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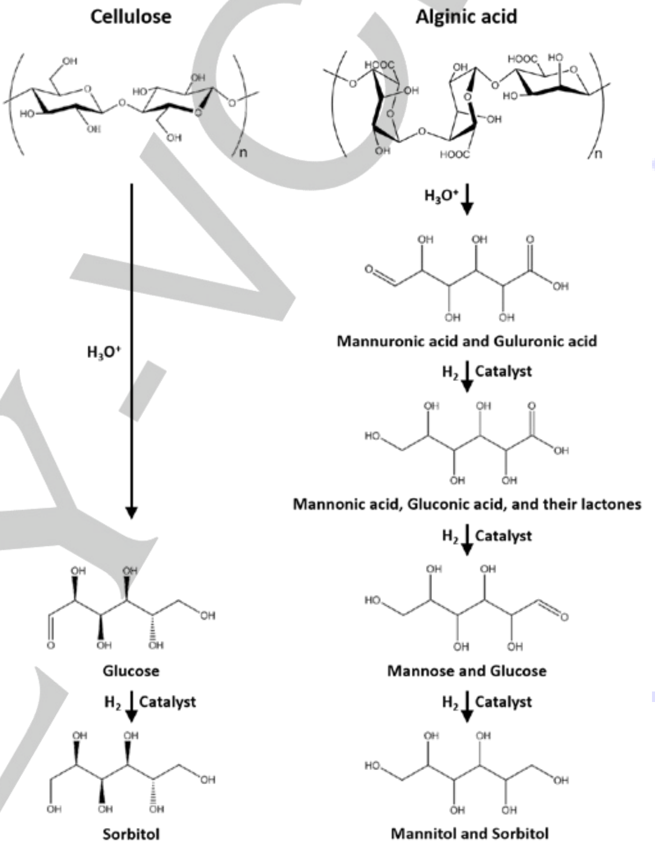
Catalytic Hydrogenation of Macroalgae-derived Alginic Acid into Sugar Alcohols

Chunghyeon Ban,[a] Wonjin Jeon,[b] Hee Chul Woo,[c] and Do Heui Kim*[a]

Abstract: Alginic acid, a major constituent of macroalgae, was hydrogenated into sugar alcohols over carbon-supported noble metals for the first time. Mannitol and sorbitol were mainly produced via the catalytic hydrogenation of alginic acid, which consists of two epimeric uronic acids. The main reaction pathway is the consecutive hydrogenation of aldehyde- and carboxyl-end of alginic acid dimers followed by the cleavage of C-O-C linkage into monomeric units via hydrolysis. The highest yield of C_6 sugar alcohols is 61% (sorbitol: 29%, mannitol: 28%, and galactitol: 4%). The low value of sorbitol to mannitol ratio differs to the case of cellulose hydrogenation due to the composition of alginic acid and isomerization between sugar alcohols under the catalytic system. Such a new and green route to produce sugar alcohols from alginic acid would provide opportunities to diversify biomass resources.

Introduction

The sustainable production of fuels and chemicals from renewable resources has attracted worldwide attention to resolve critical energy and environmental issues such as limited fossil fuel reservoir and fossil fuel-related pollution. Among various renewables, biomass is the only renewable source of carbon that can be directly converted to fuels and valuable chemicals.[1] Lignocellulosic biomass among the renewables has been frequently utilized for the production of green fuels and chemicals. Especially, catalytic conversion of cellulose has been extensively studied over the last century.[2] Cellulose could be hydrolyzed to produce glucose selectively over various acid catalysts such as sulfonated activated carbons[3] and metals supported on mesoporous carbon.[4] Cellulose could also be converted into value-added platform chemicals such as 5-hydroxymethyl furfural,[5] lactic acid,[6] and levulinic acid[7] via catalytic thermal reaction. In addition, glucose could be further hydrogenated to produce sugar alcohols or the polyols can directly be produced via the catalytic hydrogenation of cellulose over various metal catalysts with tunable selectivities between sugar alcohols. For instance, sugar alcohols can be produced via hydrogenation of cellulose over supported noble metal catalysts such as Pt,[8] Ru,[9] and Ir,[10] and over non-noble metal catalysts such as Ni[11] and Cu.[12] Among sugar alcohols, sorbitol and mannitol are valuable sugar alcohols which are used not only as a valuable sweetener but also as a building block chemical to produce hydrogen for fuel cell, vitamin C, and resin monomers such as ethylene glycol, propylene glycol, and isosorb-(or mann-)ide.[13] The commercial production of sorbitol and mannitol occurs by hydrogenation of glucose and glucose/fructose mixture, respectively, over Raney nickel as a catalyst.[14]



Scheme 1. Schematic reaction paths of sugar alcohol production via hydrogenation of cellulose and alginic acid.

