Biorefinery

Catalytic Conversion of Cellulose into Sugar Alcohols**

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The production of energy, fuels, and chemicals from renewable biomass is important to prevent global warming by decreasing atmospheric CO_2 generated from the consumption of fossil fuels.[1] Biomass includes various plant components, such as starch and cellulose, that were originally formed by photosynthesis. Starch, a polymer of D-glucose with α-1,4-glycosidic bonds, is soluble in water and a main constituent of corn, rice, potato, and so forth. Attention has been paid to the use of starch to produce fuels and chemicals,[2,3] but starch should primarily be used as a source of food. On the contrary, cellulose is neither soluble in water nor digestible for humans because of its robust structure composed of β-1,4-glycosidic bonds of D-glucose.[4–6] The annual net yield of photosynthesis is 1.8 trillion tons, approximately 40% of which is cellulose.[4]

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This figure shows that cellulose is the most abundant organic compound in nature.

However, the utilization of cellulose has been limited to lumber, fuel, textile, paper, plastics, and so on because cellulose is resistant to degradation. Until now, a great deal of effort has been put toward the degradation of cellulose with enzymes,[4,6] mineral acids,[4,7] bases,[8] and supercritical water.[9] Among the serious drawbacks of these pathways are low activity and/or selectivity, separation of products and catalysts, corrosion hazard, generation of a large amount of neutralization waste, and harsh conditions. Therefore, a new "green" catalytic process is a challenge for the conversion of cellulose to value-added chemicals. In our study of biorefinery with heterogeneous catalysis,[10] we explored the catalytic degradation of cellulose. Herein, we report that supported Pt or Ru catalysts show high activity for the conversion of cellulose into sugar alcohols.

Scheme 1 shows the system studied which includes the hydrolysis of cellulose to glucose and the reduction of glucose
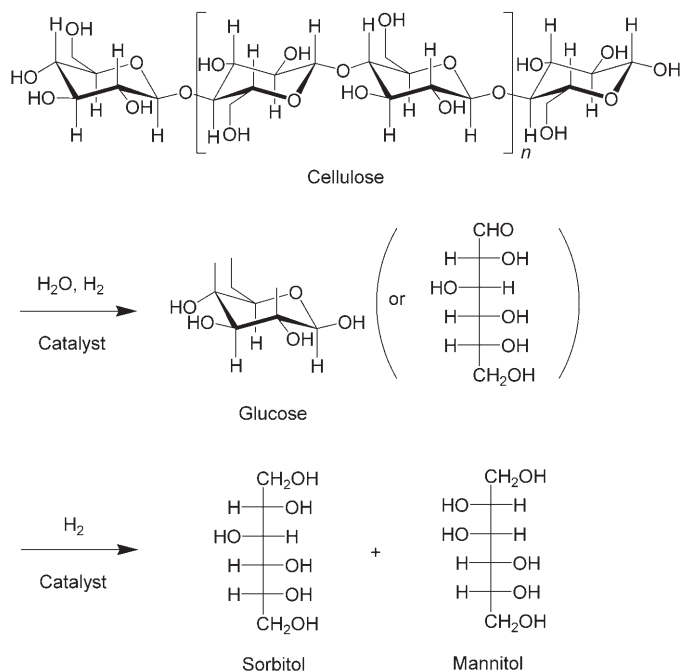
Scheme 1. Catalytic conversion of cellulose into sugar alcohols.

to sorbitol and mannitol. Water was used as the reaction media, and the separation of soluble products and the insoluble catalyst/substrate was readily carried out by filtration. Sorbitol is produced by the hydrogenation of glucose over Raney Ni[3,11] and is used not only as a sweetener but also as a precursor to isosorbide, 1,4-sorbitan, glycols, glycerol, lactic acid, and vitamin C.[3,12] Isosorbide increases the glass-transition point of poly(ethylene terephthalate). Recently, Dumesic and co-workers reported that H_2 for fuel cells[13] and C_{5-6} hydrocarbons[14] can be produced from sorbitol with higher selectivity than from glucose. Mannitol is also a sweetener and a precursor to useful compounds. Accordingly, the production of sorbitol and mannitol from cellulose would

be industrially important. The formation of sorbitol from soluble starch was reported in a patent that used Ru catalysts,[15] but no report has shown the catalytic conversion of insoluble cellulose into sugar alcohols.

