Production of value-added platform chemicals via catalytic conversion of macroalgae-derived alginic acid

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Abstract: Alginic acid, a major constituent of brown algae, was converted into value-added platform chemicals such as uronic acid and sugar alcohols over solid acid catalysts and noble metals, respectively. Uronic acids were produced over sulfonated glucose-derived carbons with the highest yield of 19.6%. A linear correlation between acid density and the yield of uronic acids was exhibited during the hydrolysis of alginic acid. Sugar alcohols were produced over carbon-supported noble metals with the highest yield of C_6 polyols of 61%. Two epimeric monomers of alginic acid and isomerization between polyols resulted in the low value of sorbitol to mannitol ratio.

Keywords: alginic acid, hydrogenation, heterogeneous catalysis.

1. Introduction

Algal biomass known to be a third-generation biomass, has been attracting a world-wide attention as a prominent resource because of its inedibility, rapid growth, and lignin-free structure. Alginic acid, a major constituent of macroalgae, consists of two different uronic acids linked by β-1,4-glycosidic bond, which is analogous to the structure of cellulose composed of glucoses also linked by the ether bond.[1] Alginic acid, on account of the structural similarity with cellulose, could be subjected to biorefinery technologies to produce versatile building block chemicals such as organic acids and furfural.[2]

As a surrogate for cellulose, alginic acid is expected to play a crucial role in diversifying the range of biomass-derived products and alleviating the large dependence on lignocellulosic biomass. In this work, hydrolysis and hydrogenation of alginic acid to produce uronic acids and sugar alcohols, respectively, over various solid catalysts were conducted for the first time.

2. Experimental

Hydrolysis reactions were performed using water-soluble sodium alginate in a stainless-steel tubular reactor in an oil bath at desired temperatures (100, 120, and 140 °C). After desired reaction times, the reactors were quenched with cold water and uronic acids in liquid products were analyzed by HPLC.

Hydrogenation reactions were performed using alginic acid in a stainless-steel autoclave. The reactor was pressurized with 50 bar of H_2 after air in the reactor was removed by flushing the reactor with 50 bar of helium 3 times. After desired reaction times at desired reaction temperatures (150, 180, 210 °C), the reactor was quenched with cold water. Products were analyzed by GC after silylation of polyols.

3. Results and discussion

The hydrolysis of alginic acid into uronic acids was performed over various solid acid catalysts such as sulfuric acid, activated carbons, zeolites, Amberlyst-15, and sulfonated glucose-derived carbons. A linear correlation between acid density and the yield of uronic acids was found as shown in Figure 1. Sulfonated glucose-derived carbons exhibited the highest yield of uronic acid (19.6%) because of the presence of the strong Brønsted acid site, $-SO_3H$, and its high local acid density. The carbohydrate-π interaction together with the high local acid density of the sulfonated glucose-derived carbon facilitated the adsorption of alginic acid onto the catalyst and the cleavage of C-O-C bond. The catalyst showed deactivation over the repeated use owing to the leaching of sulfonate group.

The hydrolytic hydrogenation of alginic acid into polyols was performed over noble metal supported carbons. A plausible reaction pathway was proposed based on analysis of intermediates using mass spectrometry. The consecutive hydrogenation aldehyde- and carboxyl-end of dimeric units of alginic acid led to the formation of 5 different partially hydrogenated intermediates before cleaved into monomeric units and hydrogenated into hexitols. As shown in Figure 2, the highest yields of C_6 polyols (61%) were obtained over Ru supported carbons. Hexitols were mainly produced over Ru supported carbons whereas the formation of byproducts via hydrodeoxygenation was observed on Pd, Pt, Rh, and Ir supported carbons as determined by GC-MS and LC-MS (data not shown). Unlike the case of cellulose hydrogenation, mannitol was produced as much as sorbitol owing to the composition of alginic acid and isomerization of sugar alcohols produced[4] under this catalytic system. Over the repeated use the leaching of active metal and aggregation of Ru caused the deactivation of the catalyst.

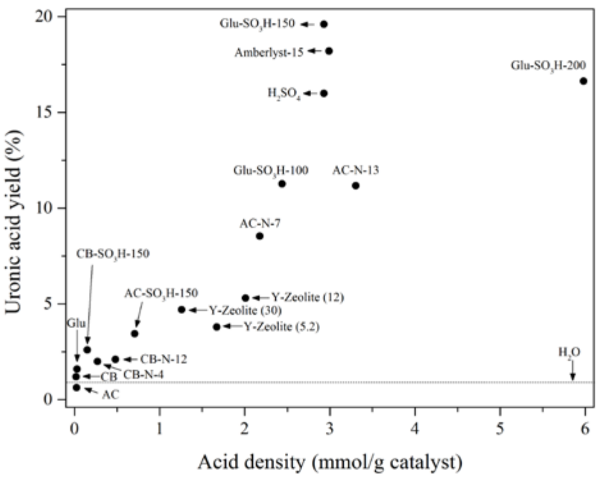

Figure 1. Yield of uronic acids with respect to acid density.

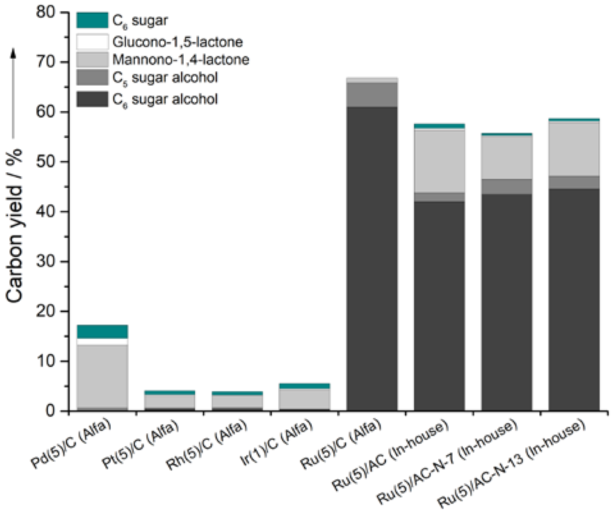

Figure 2. Yield of products over different carbon-supported noble metals.

4. Conclusions

Products of two different classes, uronic acids and sugar alcohols, were produced via hydrolysis and hydrogenation of alginic acid, respectively. Hydrolysis of alginic acid over sulfonated glucose-derived carbon resulted in the highest yield of uronic acid of 19.6% whereas hydrolytic hydrogenation of alginic acid under pressurized H_2 over Ru supported carbon produced the highest yield of hexitols of 61%. A plausible reaction pathway for each reaction was proposed. Leaching of active sites, sulfonate groups and ruthenium, and aggregation of the active metal caused the deactivation of catalysts during the hydrolytic conversion of alginic acid.

References

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