# AGRICULTURAL AND FOOD CHEMISTRY

# Efficient Hydrolysis of Cellulose over a Novel Sucralose-Derived Solid Acid with Cellulose-Binding and Catalytic Sites

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**Supporting Information** 

**ABSTRACT:** A new sucralose-derived solid acid catalyst (SUCRA-SO<sub>3</sub>H), containing -Cl and  $-SO_3H$  functional groups, has been shown to be highly effective for hydrolyzing  $\beta$ -1,4-glucans, completely hydrolyzing cellobiose (1) into glucose (2) in 3 h and converting the microcrystalline cellulose pretreated by the ionic liquid into glucose (2) with a yield of around 55% and a selectivity of 98% within 24 h at a relatively moderate temperature (393K). The enhanced adsorption capacity that the catalyst has for glucan by virtue of the presence of chloride groups that act as cellulose-binding sites offers the possibility of resolving the existing bottleneck in heterogeneous catalysis to hydrolyze cellulose, namely, the low accessibility of cellulose to the reaction position in typical solid catalysts. The apparent activation energy for hydrolysis of cellobiose (1) with SUCRA-SO<sub>3</sub>H was 94 kJ/ mol, which was much lower than that with sulfuric acid (133 kJ/mol) and the corresponding sucrose-derived catalyst (SUCRO-SO<sub>3</sub>H) without chlorine groups (114 kJ/mol).

KEYWORDS: cellulose-binding site, cellulose hydrolysis, chloride group, solid acid catalyst

# INTRODUCTION

Production of energy fuels and chemical feedstock from biomass resources has the potential to reduce CO<sub>2</sub> emission through the use of renewable carbon sources.<sup>1</sup> To produce chemicals either from a mixture of lignocelluloses or from separated carbohydrate polymers, the breakdown of polymers into individual sugar molecules must occur.<sup>2</sup> Sulfuric acid is the most widely used catalyst for converting cellulose in industry.<sup>3</sup> However, this process is costly, and it is inefficient to separate the catalyst from the homogeneous reaction mixtures, resulting in a large consumption of energy and large amounts of waste products; it also requires the use of expensive, corrosionresistant reactors. Furthermore, the largest drawback to using sulfuric acid is that it also readily degrades glucose (2) at the high temperatures required for cellulose hydrolysis.<sup>4</sup> When the reaction is performed using a biocatalyst, cellulose is typically enzymatically hydrolyzed by cellulase.<sup>5</sup> This enzyme-catalyzed approach can be performed under moderate conditions with high glucose (2) selectivity, but still has significant drawbacks, including low activity, significant reaction time, costly enzymes, and unstable enzymes.<sup>6</sup> Thus, solid catalysts are widely used, which show superiority due to a catalytic functional group such as a Brønsted or Lewis acid to imitate the liquid acid-catalyzed hydrolysis reaction.<sup>7,8</sup>

Utilization of heterogeneous catalysts is an effective approach for biomass conversion and numerous other green chemical processes due to the ease of separating the catalysts from the products and the potential of the catalyst to be recyclable.<sup>9</sup> Recent developments, such as functionalization of carbon materials to improve substrate adsorption<sup>10</sup> and use of ionic liquids (ILs) for cellulose dissolution and depolymerization,<sup>11,12</sup> are used to address problems of substrate access to the catalyst that can occur with heterogeneous catalysts. Nonetheless, a bottleneck remains in the heterogeneous reaction system due to the low accessibility of the catalyst active group to the reactive position comprising the  $\beta$ -1,4-glucan linkage in cellulose. Thus, designing a solid acid catalyst with a cellulose-binding site to lower the reaction energy is desirable in order to reduce the energy requirements of the reaction.<sup>13</sup>

Suganuma et al.<sup>14</sup> reported the use of cellulose-derived amorphous carbon as an efficient catalyst for hydrolyzing cellulose. This catalyst has a high density of sulfonic acid groups and abundant hydroxy groups, which can adsorb  $\beta$ -1,4-glucans to increase substrate concentration near the catalytic active position to favor the hydrolytic reaction. However, a high catalyst/cellulose ratio (12:1) was needed to conduct the reaction. Jacobs et al.<sup>15</sup> successfully synthesized a sulfonated silica-carbon nanocomposite via the evaporation-induced triconstituent self-assembly of tetraethyl orthosilicate that takes advantage of a similar adsorption effect, yielding up to 50% glucose (2) at 61% conversion of ball-milled cellulose. A cellulase-mimetic solid catalyst, sulfonated chloromethyl polystyrene resin, containing cellulose-binding sites (-Cl) and catalytic sites  $(-SO_3H)$ , was synthesized by Shuai et al.<sup>16</sup> This bifunctional catalyst showed excellent catalytic activity for hydrolyzing cellulose into glucose (2) and significantly shortened the reaction time by effectively lowering the activation energy of the reaction.