In recent years, algal biomass, known as a third-generation biomass, has been attracting considerable attention as a promising renewable resource since it has more advantageous features than its terrestrial counterpart, cellulose, with respect to rapid growth, inedibility, and lignin-free composition. Marine biomass has been utilized in biorefinery

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processes such as liquefaction, pyrolysis, and gasification to produce value-added renewable chemicals, contributing to alleviate the heavy dependence on petroleum-based chemicals.[15] Recently, attempts have been made to produce value-added chemicals from alginic acid, a major constituent of macroalgae, via thermochemical methods.

Alginic acid, a renewable biopolymer, consists of two different uronic acids, mannuronic acid(M) and guluronic acid(G) linked by β-1,4-glycosidic bond, which is analogous to the structure of cellulose composed of glucoses also linked by the ether bond. The ratio of M/G varies with the season, location, and species.[16] Recent studies reported that versatile platform chemicals such as uronic acids, lactic acid, and furfural could be produced from alginic acid via catalytic hydrothermal treatment.[17] However, to the best of our knowledge, catalytic hydrogenation of alginic acid into sugar alcohols over metal catalysts has never been reported. Scheme 1 shows a comparison of the structure between cellulose and alginic acid, and their conversion to sugar alcohols. Unlike the case for cellulose, additional hydrogenation steps are required for the production of sugar alcohols from alginic acid due to the presence of carboxylic groups. In addition, mannitol is produced along with sorbitol, since alginic acid consists of two different monomers (see Scheme S1 for a detailed reaction network).

In this present work, we introduce for the first time macroalgae-derived alginic acid as a green alternative to cellulose for the production of sugar alcohols via hydrogenation of alginic acid over ruthenium supported on carbon. A screening of noble metals, kinetic study, isomerization of hexitols, and durability test of the catalyst were performed. A reaction network for the hydrogenation of alginic acid is then proposed.

Results and Discussion

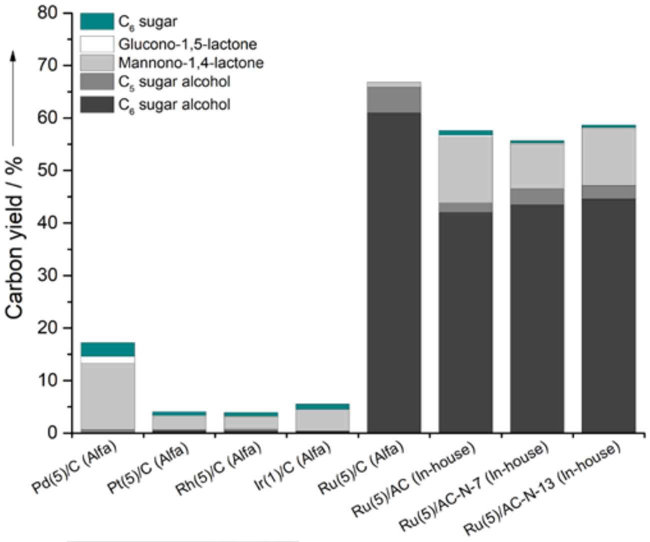

Figure 1. Product distribution over different carbon-supported noble metals at 150 °C for 12 h under 50 bar of H_2.

Table 1. Total organic carbon in liquid product after hydrogenation at 150 °C for 12 h under 50 bar of H_2

Catalyst	Total organic carbon remained in liquid product (mg/L)	Total organic carbon remained in liquid product [a] (%)
Ru(5)/C (Alfa)	17.4	99.4
Pd(5)/C (Alfa)	19.0	108.6
Pt(5)/C (Alfa)	15.6	89.1
Rh(5)/C (Alfa)	17.2	98.3
Ir(1)/C (Alfa)	14.5	82.9

[a] The values were calculated based on total organic carbon of 1% alginic acid solution (17.5 mg/L)

The batch-wise hydrolytic hydrogenation was performed over various carbon-supported metals to produce sugar alcohols from alginic acid. As shown in Figure 1, the highest yield of C_6 sugar alcohol (61%) was obtained over Ru whereas carbon-supported Pd, Pt, Rh, and Ir catalysts hardly produced any C_6 sugar alcohols although the complete conversion of alginic acid over the noble metal supported on carbon was observed by GPC analysis (Figure S1). This resulted in a significant loss in carbon balance for the Pd, Pt, Rh, and Ir supported catalysts. However, as summarized in Table 1, TOC analysis revealed that most of organic carbons (>80%) were preserved in the liquid products, indicating that carbon loss to gas phase could be regarded as marginal. In other words, several byproducts are produced during the catalytic hydrogenation of alginic acid. It is known that different metals show different selectivities towards hydrogenation, C-C cleavage and C-O cleavage. For example, a reaction of glycerol over ruthenium resulted in the formation of a fully hydrogenated product, propane,[18] or a C-C cleaved product, ethylene glycol.[19] However, the production of a C-O cleaved product, propylene glycol, was favored over Pt.[20] This was evidenced by the detection of dideoxy-aldonic acid and dideoxy-aldonic acid lactones by GC-MS only for the cases of carbon-supported Pd, Pt, Rh, and Ir (data not shown). This was further analyzed by LC-MS and the result indicates a distinctive difference between carbon-supported Ru and the other noble metals as shown in Figure S2. Dideoxy-aldonic acid lactone (m/z=169.05) was observed for all noble metal supported catalysts whereas C_6 sugar alcohols (m/z=205.08) were the main product for Ru(5)/C(Alfa). Thus, the cause of carbon loss could be attributed to the formation of byproducts via the hydrodeoxygenation of aldonic acid or its lactone over Pd, Pt, Rh, and Ir supported catalysts. Furthermore, unidentified compounds having low m/z were also produced over Pd, Pt, Rh, and Ir supported catalysts. Unfortunately, the quantification of these byproducts was not possible due to the absence of standard samples.

