学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Catalytic Conversion of Biomass-Derived Sugars to Renewable Chemicals

（バイオマス由来糖から再生可能化学品への触媒変換の研究）

The development of human society since the Industrial Revolution in the 18th century has been driven by using fossil resources. However, the mass consumption leads to their rapid depletion and may cause irreversible climate change due to quick global warming. For achieving the goal of sustainable development, it is necessary to promote the utilization of non-depleting, renewable resources. Recently, biomass has attracted much attention as a renewable carbon resource, because it is abundant and its use is carbon neutral. Sugars derived from biomass can be converted to versatile platform chemicals, but the conventional methods rely on edible foods such as starch. They are relatively easy but compete with food production, which I believe is unsuitable for SDGs. Therefore, in this work, I used sugar compounds contained in inedible food wastes to synthesize chemicals. To achieve the objective, the author proposed using artificial catalytic reactions, as they are designable and applicable for varied reaction conditions to maximize the efficiency for particular objectives. As a product, the author is interested in plastics as they are value-added and can be used for a long time different from fuels. Moreover, biomass-derived plastics often show superior characteristics to petroleum-based ones. An obvious example is isosorbide, a fused five-membered ring compound derived from glucose, which is a precursor to engineering plastics such as the polycarbonate with outstanding physicochemical properties named Durabio. This inspired the author an analogy to use N-containing sugars, where the corresponding five-membered ring compound may be a source for N-containing plastics, thus expanding the chemistry and the diversity of plastics. Based on the background, the author focused on the catalytic conversion of both typical and N-containing sugars to five-membered ring compounds as precursors to plastics.

Chapter 1 describes the background of the study and the objective of this work in detail. A broad overview is provided to show the significance of this work.

In Chapter 2, the author studied the dehydration of a chitin-derived N-containing sugar alcohol (2-acetamido-2-deoxysorbitol, denoted ADS) to a fused five-membered ring compound (2-acetamide-2-deoxyisosorbide, ADI). The dehydration reaction takes place in two steps: (i) that of ADS to anhydro-ADS (AHADS) and (ii) that of AHADS to ADI. In previous works, a predominant issue was that basic amide groups in ADS and AHADS capture protons strongly to weaken the activity, and therefore a large

amount of superstrong acid was needed. In this work, I found that H_3PO_3 shows remarkably high activity in spite of the weak acidity. The second step is very slow in conventional acid-catalyzed reactions, whereas H_3PO_3 provides a rather higher rate constant for the step than that of the first step due to a different reaction mechanism. The author clarified the new mechanism by spectroscopies and DFT calculations. Specifically, H_3PO_3 produces phosphite esters with ADS and AHADS, and P=O groups in the esters are easily protonated so that the phosphite groups are eliminated for producing the desired product by S_N2 reactions. I emphasize the significance of a new reaction mechanism of sugar dehydration condensation given by H_3PO_3 catalyst.

In Chapter 3, the author applied the H_3PO_3 system to the dehydration condensation of sorbitol to isosorbide. Again, H_3PO_3 showed the highest activity among the weak acids tested. A mechanistic study suggested that the reaction passes through the H_3PO_3 ester mechanism. The reaction gives phosphite esters of sorbitan and isosorbide to some extent as final products, but they can be readily hydrolyzed by reflux in water to improve the yield of isosorbide and to recover H_3PO_3.

In Chapter 2 and 3, I studied the catalytic conversion of ADS and sorbitol to five-membered ring compounds. As the source of sorbitol, the conventional industry uses food crops, which compete with the food supply. Therefore, in Chapter 4, I studied the pretreatment and catalytic conversion of an inedible food waste (molasses) to supply sorbitol efficiently. Molasses contains abundant biomass-derived sugars, but it also includes a large amount of impurities. I found that organosulfur compounds involved in molasses strongly suppress the hydrogenation of the sugars to sorbitol with Raney Ni catalyst under H_2 pressure. A clay material, montmorillonite K10 (MK10) selectively adsorbed the catalyst poisons, and the MK10-pretreated sample significantly increased the yield of sorbitol. Kinetic analysis of the reaction shows that the hydrogenation of sugars is the rate-determining step, and the reaction prefers a lower temperature to produce sugar alcohols because the formation of by-products has higher activation energies than that of the hydrogenation.

Chapter 5 summarizes the important results. In this dissertation, I explored the catalytic conversion of biomass-derived sugars to synthesize value-added chemicals, particularly the fused five-numbered ring compounds as precursors to engineering plastics. H_3PO_3, a weak acid, showed characteristic activity for the dehydration condensation of sugar alcohols, via a special mechanism containing phosphite esters. The low-cost and low-corrosion property of H_3PO_3 makes it useful as an alternative to strong acids. This dissertation also established an efficient method of obtaining sugar alcohols from an inedible food waste, which hopefully enhances the utilization of such wastes for chemical production and contributes to ensuring food supply. I believe that this dissertation will help in the further development of sugars-based biorefinery to sustain our civilization continuously.