In this study, the chloride group was chosen as the cellulosebinding site based on a study by Li et al.,<sup>17</sup> who found that hydrochloric acid/1-*n*-butyl-3-methylimidazolium chloride

Received:	August 7, 2013						
Revised:	January 30, 2014						
Accepted:	February 10, 2014						
Published:	February 11, 2014						

 $(C_4 \text{mim} \cdot \text{Cl})$  was an efficient system for hydrolyzing lignocellulosic biomass. These authors attributed the excellent behavior of the system to the dispersion of most of the cellulose and hemicellulose molecules within the ionic liquid. Amarasekara et al.<sup>18</sup> successfully immobilized the sulfonic acid functionalized ionic liquid, C<sub>4</sub>mim·Cl, on a silica surface to synthesize a silicasupported acid catalyst, showing that an effective heterogeneous acid catalyst can be produced by tethering an imidazolium moiety functionalized by attachment of a sulfonic acid group to a solid support. To better understand the mechanism of cellulose solvation by the above-mentioned ionic liquid, Remsing et al.<sup>19</sup> conducted a study and found that there was a 1:1 stoichiometry for the hydrogen-bonded interaction between the hydroxyl protons of carbohydrate and the chloride ions of ionic liquid. The chloride concentration in this system was as high as 20%. To expand on this bifunctional strategy, we have produced a unique artificial catalyst that mimics the structure of not only the catalytic active sites found in homogeneous acid catalysis but also the active sites of enzymes in the biocatalytic transformation of lignocellulose. In this present study, sucralose was chosen as a satisfactory carbonaceous material for the introduction of chlorine groups in carbon-based solid acid catalysts that can be prepared expediently by carbonization and sulfonation of various sugar in a manner that gives a relatively stable solid acid catalyst for hydrolyzing cellulose to glucose (2).<sup>14</sup> The incorporation ability of hydrophilic molecules will make it more easy for a cellulose chain in solution to be in contact with the -SO<sub>3</sub>H groups in the carbon material, thus giving rise to higher catalytic performance.<sup>20</sup> We propose that this study will enable the future rational design of new catalytic strategies by bonding chloride as a functional group to promote binding of cellulose to catalysts to overcome the intrinsic bottleneck of biomass hydrolysis, the severe mass-transfer limitation hampering progress, and thus enable the development of methods for processing widely available water-insoluble polymeric biomass under heterogeneous conditions.

#### EXPERIMENTAL SECTION

**Materials.** Sucralose (4) (biological reagent grade) was purchased from Shiyuanye Co., Ltd. (Shanghai, China). Sucrose was purchased from Jinhuada Chemical Reagent Co., Ltd. (Guangzhou, China). Microcrystalline cellulose (Avicel PH101) was obtained from FMC (Philadelphia, PA), and its degree of polymerization (DP) was 220. Starch (29.0% amylose content), was supplied by Huanglong Food Industry Co., Ltd. (Jilin, China). Rice straw and hardwood obtained locally was mechanically powdered to a particle size of 50–400  $\mu$ m. C<sub>4</sub>mim·OAc was from Lanzhou Institute of Chemical Physics (Lanzhou, China). Cellulase from *Trichoderma reesei* (6 U/mg) was bought from Sigma (St. Louis, MO, USA). All other chemicals were obtained from commercial sources and were of the highest grade available.

**Catalyst Preparation and Characterization.** The SUCRA-SO<sub>3</sub>H catalyst and SUCRO-SO<sub>3</sub>H catalysts were prepared from sucralose (4) and sucrose (5), respectively, according to a method similar to that reported previously by Hara et al.<sup>14</sup> Characterization of the carbon-based solid acid catalysts was carried out by a combination of Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), Branauer–Emmett–Teller analysis (BET), scanning electron microscopy (SEM), temperature-programmed desorption of ammonia anaysis (NH<sub>3</sub>-TPD), and acid– base titration.