The activity of the commercial catalyst, Ru(5)/C(Alfa) was also compared to that of activated carbon-supported Ru catalysts synthesized in-house. In the preparation of the Ru catalysts, activated carbon was oxidized with nitric acid of different concentrations to vary its acid density. Textural

Table 2. Textural properties of catalysts.

Catalyst	Surface area (m^2/g catalyst) [a]	Total acid density (mmol/g catalyst) [b]
Ru(5)/C (Alfa)	816.2	0.85
Pd(5)/C (Alfa)	810.5	0.51
Pt(5)/C (Alfa)	886.7	0.43
Rh(5)/C (Alfa)	872.5	0.62
Ir(5)/C (Alfa)	1017.5	0.43
Ru(5)/AC	941.8	0.26
Ru(5)/AC-N-7	894.0	1.11
Ru(5)/AC-N-13	824.7	1.11

[a] Surface area was measured by Brunauer-Emmet-Teller method.

[b] Total acid density was determined by back titration.

properties of the synthesized catalysts (Ru/AC-N-x) are listed in Table 2. As displayed in Figure 1, among Ru/AC-N-x catalysts, a catalyst oxidized with higher concentration of HNO_3 exhibited a higher yield of sugar alcohols. The result suggests that oxygenate functional groups which were induced after nitric acid treatment such as phenolic OH, =O, and –COOH have a promotional effect on the hydrolysis of alginic acid. Especially, amounts of weak acid site, carboxylic groups, was obviously formed after the modification as evidenced by the evolution of C=O stretching vibration band at 1718 cm^{-1} (Figure S3).[21] Similarly, the capability of carboxylic groups to effectively hydrolyze biomass feedstock was reported both in cellulose and alginate valorization.[17d, 22] However, the commercial Ru(5)/C (Alfa) catalyst having lower acid density exhibited higher activity towards the production of polyhydric alcohols. The result implies that a metal site could act as an effective acid site to hydrolyze alginic acid under pressurized H_2 atmosphere without any acid site. Therefore, it can be deduced that protonic acid sites formed by spilled-over H_2 on ruthenium could hydrolyze alginic acid effectively as in the case of hydrolytic hydrogenation of cellulose on Pt.[23] In addition, the role of ruthenium as an acid site was verified in hydrolysis of oligosaccharides into glucose.[4] The higher yields of sugar alcohols over the commercial catalyst can also be explained by the highest dispersion and the smallest size of Ru as listed in Table S1. As the effect of the crystallite size of Ru has already been determined, smaller Ru favored the formation of hydrogenated intermediate of cellobiose[24] and exhibited higher TOF on hydrogenation of glucose[25]. Hence, both the crystallite size of Ru in addition to the acidity of the catalyst should be taken into account for the conversion of alginic acid into sugar alcohols. The loss in carbon yield for ruthenium supported carbon catalysts were ascribed mainly to byproducts such as n-deoxy hexitols and pentitols, and to few C_2-C_4 sugar alcohols as analyzed by GC-MS (data not shown). The short chain sugar alcohols (C_2-C_4) accounted for less than 2%. Unfortunately, the quantification of the other byproducts could not be realized due to the absence of authentic samples.

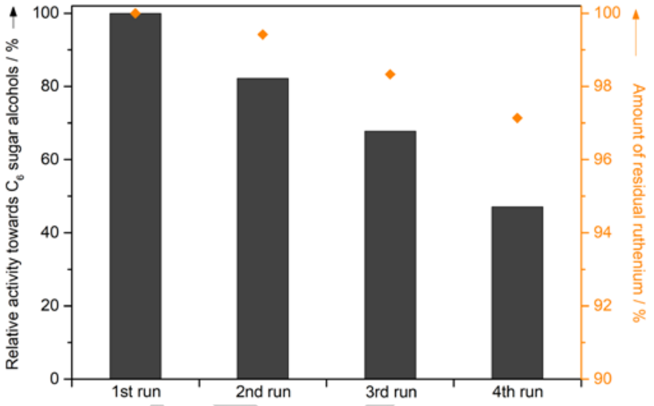

Figure 2. Recycling of Ru(5)/C(Alfa) at 180 °C for 2 h under 50 bar of H_2.

