A GLUCOSE-DERIVED CARBONACEOUS SOLID ACID CATALYST FOR CELLOOLIGOSACCHARIDES HYDROLYSIS IN AN AQUEOUS REACTION SYSTEM

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An amorphous carbon based catalyst was prepared by carbonation and sulfonation of several typical biomass materials, including glucose, microcrystalline cellulose, sugarcane bagasse, eucalyptus, switchgrass and microalgae. Preliminary experimental results on cellobiose hydrolysis indicated that the catalyst prepared from glucose exhibited the highest catalytic activity. Thus, methods, including SEM, XRD, FT-IR, NH_3-TPD and elemental analysis, were employed to characterize the catalyst before and after sulfonation. Compared with other conventional solid acid catalysts, the catalyst bearing $–SO_3H$, -COOH, and -OH groups exhibited remarkable activity in the hydrolysis of β-1,4-glycosidic bonds and no other by-reactions were detected in further hydrolysis experiments. After the hydrolysis reaction, the solid acid catalyst could be readily separated from the saccharide solution for reuse without any significant loss of activity.

Keywords: carbonaceous solid acid, hydrolysis, cellooligosaccharides

INTRODUCTION

Cellooligosaccharides, which are abundant in agricultural and industrial waste, represent carbon–neutral renewable resources for the production of biofuels and valuable chemicals, including ethanol, hydrocarbons and starting materials for polymers.[1,2] Cellooligosaccharides are polymers composed of glucose linked by β-1,4-glycosidic bonds. Oligomers comprising 2 to 6 units may be water soluble, however, polymers containing 7-13 units are often only partially soluble in hot water. Bigger molecules, with inter- and intra-molecular hydrogen bonds, afford high chemical stability and insolubility in most solvents, including water.[3,4] The hydrolysis of cellooligosaccharides to glucose can be catalyzed by enzymes or acids. The enzymatic route remains a slow, energy intensive and expensive process.[5] Sulfuric acid has been used as another typical catalyst for this hydrolysis reaction. However, this process often suffers from the corrosive property of the acid, complicated products separation and neutralization requirements of the waste acids produced.[6] Other reports can be found in the literature on the conversion of cellooligosaccharides by heteropolyacids and ionic liquids. However, such methods exhibit certain limitations, *e.g.*, separation issues, low recyclability, corrosive properties and low yields.[2]

Solid acids may be selected as effective catalysts used in this type of hydrolysis reaction due to characteristics including reduced corrosiveness, increased safety, reduced waste, ease of separation, and recovery.[7] The SO_3H groups, bearing carbonaceous solid acid (CSA) and prepared via sulfonation of the amorphous carbon or active carbon at high temperature, exhibit a considerable catalytic activity for the hydrolysis of cellulose. Suganuma *et al.* first employed the hydrolysis of cellulose and several

solid acids prepared from a variety of raw materials and under different conditions have been developed to facilitate the hydrolysis of cellulose, starch, or other polysaccharides with moderate to good glucose yields.[1,8] Due to the complex structure of cellulose, the mechanisms of CSA preparation and hydrolysis reaction still remain largely unknown.

In this article, a highly dispersive CSA catalyst prepared from glucose for polysaccharide hydrolysis has been successfully synthesized. Methods including SEM, XRD, FT-IR, NH_3-TPD and elemental analysis were employed to characterize the catalyst before and after sulfonation. Compared with traditional catalysts, the obtained CSA exhibited a higher activity in the hydrolysis of cellooligosaccharides due to high acid density, large surface area and water dispersibility.

EXPERIMENTAL

Catalyst preparation

A typical preparation of the catalyst included two steps, carbonation and sulfonation. First, 3 g of raw material powder was heated in a tube furnace under N_2 flow. The temperature increasing rate was 5 °C/min and was maintained at 400 °C for 1 hour. Then, 0.2 g of the carbon precursor obtained from inadequate carbonation of the raw material was heated in 10 mL sulfuric acid at 80 °C for 12 h to for the introduction of $–SO_3H$ groups. After cooling to room temperature, the suspension was filtered and washed repeatedly with boiling distilled water until no impurities, *e.g.* sulfate ions, could be detected in the aqueous wash. Since only a small amount of the excess sulfuric acid was consumed during the sulfonation, the sulfuric acid recovered after filtration could be reused.