The catalytic results are summarized in Figure 1, in which the values given in parentheses for the H form of ultrastable Y zeolite (HUSY) are the Si/Al ratios. $Pt/\gamma-Al_2O_3$ gave sugar
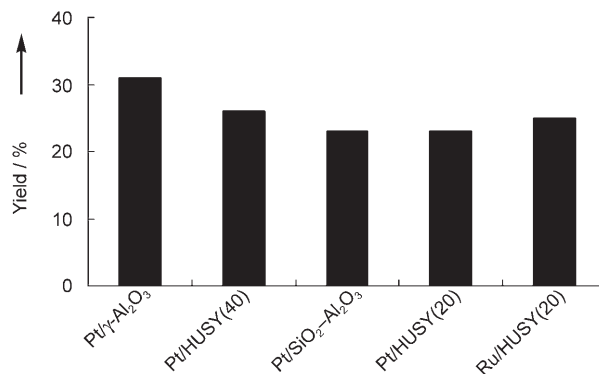

Figure 1. Conversion of cellulose into sugar alcohols by supported metal catalysts. Reaction conditions: cellulose (0.48 g), Pt catalyst (0.21 g), Ru catalyst (0.11 g; Pt, Ru 2.5 wt%), water (60 mL), initial H_2 pressure at RT = 5 MPa, 463 K, 24 h.

alcohols in 31% yield (sorbitol: 25%, mannitol: 6%), and sorbitol was the main product, with a molar ratio of sorbitol/mannitol of 4:1 or higher. The formation of mannitol suggests the epimerization of sorbitol by solid acids. In fact, a small amount of mannitol was formed by using sorbitol as a substrate over the Pt catalysts under the reaction conditions. Among the supported metal catalysts we tested, Pt and Ru catalysts gave high yields of the sugar alcohols, but Pd, Ir, and Ni catalysts showed low activity (see the Supporting Information). The choice of support material was important, with $\gamma-Al_2O_3$, HUSY(40), $SiO_2-Al_2O_3$, and HUSY(20) giving high yields (other supports showed low activity as reported in the Supporting Information). From these results, solid acidity[16] seems to be effective for the catalytic reaction, but the activity does not correspond well with the apparent strength of the acid. It was reported that Ru/HUSY prepared from NaY zeolite (LZY-52) is active in the conversion of starch to sorbitol,[15] but this catalyst showed low activity (0.7% yield) in our reaction of cellulose.

In the optimization of the reaction temperature, the highest yield was observed at 463 K in the range of 443–473 K over $Pt/\gamma-Al_2O_3$ (see the Supporting Information). The catalysts were recyclable in repeated runs. After the first run with $Pt/\gamma-Al_2O_3$, the catalyst and the remaining cellulose were filtered and washed with water, fresh cellulose and water were added, and the mixture was used for the next run. Similar yields of the sugar alcohols were obtained in up to three cycles (see the Supporting Information). These results indicate that the catalyst is not deactivated in the course of the catalytic runs.