Regarding a practical application of heterogeneous catalysts, durability of catalysts is of great importance. To check the recyclability of the catalyst, Ru(5)/C(Alfa), in the reaction system, several identical batch reactions were performed, and liquid aliquots and spent catalysts were analyzed. As shown in Figure 2, ruthenium was leached from the catalyst after repeated reactions. The decrease of the yield of C_6 sugar alcohols is in line with the decrease in the amount of residual ruthenium over repeated reactions. Furthermore, as listed in Table 3, the CO chemisorption result shows that dispersions of Ru on carbon decreased from 36% to 11% along with the increase in crystallite size of the metal from 3.7 nm to 12.2 nm after 4th recycle run. Thus, the deactivation of the catalyst could be ascribed to the aggregation of ruthenium as well as to the leaching of the metal. In addition, Durability of the catalyst in a concentrated alginic acid solution was also examined since an industrial conversion of biomass occurs mostly in bulk. As listed in Table S2, the leaching of ruthenium was accelerated in concentrated solutions of alginic acid. Ruthenium was leached gradually from 0.5 to 2.40% in alginic acid solutions of concentration below 10%. However, a sharp leaching of Ru was observed in the reactant concentration of 30%. The reason for the intense leaching lies in the acidic nature of the reactant, alginic acid, which can behave as a ligand to form a metal-alginic acid complex.[26] The above results left us a future work of the development of a more robust and industrially

Table 3. Dispersion and crystallite size of ruthenium after the recycle reactions.[a]

Recycle Run	Dispersion [b] (%)	Crystallite size [b] (nm)
1st (Fresh catalyst)	36	3.7
2nd	29	4.6
3rd	19	6.9
4th	11	12.2

[a] the recycle reactions were performed at 180 °C for 2 h under 50 bar of H_2.

[b] Dispersions and crystallite sizes were measured by CO chemisorption.

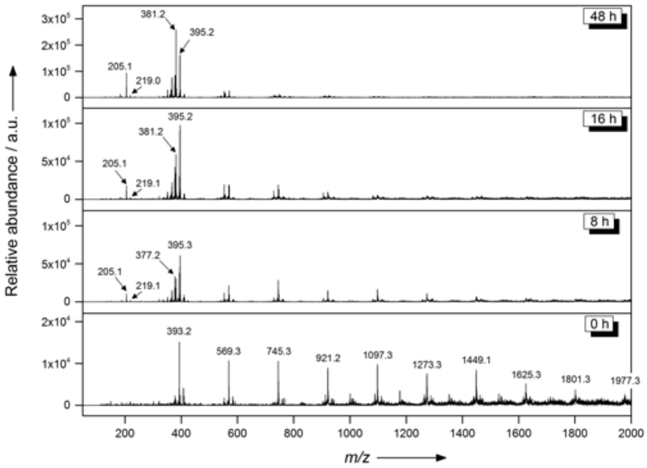

Figure 3. LC-MS spectra of products obtained at 90 °C under 50 bar of H_2 for different reaction times over Ru(5)/C(Alfa).

feasible catalyst for a bulk conversion of alginic acid to produce value-added chemicals.

To investigate plausible reaction pathways for the hydrogenation of alginic acid, kinetic studies were performed over Ru(5)/C(Alfa). Alginic acid was hydrolytically hydrogenated at 90 °C, and the resultant liquid products were then analyzed by LC-MS, as shown in Figure 3. It was observed that alginic acid was decomposed into chunks of oligomers ranging from dimer (m/z=393) to undecamer (m/z=1977) with a difference of 176 in m/z between neighboring peaks. At the early stage of the reaction, however, no sign of a peak corresponding to monomeric units (uronic acids, m/z=217) was observed. The above results suggest that the glycosidic bonds of alginic acid are cleaved in a random fashion; not in an ordered way releasing the outermost monomer unit one by one. As the reaction time was prolonged, aldonic acids (m/z=219) and sugar alcohols (m/z=205) started to be evolved along with the production of intermediates (m/z=377, 381, 393, 395) composed of two monomeric units. Unlike the case for the hydrolytic hydrogenation of cellobiose having one reducing aldehyde group where formation of only one intermediate, glucopyranosyl-glucitol, was observed,[24] the additional carboxylic group on monomeric unit causes the evolution of 5 different partially hydrogenated intermediates. From the result above, it could confidently be suggested that the formation of C_6 sugar alcohols from alginic acid occurs through the consecutive hydrogenation of both aldehyde- or carboxyl-ends in oligomeric compounds, which is then followed by the cleavage of the glycosidic bonds between alginic acid monomers to yield C_6 sugar alcohols. A reaction pathway for the formation of sugar alcohols through these intermediates was proposed in Scheme S2. Furthermore, relative amounts of each intermediates are shown in Figure S4. Only a small amount of aldonic acid (m/z=219) was produced, whereas the accumulation of intermediates (m/z=381 and 395) was observed. This implies that the hydrolysis of the glycosidic bond would be a rate-determining step in the catalytic conversion of alginic acid to sugar alcohols. Similarly, the cleavage of the ether linkage between glucose in cellulose, viz.