Characterization

Structural information about the prepared carbon precursor and the solid acid catalyst was obtained by scanning electron microcopy (SEM, S4800, Japan), powder X-ray diffraction (XRD, X'Pert Pro MPD, PANalytical), Fourier transform infrared spectroscopy (FT-IR, TENSOR27, BRUKER), and temperature programmed desorption (TPD, ASIQACIV200-2, USA) spectral analysis. The sample composition was determined by elemental analysis (C, H, N, S and O) using an elemental analyzer (Vario MICRO cube, Elementar).

Hydrolysis of cellooligosaccharides

The hydrolysis of cellobiose was performed in a PTFE cylindrical reactor by reacting 0.05 g of the catalyst, 0.06 g of cellobiose and 3 mL of distilled water. In the case of cellulose hydrolysis, 0.15 g of the catalyst, 0.05 g of cellulose and 20 mL of distilled water were added to the reactor. The mixture was heated at 120 °C for 12 h with stirring and then cooled to room temperature. The reaction contents were filtered and the solution was analyzed by high-performance liquid chromatography (HPLC with UV detector, Waters). The solid was collected for further analysis and reuse.

Cellooligosaccharides conversion and the yield of glucose were determined using the following equations: Cellooligosaccharides conversion (%) = 100 x (B+C)/A, while Glucose yield (%) = 100 x B/A where A is the total amount (mg) of glucose monomer in cellooligosaccharides; B is the amount (mg) of glucose produced by acid-catalyzed hydrolysis and C is total amount (mol) of glucose monomer soluble in water.

RESULTS AND DISCUSSION

Preliminary experiments on raw material

Glucose, microcrystalline cellulose, sugarcane bagasse, eucalyptus, switchgrass and microalgae are several typical types of biomass selected as raw material for CSA preparation in the present work. Glucose is one of the most common monosaccharide featuring a simple structure and originating from a wide range of sources.[9] Microcrystalline cellulose is the basic constituent for all types of biomass feedstock.[10] The results of component analysis shows that the content of cellulose in bagasse, switchgrass, eucalyptus was 42%, 37% and 40.8%, respectively. Bagasse and eucalyptus are regular biomass feedstocks, resulting from post-industrial waste and forestry processing.[11-13] The materials represent typical herbaceous and woody materials. Switchgrass and microalgae are both novel biomass feedstocks investigated in various experimental studies, mainly applied to prepare biogas and refined carbohydrates or fats. Considering modern trends in large-scale applications, switchgrass and microalgae were also used in this experiment for the preparation of the catalysts and preliminary studies were carried out to determine the catalytic activity in the hydrolysis of glycosidic bonds. As shown in Figure 1, among all CSAs synthesized by the same preparation method, glucose-derived CSA exhibited the highest catalytic activity in cellobiose hydrolysis. Both the cellobiose conversion and glucose yield could be achived with high yields, *i.e.* 91.51% and 85.42%,

respectively. The results of another set of experiments were much lower, of approximately 50%. The reason for this finding may be due to the experimental conditions of carbonization and sulfonation, including material ratio, heating temperature and duration. All these parameters were adjusted according to the characteristics of glucose[14] and the glucose-derived catalyst was formed in line with the requirements of the experiment.

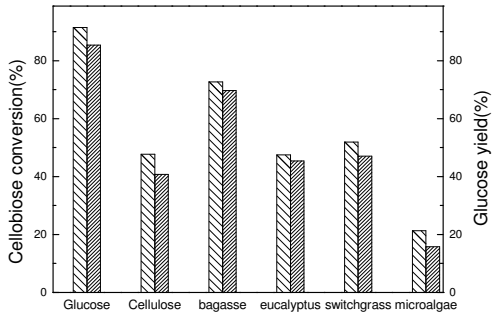

Figure 1: Catalytic activity of the CSAs prepared from different raw materials

However, under the same conditions, only a dehydration reaction was determined to occur on the other raw materials used in the experiments and the internal molecules did not rearrange to meet the structural requirements of the catalyst. Additionally, the molecular structure of glucose is simple, which is why we decided to select glucose as a raw material for the in-depth study of CSA. This was done in an effort to fully understand the spatial structure and composition of the active groups to obtain a high catalytic activity for cellooligosaccharides hydrolysis and in order to provide a more theoretical basis for suitable CAS preparation.