Hydrolysis of Cellobiose and Cellulose. The standard reaction conditions for the hydrolysis reactions were as follows: cellobiose (1) (0.1 g) or cellulose (0.05 g), catalyst (0.1 g) or 1 mL of 4% dilute

sulfuric acid and water (4 mL) were loaded into a 10 mL flask with a suitable rubber plug sealed with an aluminum cap to prevent loss of water by evaporation. After stirring (500 rpm) for 1 min the mixture was heated for 0-48 h to the temperature specified for each reaction. The flask was then placed into a mixture of ice and water for 10 min to stop reaction, and the mixtures (1-1.5 mL) were transferred into a 2 mL microcentrifuge tube and separated by centrifugation (1150g, 10 min). Aliquots (100  $\mu$ L) were withdrawn from the supernatant prior to HPLC analysis. The residual solids in the pipet, microcentrifuge tube, and flask were all collected together by filtration. Reasonable leaching water volume was heated to 80 °C to elute the remaining sugars adsorbed on the surface of the catalyst. The resultant liquor volume was concentrated down to 2 mL for subsequent HPLC analysis. In the reactions containing sulfuric acid, the solution was neutralized with CaCO<sub>3</sub> powder after the reaction, the CaSO<sub>4</sub> precipitate was removed by centrifugation, and the supernatant solution was analyzed. All reactions were performed in duplicate, and yields of glucose (2) had margins of error of up to  $\pm 3.4\%$ .

Saccharide Adsorption Capacity of the Prepared Catalysts. Glucose (2) (600 mg) or cellobiose (1) (600 mg) was added into 12 mL of water and vortexed. The mixture was divided into 12 equal portions in microtubes. Then 100 mg of the catalyst was loaded into each microtube, and the contents were mixed well. All microtubes were kept at room temperature and vortexed for 2 min every 5 min. One microtube was taken and centrifuged at each of the following reaction times: 10, 20, 30, 60, 90, and 120 min. 2 and 1 in the supernatant were determined via high performance ion chromatograph to calculate the adsorption capacity of the catalyst. Other catalysts were treated in the same manner with a reaction time of for 2 h to investigate their adsorptive properties. Error bars represent standard deviations from three experiments.

Hydrolysate Analysis. Glucose (2) and cellobiose (1) were determined using an HPLC system consisting of a Waters 515 HPLC pump, a Bio-Rad organic acid column, and a Waters 2410 refractive index detector. The column used was a 300 mm × 7.8 mm i.d., Aminex HPX-87H (BIO-RAD Laboratories, Hercules, CA, USA). The mobile phase consisted of 5 mmol/L sulfuric acid aqueous solution with a flow rate of 0.5 mL/min. The column temperature was 65 °C. The cellulose and xylan contents were calculated from glucose (2) and xylose (3) contents multiplied by conversion factors of 0 0.90 and 0.88, respectively. The concentration of each compound in the liquid phase was determined using calibration curves obtained by analyzing standard solutions with known concentrations. TOC (total organic carbon), which is mostly composed of water-soluble polysaccharide and products from the dehydration of saccharides, was analyzed using a model 5000A TOC Analyzer (Shimadu, Tokyo, Japan). Y<sub>WSOC</sub>, which represents the yield of total amount of water-soluble organic compounds in the reaction liquid, was calculated based on the data from TOC analysis. Concentration curves ranging from 1 to 150 ppm were prepared from a TOC standard solution (100 ppm) purchased from Sigma with a resulting  $R^2$  value of 0.998.

Glucose yields were calculated as follows:

glucose yield (%) = {[mol of glucose (produced)]

/(theoretical yield of glucose in mol)}  $\times$  100

Glucose selectivity was calculated on the basis of TOC results as follows:

glucose selectivity (%)

= (mol of carbon present in the form of glucose)

/(mol of total water – soluble organic carbon)

**Estimation of the Activation Energy of Glycosidic Bond Cleavage.** The activation energy of cellobiose (1) hydrolysis using the sucralose- and sucrose-derived carbon-based solid acid catalysts was studied by comparing the reaction rate at four temperatures (373 K, 383 K, 393 K, and 403 K). Results were plotted as Arrhenius plots in the form of rate constants at each temperature, and activation energies were calculated by multiplying the slope by the gas constant R.

**Reuse Experiment.** The catalyst reuse experiments were performed at 393 K. Reaction conditions were as follows: 0.1 g of cellobiose, 0.1 g of catalyst, 4 mL of deionized water, and reaction time 3 h, reaction temperature 393 K. The solid catalysts were washed by filtration with distilled water until sulfate ions could no longer be detected in the washings, after which the catalyst was reused in the next cycle of the reaction.

