Cellulose Conversion by Supported Metal Catalysts

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Introduction

Currently much attention has been focused on the synthesis of fuels and chemicals from nonfood biomass. Cellulose is the most abundant organic compound in nature as a main component of plants. However, cellulose is resistant to degradation due to its robust crystal structure. The degradation of cellulose has been carried out using enzymes or mineral acids, but these processes have drawbacks of the difficult separation of products/catalysts and the generation of lots of waste. In our study of the catalytic conversion of sugar compounds [1], we explored the conversion of cellulose by supported metal catalysts (Figure 1) [2-4].

Materials and Methods

Supported metal catalysts were prepared by the impregnation method. Catalytic reactions were performed in a stainless-steel high-pressure reactor, in which cellulose (Avicel), catalyst (metal 2-3 wt.%) and water were charged. Then the reactor was pressurized with H_2 (5 MPa) and heated at 463 K for 24 h. Products were analyzed by HPLC, LC-MS, GC-MS and NMR.

Results and Discussion

Figure 2 summarizes the typical catalytic results using supported Pt or Ru catalysts. Pt/γ-Al_2O_3 gave sugar alcohols in 31 % yield (sorbitol 25 %, mannitol 6 %), and the selectivity of the two sugar alcohols was 88% based on the converted glucose units. Among the catalysts tested, supported Pt and Ru catalysts gave high yields of the sugar alcohols, while Rh, Pd, Ir and Ni ones showed low activity. The choice of support material is important; γ-Al_2O_3, HUSY and SiO_2-Al_2O_3 gave high yields. The separation of products and catalysts was easy by filtration, and the recovered catalysts were recyclable in repeated catalytic runs.

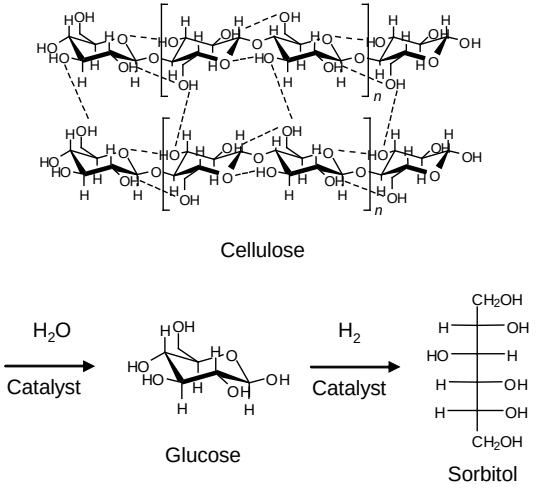

Figure 1. Catalytic conversion of cellulose into sorbitol.

The support materials without metal showed only 4 % yield of glucose. Therefore, it is proposed that in situ generated acid sites are responsible for the hydrolysis of cellulose. Then glucose is readily converted to sorbitol by the reduction over the metal catalysts with H_2. Presumably, the former hydrolysis is the rate determining step, because under the reaction conditions glucose gave almost a stoichiometric amount of sorbitol and mannitol (ca. 4-5:1 molar ratio) over the Pt or Ru catalysts.

Pre-treatment of cellulose with ball-milling is significantly effective; the yield of soluble sugar alcohols (sorbitol, mannitol, sorbitan) is 50-60% yield. The pre-treatment increases the ratio of the amorphous part of cellulose, which is a key to the high conversion of cellulose.

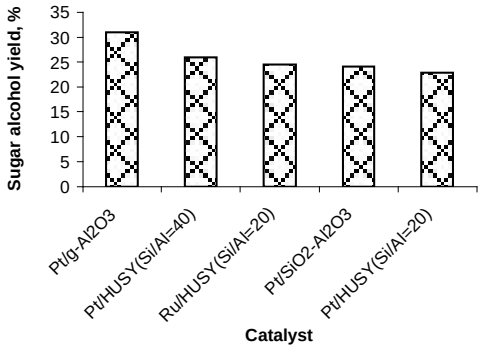

Figure 2. Yields of sugar alcohols from cellulose by supported metal catalysts.

In summary, we have demonstrated that supported metal catalysts are able to convert cellulose into sorbitol and related sugar compounds with high activity and selectivity. Sorbitol is thermally more stable than glucose and would be a good precursor to a variety of chemicals [3-4]. In fact, sorbitol is practically used as a sweetener and potential precursors to glycols for plastics, hydrogen for fuel cells and ethanol by fermentation. Therefore, this finding has opened new opportunities for heterogeneous catalysis in the conversion of cellulose to sustainable chemicals.

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Significance

We showed the world-first catalytic, selective conversion of cellulose into soluble chemicals. Our work has been a trigger of others on the catalytic conversion of cellulose which has become an active topic in the past two years.

References

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