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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（理学）

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学 位 論 文 題 名

Carbon-catalyzed hydrolysis of cellulose to cello-oligosaccharides

(炭素触媒によるセルロースのセロオリゴ糖への加水分解反応)

Cellulose, a polymer composed of repeated anhydro-glucose units linked by β -1,4-glycosidic bonds, is the most abundant component in lignocellulosic biomass. Cello-oligosaccharides are short chain linear polymers that can be produced by partial depolymerization of cellulose. They exhibit biological activity that can benefit the growth and health of plants, animals, and humans, and thus provide multiple benefits to healthcare and agriculture industries. Commercial application of cello-oligosaccharides is limited due to the high-cost of their synthesis. Therefore, cost-effective production of cello-oligosaccharides from cellulose is attractive. During the hydrolysis of cellulose cello-oligosaccharides are formed as intermediates. Selective synthesis of cello-oligosaccharides is difficult because they are water soluble and undergo hydrolysis at a faster rate in comparison to cellulose in the presence of a homogeneous acid catalyst, resulting in formation of glucose. However, when cellulose is adsorbed on heterogeneous carbon catalyst, its hydrolysis is faster than the subsequent hydrolysis of cello-oligosaccharides. Given this, I chose carbon materials as catalysts to synthesize cello-oligosaccharides by hydrolysis of cellulose. An innovative semi-flow reactor was developed for the reaction in which the products could be rapidly removed from the reaction system, preventing their successive hydrolysis. In addition, a kinetic study was performed to understand the underlying mechanism of cellulose hydrolysis.

In Chapter 1, the purpose of this dissertation and background of the study are described in detail. A broad overview is provided to establish the benefits of using cellulose as a renewable resource for various chemicals. Current research in cellulose conversion is discussed in the context of different value-added products including cello-oligosaccharides. Various strategies are then analyzed for partial hydrolysis of cellulose such as the use of enzymes, homogeneous acids and heterogeneous catalysts. Problems relating to cello-oligosaccharides synthesis are defined and then used to frame the objective of this thesis and its scope.

Chapter 2 describes the synthesis and characterization of carbon catalyst and its activity for cellulose hydrolysis to cello-oligosaccharides. This carbon catalyst (AC-Air) was prepared by oxidation of activated carbon to introduce weakly acidic functional groups without altering the microporous structure. 72 % yield of cello-oligosaccharides was obtained after hydrolysis at 473 K for 40 min over AC-Air in the semi-flow reactor with limited yield of dimer and monomer. The presence of acidic functional groups and the adsorption of cellulose on carbon by mix-milling were both crucial for this high activity. In addition, a method for

quantitative analysis of individual cello-oligosaccharides was developed by using MALDI-TOF mass spectrometry, which holds high significance in the cello-oligosaccharides research owing to the dependence of efficacy on chain length. Cello-oligosaccharides with a degree of polymerization (DP) up to 13 were observed with celohexaose and celloheptaose obtained as the major products at a space velocity of 70 h⁻¹. The product distribution was controlled by adjusting the reaction conditions. For example, by reducing the space velocity, cellotriose can be obtained as the primary product instead of celohexaose. ¹H NMR and FTIR analysis confirmed the structure of β -1,4 linked straight-chain cello-oligosaccharides and the absence of branching or impurities.

In Chapter 3, a kinetic analysis was performed to understand the mechanism for hydrolysis of β -1,4-glycosidic bonds in cellulose. Cello-oligosaccharides were chosen as model compounds to evaluate the change in hydrolysis rate with respect to molecule size and elucidate the underlying factors from a mechanistic perspective. Only in the presence of carbon catalyst, the rate of hydrolysis of individual cello-oligosaccharides was strongly dependent on their chain length. Larger cello-oligosaccharides underwent hydrolysis at a much faster rate. This behavior was unique to carbon catalyst, and other solid catalysts showed no such trend. The difference in rate constant of hydrolysis with chain length explains the accumulation of cello-oligosaccharides in the presence of carbon catalyst with low yield of glucose during the cellulose hydrolysis in Chapter 2. Stronger adsorption affinity and a reduction in apparent activation energy for hydrolysis were observed with the increase in cello-oligosaccharides size. Based on these observations, a plausible mechanism was proposed that larger molecules experience a greater degree of conformational distortion during their adsorption within the micropores of carbons. This leads to reduction in activation energy required to cleave the glycosidic bond and enhances the rate of reaction.

In Chapter 4, I modified the synthesis method of carbon catalyst to increase the hydrolysis activity with the aim of obtaining high yield of water-soluble cello-oligosaccharides with lower molecular size (DP ranging from 3-6). These short chain cello-oligosaccharides exhibit high bioactivity as elicitors for improving the growth of plants. Chemical oxidation of activated carbon by ammonium persulfate (APS) was an efficient method which introduced large amount of weakly acidic functional groups, especially carboxylic groups. 70 % yield of cello-oligosaccharides was achieved from cellulose hydrolysis over this catalyst in the semi-flow reactor. The product distribution showed higher yield of desired cello-oligosaccharides (cellotriose to celohexaose). The high activity of this catalyst was attributed to the high density of carboxyl functional groups. Based on temperature programmed desorption analysis, we also postulate the formation of vicinal carboxyl groups which are most active for this reaction. In addition, it was important to note that only 30 min of mix-milling pretreatment was required by using this catalyst, which decreased the energy consumption, whereas 1 h of mix milling was necessary when AC-Air was used as catalyst to achieve the same result.

Chapter 5 summarizes the important results discussed in the thesis. Synthesis of cello-oligosaccharides from cellulose can provide multiple benefits to agriculture and healthcare industries. This dissertation has proved that carbon materials are effective catalysts for selective formation of cello-oligosaccharides from hydrolysis of cellulose. The distribution of products can be controlled by adjusting the reaction conditions and catalyst activity, which is important for their applications in industry. The results obtained in this study provide essential insights for understanding the cellulose hydrolysis on carbon catalyst. I believe that the process developed in this dissertation is a promising and cost-efficient approach to achieve the large-scale application of cello-oligosaccharides.