# RESULTS AND DISCUSSION

Fourier transform infrared (FT-IR) spectra of the catalysts displayed peaks at approximately 1180 cm<sup>-1</sup> and 1030 cm<sup>-1</sup> which are typically attributable to the stretching modes of SO<sub>3</sub>H groups. X-ray photoelectron spectroscopy (XPS) revealed only one peak at 168 eV, assigned to the SO<sub>3</sub>H groups, implying that all sulfur in the carbon catalyst is contained in the SO<sub>3</sub>H groups. The elemental compositions of the catalysts were measured using the XPS data in order to determine the content of sulfonic acid group. The amount of sulfur per gram of catalyst was 0.28 mmol for the sucralosederived catalyst (SUCRA-SO<sub>3</sub>H), 0.47 mmol for the sucrosederived catalyst (SUCRO-SO3H), and 0.67 mmol for the sulfonated sucralose. As expected, the carbonized sucralose contained no detectable sulfur. The specific surface area of SUCRA-SO<sub>3</sub>H catalyst was 0.317 m<sup>2</sup>/g, which was similar to the 0.282  $m^2/g$  measured for the SUCRO-SO<sub>3</sub>H catalyst. Sulfonated sucralose showed a clear advantage in the amount of sulfonyl group attachment compared to other catalysts, indicating that both the carbonization and sulfonation processes cause a decrease in chloride group content, negatively affecting adsorption ability and reaction results. Here, we evaluated the best catalyst among different materials that were capable of hydrolyzing polysaccharide. Both SUCRO-SO<sub>3</sub>H and SUCRA-SO<sub>3</sub>H catalysts are composed of irregular shaped amorphous carbon particles with layer structures, and the size of catalyst particles was between 0.4 and 1.0 mm. However, there were no obvious mesoporous or microporous particles observed in the SEM micrographs. The acidic properties of SUCRO-SO<sub>3</sub>H, SUCRA-SO<sub>3</sub>H, and carbonated sucralose were investigated by temperature-programmed desorption of ammonia analysis. Both samples of SUCRO-SO<sub>3</sub>H and SUCRA-SO<sub>3</sub>H show a distinct broad peak at around 473 K due to the presence of abundant hydroxyl groups. The curve of incompletely carbonated sucralose shows a little higher intensity and desorption in the temperature range of 723-923 K than the other two samples, due to the more severe decomposition of the solid sample. Both SUCRO-SO<sub>3</sub>H and SUCRA-SO<sub>3</sub>H catalysts showed the presence of medium acid sites, as their respective desorption temperatures are around 623 K, which corresponded to the carboxyl groups.

Initially, we tested the capacity of the catalysts to hydrolyze  $\beta$ -1,4-glycosidic bonds by using cellobiose (1) as the substrate, which is commonly used as model compound for cellulose. Figure 1 shows time courses for D-glucose (2) formation from cellobiose (1) by the SUCRA-SO<sub>3</sub>H catalyst. As a comparison, the results for the SUCRO-SO<sub>3</sub>H catalyst are also included. Conversion of cellobiose (2) reached 100% after 3 h with both catalysts. Taking the sulfur content of the catalysts into account, which based on the XPS results equates to the content of sulfonic acid groups in the catalysts, the SUCRA-SO<sub>3</sub>H catalyst (containing 0.28 mmol/g of sulfur) performs much better than the higher sulfur content SUCRO-SO<sub>3</sub>H catalyst (containing 0.47 mmol/g of sulfur).



Figure 1. Time courses for D-glucose formation from cellobiose.Yield of glucose (2) (circular symbols) and selectivity of glucose (2) (square symbols and triangles) during hydrolysis of cellobiose (1) over SUCRA-SO<sub>3</sub>H (closed symbols) and SUCRO-SO<sub>3</sub>H (open symbols).

To investigate the performance of the new catalysts in comparison to other catalytic systems, their performance was compared with that of sulfonated sucralose, sulfonated sucrose, Amberlyst-15, and niobic acid (Figure 2). Only trace amounts



Figure 2. Hydrolysis of cellobiose (1) catalyzed by various catalysts.

of cellobiose (1) were converted over niobic acid, presumably due to the lack of efficient acid catalytic sites,<sup>21</sup> while the catalysts bearing Brønsted acid sites (Amberlyst-15 and the sulfonated carbon materials) generally exhibited good catalytic performance. Furthermore, the addition of halogen as cellulose binding sites in SUCRA-SO<sub>3</sub>H significantly enhanced the reaction activity compared to the SUCRO-SO<sub>3</sub>H catalyst, which does not contain halogen.

