Understanding the Surface Modification of Heterogeneous Catalyst for Hydrolytic Depolymerization of Cellulose: Correlation among Average Molecular Weight, Crystallinity of Polysaccharides and Hydrolytic Efficiency

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Abstract: Carbonaceous catalysts with high coverage of acidic functionality on the surface were developed and this catalytic system could depolymerize amorphous cellulose to 39% production yield of glucose while acidic functionality was presented at a catalytic ratio of 4.8 mol%. In addition, further modification of basic surface could catalytically isomerize glucose to fructose up to 90% selectivity with the base surface functionality at 2 mol% of catalytic ratio. Surprisingly, peak molecular mass of glucans larger than regular amorphous cellulose was observed in gel permeation chromatography (GPC) analysis after hydrolytic reaction and it suggested that glucan polymerization might occur as well while using the aforementioned carbonaceous catalyst. In addition, recrystallization of amorphous cellulose was observed in powder X-ray diffraction (PXRD) pattern and it might limit hydrolytic efficiency of cellulose. Even though, the carbonaceous catalyst might lead to new application, such as glycosylation of sugar derivative and synthesis of functional oligosaccharides.

Keywords: depolymerization, cellulose, hydrolysis.

1. Introduction

Most of the industrial organic precursors used to make plastics, solvents, commodity products, and numerous essential chemicals are currently derived from fossil fuels. With the dwindling fossil fuel of nature resource, glucose production derived from lignocellulosic biomass is one sustainable alternative and converting glucose into other chemicals through different catalytic pathways has been intensively studied in the past few years.[1] Previously, the adsorption and depolymerization of β-glucan molecules derived from cellulose on porous carbon materials have been explicitly studied recently[2-5] and herein, to better understand the influence of surface modification on heterogeneous catalyst, especially for depolymerizing the cellulose, we have investigated acid/base functionality with high coverage on carbon surface could lead effective hydrolytic reaction of converting amorphous cellulose to glucose as well as isomerization of glucose to fructose as shown in Figure 1(a).

2. Experimental

The carbonaceous surface was chemically modified by a variety of oxygenated species denoted as C1, C2 and C3 for acid-factionalized surface and C1-CB, C2-CB and C3-CB for base-functionalized surface. All hydrolytic reactions were carried out in a glass tube at 180 °C for 3 hours, followed by the simple filtration the glucose yield was quantified by HPLC. For the isomerization of glucose, glucose aqueous solution was carried out at 100 °C for 1 hour, followed by the filtration and the fructose selectivity were evaluated by high performance liquid chromatography (HPLC) analysis. Furthermore, the spent residue was washed by Dimethylacetamide/LiCl solvent and the soluble specie was analyzed by gel permeation chromatography (GPC) to understand the polymer distribution of remaining glucan. The crystallinity of cellulose in the spent residue was determined using powder X-ray diffraction (PXRD).

3. Results and discussion

The carbonaceous catalysts with high coverage of acid functionality could depolymerize amorphous cellulose and to understand the efficiency of depolymerization, it could reflect on the glucose production which reached up to 39% as shown in Figure 1(a). On the other hand, the distribution of polymer or oligomer derived from depolymerized cellulose was studied by gel permeation chromatography (GPC) as well and surprisingly, as shown in Figure 1(b), peak molecular mass of glucans larger than regular amorphous cellulose was observed in GPC analysis after hydrolytic reaction and it suggested that glucan polymerization might occur simultaneously while using the aforementioned carbonaceous catalyst. The cellulosic residues collected after acid hydrolysis were characterized by powder X-ray diffraction (PXRD) and it revealed the trend of structural transformation for amorphous cellulose to recrystallized cellulose escalated during hydrolysis, as shown in Figure 1(c). These observations above indicated that recrystallization of amorphous cellulose indeed took place to impede the depolymerization during acid hydrolysis, which might lead to ineffective monosaccharide production. Therefore, to understand the kinetics of hydrolytic depolymerization in depth could shed the light to design efficient hydrolytic depolymerization system for biomass-derived polysaccharides in the future. In addition, we simply modified base functionality through neutralization of acid groups and this base functionalized surface can isomerize glucose to fructose up to 90% selectivity and it suggested that conjugate base could be used as base-catalyzed isomerization of glucose.

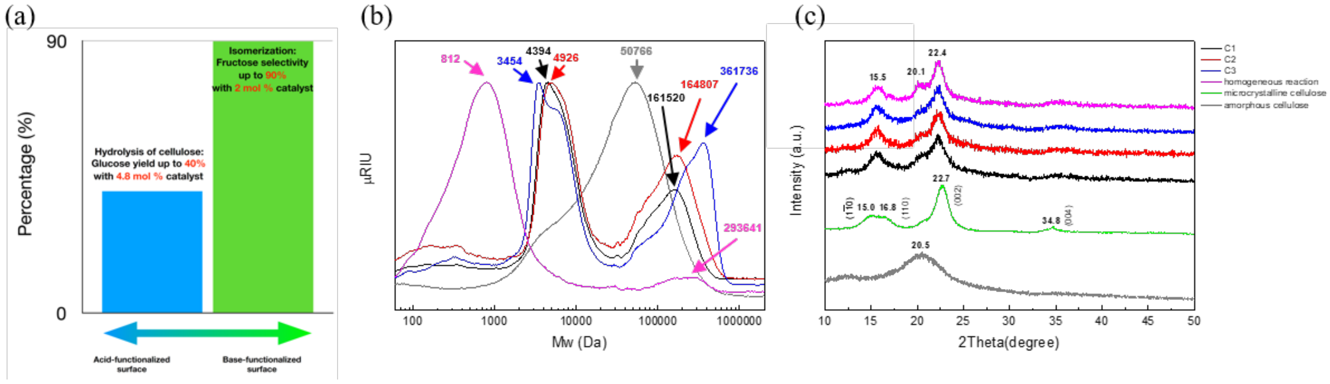

Figure 1. (a) Demonstration of glucose production yield by using acid-functionalized surface and the fructose selectivity from glucose by using base-functionalized surface, respectively; (b) molecular mass distribution and (c) powder X-ray diffraction patterns of amorphous cellulose after the hydrolytic reactions by acid-factionalized catalysts. (homogeneous reaction was carried out in the presence of 2 mol% acidity of H_2SO_4).

4. Conclusions

In summary, we have demonstrated that carbonaceous catalysts with high coverage of either acidic or basic functionality on the surface were developed and this catalytic system could depolymerize amorphous cellulose to 40% production yield of glucose and could catalytically isomerize glucose to fructose up to 90% selectivity, respectively. Moreover, peak molecular mass of glucans larger than regular amorphous cellulose was observed in GPC analysis after hydrolytic reaction and it suggested that glucan polymerization might occur as well during the hydrolysis. This unexpected discovery might lead to new application for this catalyst, such as glycosylation of sugar derivative and synthesis of functional oligosaccharides.

References

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