The support materials were also used as catalysts under the conditions that employed H_2 pressure (Figure 2). Only a
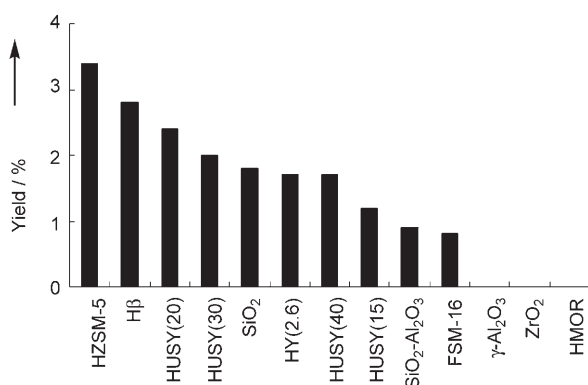
Figure 2. Hydrolysis of cellulose into glucose by support materials. Reaction conditions: cellulose (0.16 g), catalyst (0.068 g), water (20 mL), initial H_2 pressure at RT = 5 MPa, 463 K, 24 h. The yields are based on the number of moles of the initial $C_6H_{10}O_5$ unit in cellulose. HZSM-5 = H form of zeolite Socony mobil, HY = H form of Y zeolite, FSM-16 = folded sheets of mesoporous material, HMOR = H form of moredenite.

small amount of glucose was formed with yields of less than 4%, thus indicating that the metal promotes the hydrolysis of cellulose. Hence, it is suggested that the acid sites for the hydrolysis of cellulose are generated in situ from H_2 in addition to the acidic surface sites intrinsic in the support.[17] In this mechanism, H_2 is dissociatively adsorbed on the metal surface and the hydrogen species reversibly spill over onto the support surface. The acidic sites catalyze the hydrolysis of cellulose to glucose, and the C=O group in glucose is readily reduced by Pt or Ru with H_2 to form sorbitol (Scheme 1). The former hydrolysis is a rate-determining step because the reduction of glucose gave an almost stoichiometric amount of sorbitol over the Pt or Ru catalysts.

The maximum yield was not improved when the reaction was carried out over 72 hours (see the Supporting Information). This finding implies that the further degradation of cellulose was restricted as a result of its robust structure. Previous reports on the hydrolysis of cellulose recognized that the factors that control the conversion of cellulose are crystallinity, degree of polymerization, availability of chain ends, and fraction of accessible bonds.[6] These factors play a significant role in our reactions, in which both substrate and catalyst are solid.

As described above, we have demonstrated for the first time that supported metal catalysts can convert cellulose into sugar alcohols by an environmentally friendly process. This green process opens new opportunities for the use of abundant and inexpensive cellulose as a chemical feedstock with heterogeneous catalysis.

Experimental Section

Support materials and metal precursors are summarized in the Supporting Information. The supports were dried under vacuum (ca. 0.1 Pa) at 423 K for 1 h. Typically, an aqueous solution of $[Pt(H)_2Cl_6] \cdot x H_2O$ (5 mL, 15 mg) was added to a mixture of γ-Al_2O_3 (Nishio, A-11, 200 mg) and water (20 mL). The reaction mixture was stirred for 15 h, evaporated to dryness, and dried under vacuum for

24 h. The sample was calcined in O_2 at 673 K for 2 h and reduced in H_2 at 673 K for 2 h to give Pt/γ-Al_2O_3 (Pt 2.5 wt%). Ru/HUSY catalysts were prepared by the various methods given in the Supporting Information.

A typical procedure: cellulose (Merck, Avicel, microcrystalline, 0.16 g), Pt/γ-Al_2O_3 (0.068 g), water (20 mL) and a stirring bar were charged in a stainless-steel autoclave (Taiatsu TPR2, 30 mL). Three-fold scale-up reactions were also performed in an MMJ-100 reactor (OM Lab-Tech). The autoclave was heated at 463 K for 24 h after pressurization with H_2 to 5 MPa at RT. After the reaction, the reaction mixture was centrifuged and the filtered solution was analyzed by HPLC (Shimadzu LC10AT*VP*, RI detector, Shim-pack SPR-Ca column (250 × 7.8 mm), mobile phase: water). Sorbitol and mannitol were characterized by LC–MS (Shimadzu LCMS-2010 A). The yield of sugar alcohols was calculated as follows: yield (%) = (mol of sorbitol and mannitol)/(mol of $C_6H_{10}O_5$ unit in charged cellulose) × 100. Initial ratio of substrate/catalyst (S/C) was 110 (S = mol of $C_6H_{10}O_5$, C = g atom of bulk metal).

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