This encouraging progress could be attributed to increases in adsorption capacity. Catalysts with cellulose binding sites are thought to be superior at adsorbing cellobiose (1) (the shortest  $\beta$ -1,4-linked polysaccharide, which is often used to model the cellulose hydrolysis reaction) and 2 (the expected product), since the chloride group is a strong hydrogen bond acceptor that may enter into hydrogen bonding with the hydroxyl groups on cellulose, cellobiose (1), and glucose (2). To confirm this conjecture, 0.1 g portions of the solid catalyst were added to separate 2 mL aliquots of aqueous cellobiose (1) and glucose (2) solutions (50 g/L), and the mixture was oscillated at room temperature (298 K). As shown in Figure 3, 21.5% of the added cellobiose (1) was absorbed by the SUCRA-SO<sub>3</sub>H catalyst within 2 h, which was higher than the value of 18% absorbed by the SUCRO-SO<sub>3</sub>H catalyst, and the Cl-bearing catalyst SUCRA-SO<sub>3</sub>H required a shorter time before adsorption equilibrium was reached compared to the Cl-free SUCRO-SO<sub>3</sub>H catalyst. Similarly, the SUCRA-SO<sub>3</sub>H catalyst absorbed 8.5% of the added glucose (2), which was more than the 5%absorbed by the SUCRO-SO<sub>3</sub>H catalyst and agrees with the



**Figure 3.** Adsorption curve of glucose (2) (circular symbols) and cellobiose (1) (square symbols) onto SUCRA-SO<sub>3</sub>H catalyst (closed symbols) and SUCRO-SO<sub>3</sub>H catalyst (open symbols) in aqueous solution. 100% adsorption would correspond to binding of 50 mg of carbohydrate to 100 mg of catalyst in a volume of 1 mL.

results of Suganuma et al.<sup>21</sup> and Shuai et al.<sup>16</sup> The ability of the catalysts to take up large amounts of saccharides is likely caused by the simultaneous incorporation of water and adsorption of saccharides. It is possible that the formation of hydrogen bonds occurs between the hydroxyl groups of cellulose and not only the chloride groups but also the hydroxyl groups on catalyst as minor electronegative groups. Furthermore, the stronger electrophilicity of surface chloride groups than hydroxyl groups on the carbon affords better adsorption capacity.

Further, the adsorption capacity of the  $SUCRA-SO_3H$  catalyst was compared with those achieved with other heterogeneous catalysts (Figure 4). Among the range of



**Figure 4.** The adsorption capacity of the tested catalysts. 100% adsorption would correspond to binding of 50 mg of carbohydrate to 100 mg of catalyst in a volume of 1 mL.

catalysts tested, the sulfonated sucralose shows the best adsorption ability, which correlates with its highest chloride

group loading. Although niobic acid showed the third greatest saccharide-binding capacity, possibly caused by swelling of the solid acid catalyst, it exhibited poor catalysis presumably owing to its low acidity (70% that of sulfuric acid). However, Amberlyst-15, with its strong acid groups, performed conversely, indicating that only when a certain amount of acid groups and requisite electron pair acceptor are present on the catalyst will a highly effective catalyst result.<sup>22</sup>

Catalytic activity was further investigated by examining the effectiveness of the catalysts for cellulose and starch hydrolysis. Compared to starches, cellulose is more difficult to hydrolyze due to its crystalline form and the abundant hydrogen bonding present in the cellulose molecule, and the  $\beta$ -glycosidic linkage of cellobiose (1) among the various types of simple disaccharides is one of the most recalcitrant bonds to acid hydrolysis compared to maltose, sucrose, lactose, and xylobiose.<sup>23</sup> As shown in Table 1, in the case of starch, the carbon-based catalyst SUCRA-SO<sub>3</sub>H showed a glucose (2) yield of approximately 90%, with an equivalent amount of fructose observed after a 6 h reaction. For hydrolysis of unpretreated cellulose, however, only 4% glucose (2) yield was achieved after 24 h of reaction. Nonetheless, the glucose (2) yield from this reaction could be increased to 53% by converting the water-soluble polysaccharide in the resulting reaction liquid through a 48 h enzyme hydrolysis, and 48% saccharide was detected in the final product according to the TOC result based on mass.