Structural characterization

Structural information on glucose, carbon precursor and CSA was obtained by SEM, XRD, FT-IR, NH_3-TPD and elemental analysis.

Figure 2 shows SEM images of the raw material (Fig. 2a, b) and carbon precursor after carbonation (Fig. 2c, d, e, and f) with varying magnification. As can be seen from the SEM images (Fig. 2a, b), the glucose crystals are arranged loosely and irregularly, with an average particle size of about 200 μm. After heating at 400 °C for 1 h, glucose was found to be partly dehydrated and incompletely carbonized. Therefore, the polymerization degree of the carbon precursor increased remarkably (Fig. 2c, d). The main structure of the graphite sheet layer was regular (Fig. 2e) and after grinding, the surface was easily removed forming small particles with an average particle size of about 500 nm (Fig. 2f). Therefore, the surface area of the catalyst and the ratio of the contact between catalyst and substrate could be significantly increased.

Figure 3 shows the XRD patterns for the carbon precursors before and after sulfonation. Due to the presence of amorphous carbon, the XRD pattern for the carbon precursor prepared by glucose exhibited broad diffraction peaks at a 2θ angle of 10º-30º with the center at about 20°, representing the reflection of the stacking degree of the aromatic carbon sheets. After sulfonation, the (002) peak of CSA was found to be more symmetrical than that of the carbon precursor and the center moves to a relatively higher 2θ angle of about 25º, corresponding to the (002) planes of the micrographites oriented in a random fashion.[14,15] Moreover, a new weak diffraction peak at 2θ = 35º-45º appeared due to the (100) axis of the graphite structure.[15] These changes of the XRD pattern suggested that during the sulfonation step, the carbon precursor was further carbonized and the crystallite growth of the graphite proceeded, introducing amorphous carbon composed of aromatic carbon sheets.[1] Figure 4 shows the FT-IR spectrum of the carbon precursor (a) and the CSA (b). Comparing the two curves, significant differences can be observed, as follows: firstly, the relative intensity of the bands at around 3300 cm^{-1} could be assigned to the stretching vibration of O-H and increased significantly.[16] This finding indicates

the existence of a large number of residual hydroxyl groups on CSA after sulfonation.[17] Secondly, the peaks at 2800-3000 cm^{-1} may be assigned to the C–H stretching and almost disappeared.