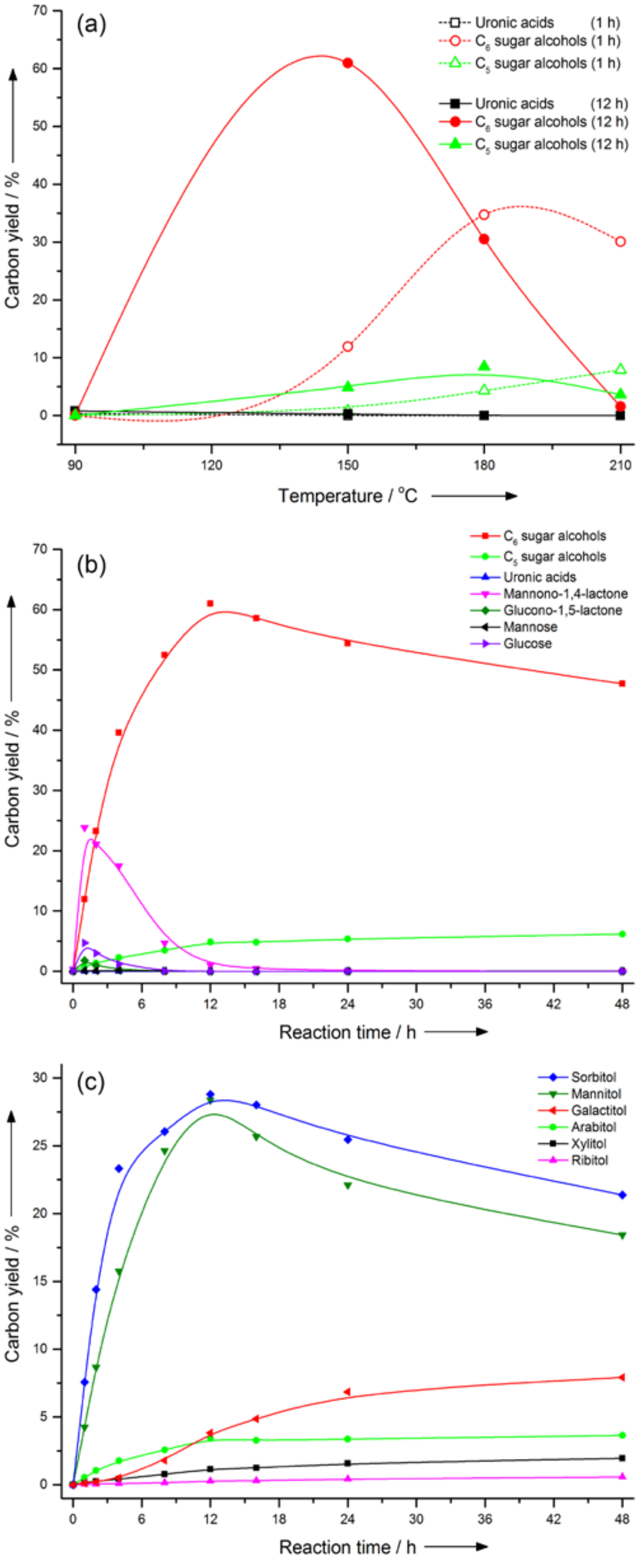

Figure 4. Yields of products as a function of reaction temperature (a), yield of products at 150 °C as a function of reaction time (b), and detailed sugar alcohol distribution at 150 °C as a function of reaction time (c) over Ru(5)/C(Alfa) under 50 bar of H_2.