To improve the accessibility of the catalytic sites of the catalyst to the  $\beta$ -1,4-glycosidic bond in cellulose, we pretreated cellulose with the ionic liquid C4mim·OAc and then regenerated it with water. It is generally accepted that the primary mechanism for dissolution of cellulose by ionic liquids proceeds through disruption of the interstrand hydrogenbonding network between adjacent polymer chains, and C4mim·OAc has been found to be an efficient ionic liquid for reducing the crystallinity of cellulose.<sup>24</sup> XRD analysis indicated that the amorphous region increased greatly in the regenerated cellulose, and thereby it is possible that the glycosidic bonds in the substrates become more exposed to the catalysts. Three diffraction peaks, at around  $2\theta$  of  $16^\circ$ ,  $22^\circ$ , and  $34^\circ$ , respectively, for untreated microcrystalline cellulose, but only one weak peak remained at around 22° after treatment with  $C_4$ mim·OAc. The most important result of pretreatment is that it enables maximum sugar yield and minimizes the loss of sugars and the subsequent formation of inhibitory products. The yield of glucose (2) increased up to 55% with a 98%

Table 1. Hydrolytic Degradation of Polysaccharides to Glucose Using Various Catalysts

entry	catalyst	substrate	time $^{a}$ (h)	temp (K)	$Y_{\text{Glu}}^{\ \ b}$ (%)	$Y_{\rm WSOC}^{c}$ (%)	$S_{\text{Glu}}^{d}$ (%)
1	SUCRA-SO <sub>3</sub> H	cellulose (Avicel PH101)	24	393	4	48	8
2	SUCRA-SO <sub>3</sub> H	IL-pretreated cellulose	24	393	55	56	98
3	SUCRA-SO <sub>3</sub> H	IL-pretreated cellulose	24	413	46	63	73
4	SUCRA-SO <sub>3</sub> H	IL-pretreated cellulose	24	423	41	67	61
5	SUCRA-SO <sub>3</sub> H	starch	6	383	92	96	47
6	SUCRO-SO <sub>3</sub> H	cellulose (Avicel PH101)	24	393	3	26	11
7	SUCRO-SO <sub>3</sub> H	IL-pretreated cellulose	24	393	49	49	97
8	Amberlyst-15	IL-pretreated cellulose	24	393	-	3	-
9	niobic acid	IL-pretreated cellulose	24	393	_	-	-
10	dilute sulfuric acid	IL-pretreated cellulose	30	393	25	34	75

<sup>*a*</sup>The optimum reaction time for the hydrolysis. <sup>*b*</sup> $Y_{Glu}$  was the yield of glucose. <sup>*c*</sup> $Y_{WSOC}$  was the yield of water-soluble organic compounds determined via a TOC analyzer. <sup>*d*</sup> $S_{Glu}$  was the selectivity of glucose on tested catalysts. – represents "not detected".

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selectivity for regenerated cellulose using SUCRA-SO<sub>3</sub>H catalyst at an optimum reaction time of 24 h and 393 K, which was superior to that with SUCRO-SO<sub>3</sub>H catalyst (49%) at an optimum reaction time of 24 h and 393 K and that with dilute sulfuric acid (25%) at an optimum reaction time of 30 h and 393 K (Table 1). Additionally, in comparison with other liquid acid catalysts reported previously such as maleic acid<sup>25</sup> and phosphoric acid,<sup>26</sup> our prepared SUCRA-SO<sub>3</sub>H catalyst gave a higher yield of glucose (2) in hydrolysis of cellulose. Figure SA–C illustrates the effects of reaction time on



Figure 5. Hydrolysis of cellulose pretreated with  $C_4$ mim·OAc over various catalysts: (A) SUCRA-SO<sub>3</sub>H, (B) SUCRO-SO<sub>3</sub>H, and (C) dilute sulfuric acid.

hydrolysis of cellulose pretreated by ionic liquid with SUCRA-SO<sub>3</sub>H, SUCRO-SO<sub>3</sub>H, and dilute sulfuric acid as the catalyst, respectively. It was found that the reaction time had significant influence on yield of glucose (2), selectivity of glucose (2), and yield of water-soluble organic compounds  $(Y_{WSOC})$  in hydrolysis of cellulose using various catalysts. The yield and selectivity of glucose (2) and the  $Y_{WSOC}$  with SUCRA-SO<sub>3</sub>H increased clearly with increasing reaction time up to 24 h, but a further increase in reaction time resulted in a significant