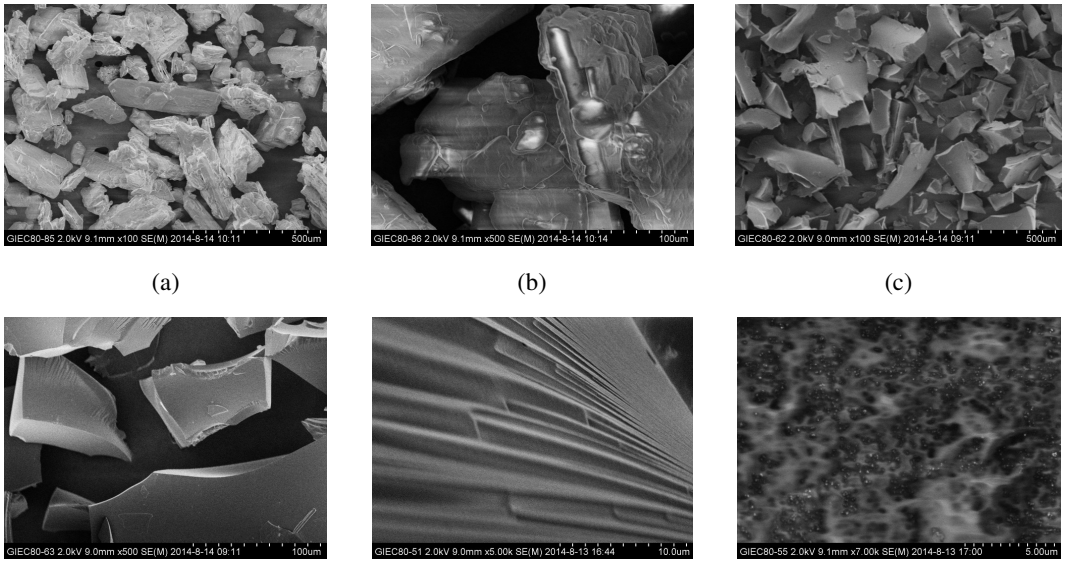

Figure 2: SEM images of (a,b) raw material and (c,d,e,f) carbon precursor after carbonation

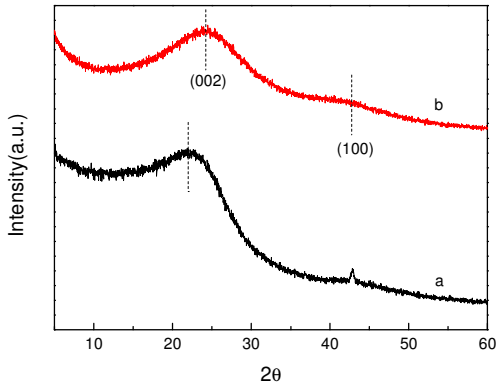

Figure 3: XRD patterns for the carbon precursor (a) and the CSA (b)

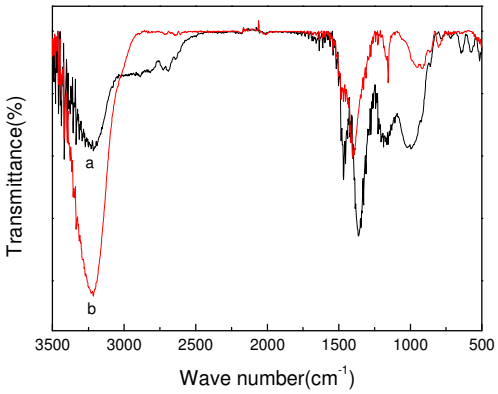

Figure 4: FT-IR spectra of the carbon precursor (a) and the CSA (b)

Furthermore, a broad band centered at about 1600 cm^{-1}, ascribable to the C=O vibration was reduced,[7,18] further confirming that the further carbonization of glucose took place during sulfonation. Interestingly, after sulfonation, some new peaks appeared simultaneously (Fig. 3b). The peaks at around 1225 and 1042 cm^{-1} could be assigned to the O=S=O symmetric stretching mode and $–SO_3H$ stretching mode,[19,20] respectively. This finding suggests that a successful sulfonation reaction took place.

Table 1 shows the elemental composition of glucose, the carbon precursor and CSA. After carbonation, the content of hydrogen and oxygen both decreased compared to glucose, indicating that the dehydration as main reaction took place. After sulfonation, sulfur was introduced to the carbon precursor and the content determined was

3.548%. As the $–SO_3H$ group represents the only form for elemental sulfur existing in CSA, the content of $–SO_3H$ was calculated to be 1.109 mmol/g. The increase of the oxygen content and the decrease of the hydrogen and carbon contents may be caused by the presence of acidic groups containing oxygen.

Temperature programmed desorption (TPD) of ammonia showed that CSA exhibited an amount of acidic groups of 1.45 mmol/g (Fig. 5), which is higher than the theoretical value for $–SO_3H$ groups. Therefore, it can be assumed that other acidic groups may be present in CSA. As shown in Figure 4, when the desorption temperatures reached 200 °C and 400 °C, respectively, the TPD signals appeared as two individual peaks. This finding confirms that two different types of groups with different acidity exist in CSA. Compared to only one type of reactive group usually present in conventional catalysts, a variety of reactive groups present in CSA may intensify the contact with the substrate and strengthen the binding. With these physicochemical properties, CSA exhibits a high catalytic activity for the conversion of cellooligosaccharides into glucosides with a high yield.