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hydrolysis, is well-reported to be the rate-determining step in the hydrolytic hydrogenation of cellulose.[10a]

Since the difficulty lies in separating unreacted alginic acid from the catalyst and liquid products, conversion of alginic acid in this work was determined qualitatively by GPC analysis. As shown in Figure S5, the depolymerization of alginic acid over Ru(5)/C(Alfa) is promoted as the reaction time and temperature were increased. At reaction temperatures higher than 90 °C, alginic acid was completely converted into smaller molecules within 1 h of reaction. The facile conversion of the biopolymer in the absence of any acid catalyst is due partly to the increase of ion product of water at elevated temperatures[27] and partly to the Brønsted acid formed in-situ from Ru on carbon under pressurized H_2.[23] The effect of reaction time and temperature on the hydrolytic hydrogenation of alginic acid is quantitatively shown in Figure 4(a). As already shown in GPC analysis (Figure S5), the depolymerization of alginic acid proceeded tardily at low temperature, 90 °C, resulting in low yields of uronic acids (4.4%) and C_6 sugar alcohols (3.2%) even after a prolonged reaction (48 h). The yield of C_6 sugar alcohols increased sharply upon elevating the reaction temperature from 90 °C to 150 °C and the reaction time from 1 h to 12 h. The highest yield of C_6 sugar alcohols, 61.0%, was obtained when alginic acid was hydrolytically hydrogenated at 150 °C for 12 h over Ru(5)/C(Alfa) under 50 bar of H_2. However, further increase in temperature to 210 °C reduced the yield of C_6 sugar alcohol due to the decomposition of C_6 sugar alcohols into lower alcohols.[9a] In the early stage of the reaction, it was observed that aldonic acid lactones and sugars were evolved first as intermediates and disappeared with the production of C_6 sugar alcohols as shown in Figure 4(b). On the other hand, small amounts of uronic acids were observed, which again suggests that the consecutive hydrogenation of uronic acids into C_6 sugar alcohols is faster than the hydrolysis of alginic acid into uronic acids.

The yields of individual C_5 and C_6 sugar alcohols are shown in Figure 4(c). It was observed that both sorbitol and mannitol are mainly produced from alginic acid. In fact, the production of mannitol is a distinctive feature of the hydrogenation of alginic acid since sorbitol is predominantly produced by the hydrolytic hydrogenation of cellulose over various metal supported catalysts.[28] The difference in the distribution of sugar alcohols is most likely attributed to the composition of alginic acid since G and M can be converted to sorbitol and mannitol, respectively. To further investigate the origin of mannitol, alginic acid was analyzed by ^{13}C NMR analysis (Figure S6). The ^{13}C NMR analysis revealed that the alginic acid used in this work is M-rich, representing a ratio of M/G of ca. 2.5. In this regard, mannitol should have been produced more abundantly than sorbitol. However, as shown in Figure 4(c) and Figure 5(a), sorbitol was produced in larger quantities than mannitol for all the reaction conditions. Such discrepancy can be ascribed to two reasons: an isomerization of produced hexitols and different reaction rates of intermediates, aldonic acid lactones.

The isomerization of sugar alcohols has been frequently observed during the hydrogenation of cellulose or glucose.[9a, 10a, 28] Sugar alcohols equilibrate with each other in the presence of H_2[29] and the isomerization of sugar alcohols is catalyzed by metal sites, resulting in different sorbitol to mannitol ratios under various catalytic systems.[30] For example, the ratio was reported to be ca. 4 over Pt/γ-Al_2O_3[23] during the hydrogenation of cellulose and to be ca. 2 over Ru/C during the hydrogenolysis of sorbitol.[30] When alginic acid underwent hydrogenation in our catalytic system, the ratio was found to be ca. 1.2 over Ru/C as shown in Figure 5(a). To further investigate the equilibrium between sugar alcohols, model reactions were conducted under the same reaction condition using sorbitol, mannitol, glucose, mannose, and lactones as a reactant. As shown in Figure 5(b), regardless of the reactants used, the ratios converged to ca. 1.3. Such value is in accordance with the ratio obtained from raw alginic acid.

However, at the early stage of hydrogenation of alginic acid, the ratio reached ca. 1.8. This could be attributed to the different initial hydrogenation rates of intermediates such as

