catalytic conversion of biomass to valuable chemicals using supported metal catalysts in high-temperature water

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Abstract: We have succeeded in converting hemicellulose, cellulose, and lignin to useful chemicals using supported metal catalysts in step-by-step procedures. At first, we found a technique for the conversion of cellulose and hemicellulose in biomass chips to sugar alcohols by supported metal catalysts with hydrogen. Then, the lignin, which remained mostly as solid after the direct conversion of biomass chips into sugar alcohols, could be converted into chemicals. The supported metal catalysts were recyclable.

Keywords: Biomass conversion, Supported metal catalyst, High-temperature water.

1. Introduction

Conversion of nonedible biomass into valuable chemicals has greatly attracted attention for establishing the sustainable society because of its renewability, abundance, and inedibility. The lignocellulosic biomass is composed of cellulose, hemicellulose, and lignin, which should be feedstocks for the chemicals production. The cellulose and hemicellulose are polymers of sugars and lignin is a polymer of aromatic compounds. Direct catalytic conversion of cellulose and hemicellulose in biomass to valuable chemicals is highly desirable to utilize the all the components of cellulose, hemicellulose, and lignin. In this paper, we have succeeded in direct conversion of cellulose and hemicellulose in wood chips to six-carbon and five-carbon sugar alcohols, such as sorbitol, mannitol, and xylitol, by supported metal catalysts and hydrogen without a delignification pretreatment by acid [1, 2]. Most of lignin in the reactant biomass remained as solid after the reaction.

Next we investigated the chemistry for intramolecular dehydration of the sugar alcohols in high-temperature water into valuable chemicals to utilize biomass resources. The intramolecular dehydration of sorbitol and mannitol can provide valuable diols, isosorbide and isomannide, by bimolecular dehydration. Isosorbide and isomannide have attracted a great deal of attention because poly(ethylene terephthalate) (PET) containing isosorbide has higher glass transition temperatures than pure PET, broadening the applications of polyesters. We found that isosorbide and isomannide could be produced from sorbitol and mannitol dehydration in high-temperature water without adding any acid catalysts [3-5], which could enhance the prospect for biomass-based monomers.

At last, the lignin, which remained mostly as solid after the direct conversion of biomass chips into sugar alcohols, was converted into chemicals. More efficient use of lignin carbon is necessary for carbon-efficient utilization of lignocellulosic biomass. Conversion of lignin into valuable aromatic compounds requires the cleavage of C–O ether bonds and C–C bonds between lignin monomer units. We also report cleavage of the aromatic C–O bonds in lignin model compounds using supported metal catalysts in supercritical water without adding hydrogen gas [6].

2. Experimental

The conversion of cellulose and hemicellulose in biomass to sugar alcohols by hydrogenolysis reaction was carried out in a batch reactor, of which inner volume was 100 cm^3. The biomass 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.

The dehydration of sugar alcohols was carried out in a batch reactor (6 cm^3). Sugar alcohol aqueous solution (3 cm^3) was loaded in the reactor, and then it was purged with argon gas to remove air. The reactor was submerged into a molten-salt bath at a desired reaction temperature for a given reaction time. The quantitative analysis of the unreacted reactant and liquid products was conducted by a HPLC.

Lignin was decomposed in a batch reactor made of stainless steel 316 tube with an inner volume of 6.0 cm^3. The reactor was submerged in a molten-salt bath at 673 K for 1 h and then submerged in a water bath to quickly cool the contents of the reactor to ambient temperature after the reaction. Liquid products in the reactor were recovered with tetrahydrofuran and filtered to separate solid catalysts from the liquid fraction. Liquid products were quantitatively analyzed by gas chromatography (Agilent, HP-6890) with a flame ionization detector using a DB-WAX capillary column.

3. Results and discussion

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 the 4%Pt/C catalyst with hydrogen. Ball-milling pulverization of the lignocellulosic biomass increased the amount of total sugar alcohols from the direct conversion.

Dehydration of sugar alcohols (0.5 mol dm^{-3}) proceeded in high-temperature water at 523 K without any acid catalysts and the dehydrated products were obtained [3-5]. The major product of monomolecular dehydration obtained was only 1,4-anhydrosorbitol and the yield of isosorbide from bimolecular dehydration of sorbitol increased with reaction time (maximum yield of isosorbide 57%). 2,5-Anhydromannitol and 1,4-anhydromannitol were major products from the mannitol monomolecular dehydration and the maximum yield of isomannide was 20%. The dehydration behaviors of sorbitol and mannitol were quite different from each other [4].

Lignin, which remained mostly as solid after the direct conversion of biomass chips into sugar alcohols, could be converted into aromatic compounds in water at 673 K. The catalyst could be recovered by the simple filtration and the recovered catalyst showed the same activity for the biomass conversion. We also demonstrated that lignin model compounds undergo some unique reactions in which the C–O and C–C bonds are cleaved without adding hydrogen gas and without causing hydrogenation of the aromatic ring [6].

4. Conclusions

We have succeeded in converting cellulose and hemicellulose in the biomass chips into sugar alcohols by supported metal catalysts with hydrogen. Then, we have also succeeded in the intramolecular dehydration of mannitol and sorbitol in high-temperature liquid water without adding any hazardous acid catalysts. Lignin could be converted into aromatic compounds in water at 673 K. The supported metal catalysts were recyclable.

References

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