Catalytic performance for cellooligosaccharides hydrolysis

Cellobiose represents the shortest β-1,4-glucan in which two glucose molecules are linked by a β-1, 4-glycosidic bond. The study of the cellobiose hydrolysis reaction is the first step to reveal the conversion mechanism of glycoside bonds catalyzed by CSA. Figure 6 shows the evolution in time of cellobiose conversion and glucose formation in the cellobiose hydrolysis in aqueous media catalyzed by CSA. This catalyst exhibited a remarkable hydrolytic performance compared to other conventional solid acid catalysts,[21-24] resulting in a cellobiose conversion of 68.18% and glucose yield of 66.78% after 15 h. Neither 5-hydroxymethylfurfural nor levulinic acid, the byproduct formed through decomposition of glucose, could be observed in the aqueous solution after the reaction using CSA as carbon-based material. The conversion of cellobiose and the yield of glucose were extremely close, indicating that CSA featured a considerably high selectivity. Control experiments were also carried out, confirming that using these experimental conditions, cellobiose was not hydrolyzed to form glucose and CSA did not decompose to produce dextran, potentially interfering with HPLC results.

Table 1
Elemental composition of glucose, carbon precursor and the CSA

Sample	C (%)	H (%)	O (%)	S (%)
Glucose	40	6.67	53.33	0
Carbon precursor	79.78	4.159	16.061	0
CSA	61.53	3.548	31.374	3.548

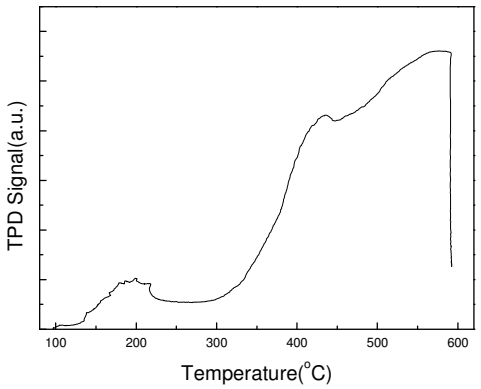

Figure 5: Temperature initiated desorption profile

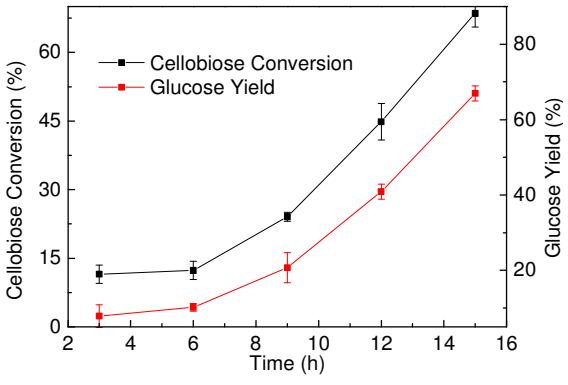

Figure 6: Glucose formation from cellobiose as a function of reaction time

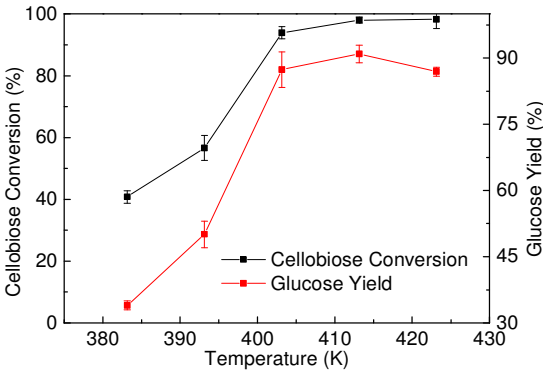

Figure 7: Temperature initiated desorption profile

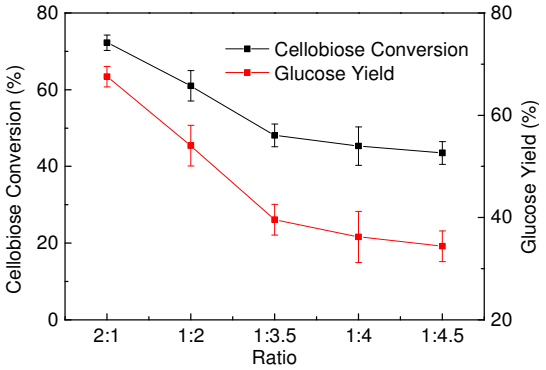

Figure 8: CSA to cellobiose ratios resulting in glucose formation from cellobiose