drop in the yield and selectivity of glucose (2) (Figure 5A). The  $Y_{WSOC}$  with SUCRA-SO<sub>3</sub>H showed only slight increase when reaction time was more than 24 h, suggesting that there is a recalcitrant portion of insoluble cellulose present in the cellulose that is not accessible to hydrolysis. This similar trend was seen with increasing reaction time in hydrolysis of cellulose catalyzed by SUCRO-SO<sub>3</sub>H (Figure 5B). Obviously, the optimum reaction time for hydrolysis of cellulose using SUCRA-SO<sub>3</sub>H or SUCRO-SO<sub>3</sub>H was 24 h. In the case of dilute sulfuric acid, the yield and selectivity of glucose (2) reached maximum values at reaction time of 30 h, being the optimum reaction time for the reaction. Similarly, no significant variation in the Y<sub>WSOC</sub> was observed when reaction time was further prolonged. Although both carbon-based catalysts and dilute acid suffered from an undesirable side reaction, namely, the conversion of glucose (2) into hydroxymethyl furfural (HMF), the yield of glucose (2) showed a sharper decline with prolonged reaction time in the case of the dilute acid catalyst, in comparison with SUCRA-SO<sub>3</sub>H and SUCRO-SO<sub>3</sub>H. The result suggests that the formed glucose (2) from cellulosic biomass may be less converted into byproducts by the carbonbased catalysts. When reaction temperature was elevated, the formed glucose (2) was further converted into HMF with high concentrations, thus lowering the selectivity of glucose (2)(Table 1). We also performed the reaction using rice straw and hardwood (Table 2) as commercially significant lignocellulosic substrate to check the practicability of tested catalysts. When rice straw pretreated with C4mim·OAc was hydrolyzed by the SUCRA-SO<sub>3</sub>H catalyst, the obtained yield of glucose (2) was much less than that of hydrolysis of pure cellulose similarly pretreated under the same conditions. As evident from the data summarized in Table 2, rice straw was more easily degraded by the SUCRA-SO<sub>3</sub>H and SUCRO-SO<sub>3</sub>H catalysts than hardwood. SUCRA-SO<sub>3</sub>H slightly surpassed SUCRO-SO<sub>3</sub>H for hydrolysis of both rice straw and hardwood. Hemicellulose as an important component of ligincellulose can be hydrolyzed by our prepared solid acid catalysts as well as by liquid acid catalysts.<sup>27</sup> Interestingly, both the cabon-based catalysts preferentially hydrolyzed hemicellulose.

It has been reported that cellulose hydrolysis can be modeled based on a pseudo-first-order reaction followed by degradation of the generated glucose (2).<sup>28</sup> The reaction rate constant obeys modified Arrhenius equations, including effects of temperature and acid concentration. The advantage of adsorbing the substrate onto the catalyst surface is that it will increase the opportunity for the substrate to come into contact with the local acid moieties dispersed on the surface of the amorphous carbon sheet, thereby increasing the rate of the reaction associated by reducing activation energy (Figure 6). Kinetic studies showed that the apparent activation of cellobiose (1) hydrolysis was 94 kJ/mol at 373–403 K for

Table 2. Hydrolytic Degradation of Lignocellulose to Glucose Using SUCRA-SO<sub>3</sub>H

					yield (%)					
	composition of regenerated lignincellulose (%)				SUCRA-SO <sub>3</sub> H			SUCRO-SO <sub>3</sub> H		
raw material	cellulose	hemic-ellulose	lignin	ash	$Y_{\rm Glu}^{\ a}$	$Y_{\rm Xyl}^{\ \ b}$	$Y_{\rm WSOC}^{c}$	$Y_{\rm Glu}{}^a$	$Y_{\rm Xyl}^{\ \ b}$	$Y_{\rm WSOC}^{c}$
rice straw	47.7	15.6	14.5	16.4	19.5	57.3	36.0	16.5	56.0	34.5
hardwood	54.3	16.5	14.4	1.3	12.7	44.4	32.0	11.2	39.8	29.8

 ${}^{a}Y_{Glu}$  was the maximum yield of glucose based on the weight of cellulose in regenerated lignincellulose.  ${}^{b}Y_{Xyl}$  was the maximum yield of xylose (3) based on the weight of hemicellulose in regenerated lignincellulose.  ${}^{c}Y_{WSOC}$  was the yield of water-soluble organic compounds determined via a TOC analyzer.



**Figure 6.** Arrhenius plot of cellobiose (1) hydrolysis over (A) SUCRA-SO<sub>3</sub>H and (B) SUCRO-SO<sub>3</sub>H. Rate constant k was calculated on the basis of the average rate during the initial reaction period (<50% conversion).