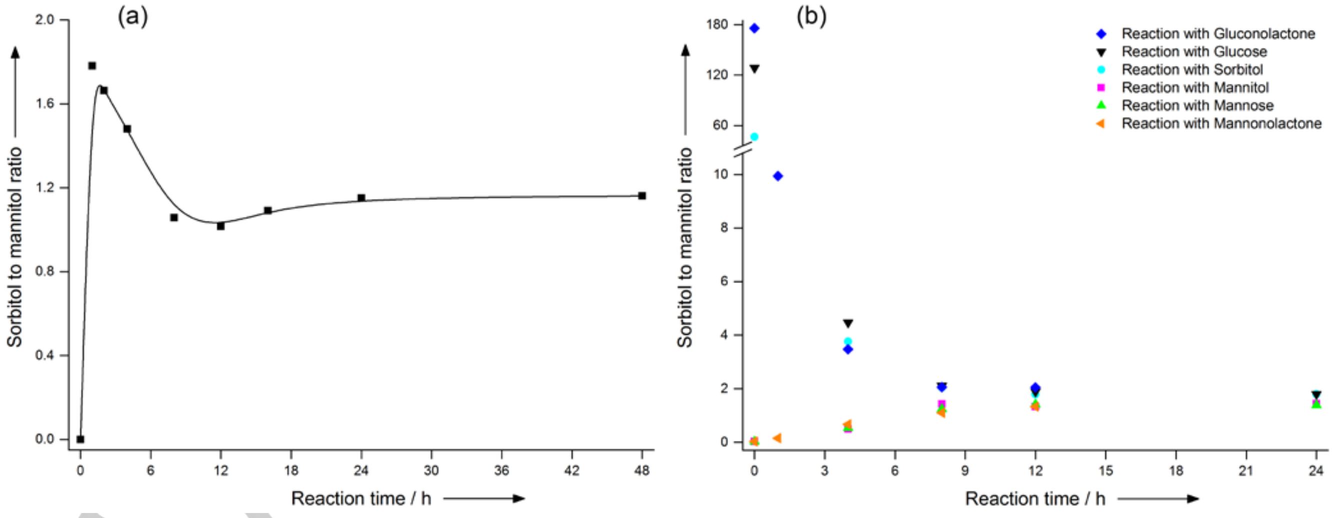

Figure 5. Time-course of sorbitol to mannitol ratio over Ru(5)/C(Alfa) during the hydrogenation of (a) alginic acid and (b) model molecules at 150 °C for 12 h under 50 bar of H_2.

mannonolactone and gluconolactone. As seen from the initial slopes of aldonolactone hydrogenation in Figure S7, gluconolactone was hydrogenated 5-fold faster than mannonolactone from which sorbitol and mannitol were produced, respectively. Thus, the ratio of sorbitol to mannitol could be higher than the value from the equilibrium at the early stage of the reaction.

Conclusions

The hydrolytic hydrogenation of alginic acid into sugar alcohols, mainly sorbitol and mannitol, was investigated for the first time over noble metal supported catalysts and a plausible reaction pathway of such was proposed. Hexitols were mainly produced over Ru supported on carbon catalysts whereas byproducts of dideoxy-aldonic acids and their lactones were produced over Pd, Pt, Rh, and Ir supported on carbon catalysts. The highest yield of C_6 sugar alcohols was obtained as 61% (sorbitol: 29%, mannitol: 28%, and galactitol: 4%) at 150 °C for 12 h under 50 bar of H_2 over ruthenium supported carbon. The consecutive hydrogenation of dimeric units of alginic acid with two reducible functional groups, carboxylic- and aldehyde-end, led to the formation of 5 different partially hydrogenated intermediates before cleaved into C_6 sugar alcohols over carbon-supported Ru. Mannitol was produced as much as sorbitol owing to the composition of alginic acid which is composed of two epimeric monomers and to the isomerization of hexitols. The leaching and aggregation of the active metal, Ru, after the reaction caused the deactivation of the catalyst. A green route proposed herein to produce sugar alcohols from alginic acid instead of cellulose could provide new opportunities to alleviate large dependence on lignocellulosic biomass and to better utilize macroalgae as an alternative renewable feedstock.

Experimental Section

Materials

Alginic acid and gluconic acid were purchased from Sigma-Aldrich. Mannuronic acid and guluronic acid were obtained from Qingda BZ Biotech. Sorbitol, mannitol, galactitol, arabitol, ribitol, xylitol, glycerol, propylene glycol, gluconolactone, mannose, and glucose were purchased from Alfa Aesar. Mannolactone was obtained from TCI Chemicals. The above authentic samples were used as received. Activated carbon was purchased from Sigma-Aldrich. The commercial catalysts, Pd(5)/C, Pt(5)/C, Rh(5)/C, and Ir(1)/C, were purchased from Alfa Aesar and used without further pretreatment.

Catalyst preparation

Activated carbon was partially oxidized with nitric acid of different concentrations to impart different amount of acid functionality. Typically, activated carbon was mixed with nitric acid with a volume to mass ratio of 10. After 3 h at 110 °C, the resultant carbon was retrieved by filtration, washed with distilled water until the filtrate became neutral, and then oven-dried at 100 °C overnight. The resulting activated carbons were denoted as AC-N-x, where x represents the molar concentration of nitric acid. 5 wt% of Ruthenium (Ru) was impregnated on the above activated carbons by conventional wet impregnation method. Ru(5)/AC-N-x was reduced at 400°C for 2 h under 10% H2 flow (50 ccm) before being used in the reaction.