The effect of temperature on the hydrolysis reaction between 110 and 150 °C was also evaluated. As shown in Figure 7, when the temperature increased to 130 °C, the conversion rate of glucose clearly exhibited a linear increase. The reaction remained stable and the catalytic efficiency was not determined to be significantly improved at temperatures between 130 and 150 °C. While the reaction temperature increased from 130 to 150 °C, the yield of glucose decreased by about 5%. This finding indicates that the high temperature started to promote the decomposition of glucose. Considering the cellobiose decomposition rate and glucose production rate, the best reaction temperature was determined to be 140 °C for CSA. Figure 8 shows the influence of CSA ratio on cellobiose conversion and glucose yield. When the ratio was between 2:1 and 1:3.5, the cellobiose conversion and glucose yield decreased significantly. When the ratio decreased further, the decrease was found to be reduced. This latter finding may be due to a decreased catalyst concentration in the reaction system. On the other hand, another possibility may be that the mass transfer became saturated. In general, when the ratio of catalyst to other reactants decreases to a certain degree, the catalytic ability of these catalysts reaches saturation and a higher cellobiose conversion and glucose yield can only be obtained through prolonged reaction times.

Cellulose represents an important raw material that can be directly used as feedstock for the production of biofuel and bio-based chemicals. However, the material easily forms a highly crystalline structure due to the presence of extensive intra- and inter-molecular hydrogen bonds and van der Waals interactions.[25,26] Cellulose cannot be hydrolyzed into glucose or water-soluble β-1,4 glucan using conventional solid acid catalysts, such as niobic acid, Amberlyst-15, and Nafion®NR-50.[27] However, the carbon catalyst exhibited a remarkable performance on the hydrolysis reaction. After heating at 120 °C for 12 h, glucose could be detected using HLPC at a concentration of 1.525 mg/mL, *i.e.* the yield of glucose could be determined to be 53.71%. Given that glucose represents the simplest compound resulting from the hydrolysis of cellulose, the overall conversion rate of cellulose may be even higher than the glucose yield. Without any pretreatment of microcrystalline cellulose and under these aqueous reaction conditions, CSA may be considered a suitable and promising catalyst for cellulose hydrolysis.

Recyclability of CSA

The recyclability of the carbon catalyst was evaluated in three cycles in the same 20 mL aqueous reaction system. After completion of each run, the CSA was filtered from the solution and the collected solid was dried at 105 °C and reused for subsequent hydrolysis reactions. The cellobiose conversion of each recycle was determined to be 89.51%, 84.11% and 86.18%, respectively. No significant differences in catalytic activity among the recycled catalysts could be determined. These results confirm that the active groups were tightly bound to the graphene sheets and further verify that CSA functions as a stable and highly active catalyst for the hydrolysis of cellooligosaccharides.

CONCLUSION

Through carbonation and sulfonation, the CSA prepared via glucose resulted in the production of a highly active and stable solid acid catalyst for cellooligosaccharides hydrolysis in an aqueous reaction system. With the use of advanced analytical equipment and methods, spatial structures and the active groups of raw materials, carbon precursor and CSA could be studied and characterized. Hydrolysis experiments of cellobiose and cellulose demonstrated that CSA is a highly active and stable catalyst for the hydrolysis of cellooligosaccharides due to the presence of versatile active groups (SO_3H, COOH and OH) in the structural scaffold. Furthermore, CSA exhibited a large effective catalytic surface area in water and the ability to adsorb β-1,4-glucan.

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