SUCRA-SO<sub>3</sub>H catalyst (Figure 6A), which is significantly lower than values for microcrystalline cellulose-derived carbon catalyst (110 kJ/mol),<sup>21</sup> SUCRO-SO<sub>3</sub>H catalyst (114 kJ/mol) (Figure 6B), and sulfuric acid (133 kJ/mol).<sup>16</sup>

Figure 7 shows the operational stability of the resulting solid catalysts by conducting sequential hydrolytic reactions with the



**Figure 7.** Reusability of SUCRA-SO<sub>3</sub>H and sulfonated sucralose in hydrolysis of cellobiose. The relative activity for both catalysts tested prior to use is defined as 100%, and activity is shown after each cycle.

same sample of catalyst using cellobiose (1) as substrate at 393 K for 3 h reaction time per cycle. The SUCRA-SO<sub>2</sub>H catalyst showed no significant loss in activity after successive reuse of six batches, but an obvious loss in activity was observed after seven batches, and the SUCRA-SO<sub>3</sub>H catalyst remained around 56% of the original activity after being repeatedly used for 10 batches, which was attributable to the partial leach of SO<sub>3</sub>H groups from the catalyst with the increase of reuse batch. We subsequently detected the pH of the reaction system after the removal of the SUCRA-SO3H catalyst by filtration during the course of each run, including those at the beginning and the end. The pH of the reaction system showed only a slight fall after successive reuse of six batches, but manifested a relatively obvious decrease after seven batches, particular at the end of the tenth batch, implying the partial leach of SO<sub>3</sub>H groups into the reaction system to form free acids through possible selfhydrolysis of the sulfonated catalysts, which was also confirmed by analyzing the S content of the catalyst (data not shown). This could well explain the observation that the SUCRA-SO<sub>3</sub>H catalyst indicated relative instability after seven batches of reuse. Moreover, as can be seen in Figure 7, the stability of the SUCRA-SO<sub>3</sub>H catalyst prepared by carbonization and sulfonation was clearly superior to that of the sulfonated sucralose, possibly due to the increase of the COOH groups and the rigidity of the carbon skeleton structure in SUCRA-SO<sub>3</sub>H by

carbonization, which was similar to the observation reported by Siril et al.<sup>29</sup> In fact, it is known that aromatic carbon-SO<sub>3</sub>H bonds in sulfoaromatic compounds bearing electron-withdrawing functional groups such as halogens, COOH, and phenol OH are more stable against loss of the sulfonyl group as a result of the increased electron density between the carbon and sulfur atoms. Moreover, the prepared SUCRA-SO<sub>3</sub>H catalyst was incubated for 24 h at a relatively higher temperature of 413 K to evaluate its thermal stability, and still maintained more than 80% of its initial activity, showing good stability which was comparable to that of the catalyst Amberlyst 35.23 A possible mechanism for the hydrolysis process over the solid acid catalysts prepared is that the stronger affinity for  $\beta$ -1,4-glucan of the novel carbon-based catalyst than the traditional solid acid catalysts may provide better access by reactants to the -SO<sub>3</sub>H groups in the carbon material to cleave the  $\beta$ -1,4-glucosidic bonds. Catalysis over the tentative carbon catalyst with -SO<sub>3</sub>H, -COOH, -Cl, and phenolic -OH groups thus resulted in high catalyst activity.

# ASSOCIATED CONTENT

# **Supporting Information**

Chlorine and sulfur content of the four catalysts (SUCRO-SO<sub>2</sub>H, SUCRA-SO<sub>2</sub>H, carbonized sucralose, and sulfonated sucralose) (Table S1). BET parameters of SUCRO-SO<sub>3</sub>H and SUCRA-SO<sub>3</sub>H (Table S2). Detail equation parameters of lnk-1/T curve (Table S3). The pH of the reaction system after removal of the catalyst for each run (Table S4). FT-IR spectra and S2p curves from XPS analysis of SUCRO-SO<sub>3</sub>H catalyst and SUCRA-SO<sub>3</sub>H catalyst (Figures S1 and S2). XRD analysis of cellulose substrate before and after pretreatment using ionic liquid (Figure S3). Nitrogen adsorption/desorption isotherms and scanning electron microscopy images of SUCRO-SO<sub>3</sub>H and SUCRA-SO<sub>3</sub>H (Figures S4 and S5). The NH<sub>3</sub>-TPD profiles of SUCRO-SO<sub>3</sub>H catalyst, SUCRA-SO<sub>3</sub>H catalyst, and carbonized sucralose (Figure S6). Glucose (2) and xylose (3) yields of hydrolysis of IL-pretreated straw catalyzed by SUCRA-SO<sub>3</sub>H and SUCRO-SO<sub>3</sub>H with time (Figure S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We wish to thank the National Science Found for Excellent Young Scholars (21222606), the State Key Program of National Natural Science Foundation of China (21336002), the National Key Basic Research Program of China (2013CB733500), and the Fundamental Research Funds for SCUT (2013ZG0003) for partially funding this work.

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