Catalyst characterization

The specific surface area of the catalysts was determined by Brunauer-Emmett-Teller (BET) method on Micromeritics ASAP 2010. The samples were degassed at 250 °C for at least 4 h before the analysis at -196 °C. FT-IR spectra of the catalysts were measured on Agilent Cary 660 with resolution of 4 cm^{-1} using KBr pellets which contains 5wt% of a catalyst. CO chemisorption was performed on BEL-Cat (BEL JAPAN Inc.) to determine crystallite sizes and dispersion of ruthenium. Typically, the sample was pre-reduced at 350 °C for 2 h under 5% H2 flow (50 ccm). After the sample was cooled to the measurement temperature, 50 °C, under He flow (50 ccm), a CO pulse (4.98% CO/He, loop volume of 0.8570 cm3) was introduced until the saturated coverage was obtained. The acid density of the catalysts was analyzed by back titration using 0.01 M of NaOH solution and 0.02 M of HCl solution with a drop of phenolphthalein solution.

Catalytic reaction

A typical reaction procedure is as follows: hydrolytic hydrogenation was performed in a stainless-steel autoclave with an inner volume of 100 mL charged with 0.3g of alginic acid, 30 mL of distilled water, and the proper amount of catalyst. The mass ratio of the reactant to metal was 105. Air in the reactor was removed by flushing the reactor with 50 bar of helium 3 times and the reactor was then pressurized with 50 bar of hydrogen. The reactor was heated to the desired temperature within 30 min in an electric furnace. The reaction mixture was agitated by a mechanical impeller at 1000 rpm during the reaction. After the desired reaction time, the reactor was quenched with ice-cold water within 10 min to prevent further reaction.

To evalutate the recyclability of the catalyst, a multi-batch procedure was designed to compensate a weight loss, which frequently occurs during the catalyst recovery. Briefly, four indentical batch reactions were performed as described above. After each reaction, spent catalysts were retrieved via filtration and washed with distilled water and acetone, and dried in an oven at 100 °C. The spent catalysts were reused for the second run in three identical reactors and recovered again after the reaction for the next run. The same procedure was repeated for the third and fourth run.

Liquid products were analyzed by LC-MS, GC-MS, GPC, TOC, and ICP as described below.

Analytical methods

Gel permeation chromatography (GPC) was conducted on Ultimate 3000 (Dionex) equipped with a refractive index detector and a series of three columns (Waters Ultrahydrogel 120, 150, and 1000) maintained at 40 °C. 0.1M of sodium azide solution as a mobile phase was eluted at a flow rate of 1.0 mL/min. The instrument was calibrated with Pullulan having a molecular weight distribution of 342-80,500. The amount of Ru leached from the catalyst was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, PerkinElmer/Optima-4300 DV). The total organic carbon was measured using Sievers 5310 (GE) with an autosampler. Liquid chromatography-mass spectrometry (LC-MS) was performed on LCQ Deca XP Plus, Thermo Finnigan equipped with an electrospray ionization module working in a positive mode. The liquid sample was infused into the equipment with 0.1% formate buffer. The values of m/z are 23 higher than the actual molecular weight of molecules due to the formation of sodium adduct during the analysis. The qualification of reaction products was conducted using gas chromatography-mass spectrometry (GC-MS) equipped with a DB-5MS column (60 m × 0.25 mm × 0.25 μm). Since the resolution of GC for the separation of various sugar alcohols is superior to that of liquid chromatography, the quantification of products was performed on GC equipped with a DB-5 column (60 m × 0.25 mm × 0.25 μm). The liquid aliquot was silylated before being injected to

GC according to the method previously reported.[31] The carbon-based yield was calculated as follows:

Carbon yield (%) = 100 × (number of carbon atoms in an organic compounds/6) × (moles of an organic compounds in the product obtained by GC/moles of a repeating unit in alginic acid)

The composition of alginic acid, i.e. the ratio of mannuronic acid(M) to guluronic acid(G), was measured by 13C nuclear magnetic resonance (NMR) analysis referring to previous studies. The NMR spectrum was recorded using an NMR spectrometer (Bruker Avance II, 500 MHz) with a 4–mm probehead with a spectrometer frequency and spinning rate of 125.7 MHz and 5 kHz, respectively. The ratio M/G was calculated by using the areas of designated peaks shown in Figure S5 as expressed in the following equation:[32]

$M/G = (AE+AF)/(AD+AG+AH)$

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Keywords: biomass • heterogeneous catalysis • hydrogenation • alginic acid • sugar alcohol

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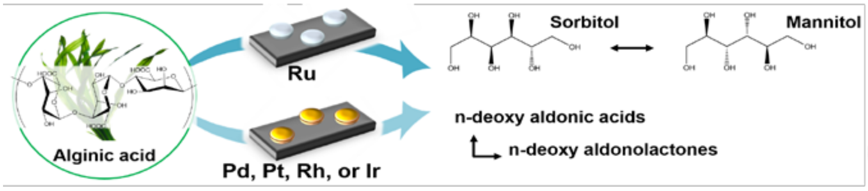

Sugar alcohols, mainly sorbitol and mannitol, were produced via the hydrogenation of macroalgae-derived alginic acid over noble metal supported on carbon. Ruthenium exhibited the highest yield of sugar alcohols among other noble metals.

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