Hydrolysis of cellulose into glucose over carbons sulfonated at elevated temperatures[†]

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Received 22nd June 2010, Accepted 22nd July 2010 DOI: 10.1039/c0cc02014a

The hydrolysis of cellulose over sulfonated carbons was promoted greatly by elevating the sulfonation temperature. With 250 °C-sulfonated CMK-3 as a catalyst, the cellulose was selectively hydrolyzed into glucose with the glucose yield as high as 74.5%, which is the highest level reported so far on solid acid catalysts.

Stimulated by the ever increasing energy crisis and environmental concerns, utilization of renewable resources for the production of energy and chemicals has attracted more and more attention. Cellulose, the most abundant source of biomass and non-digestible by humans, is being considered as a promising alternative to fossil resources.¹ Cellulose is a waterinsoluble saccharide polymer composed of glucose monomers linked by β -1,4 glycosidic bonds. Since glucose can be efficiently converted into fuels and various value-added chemicals with the commercially available fermentation or chemical processes,² the selective hydrolysis of cellulose into glucose represents a key technology in the utilization of cellulose.

The conventional processes for the hydrolysis of cellulose involve the use of mineral acids.³ The corrosion and waste disposal problems, however, significantly lower the attraction of liquid acid-catalyzed hydrolysis. In order to minimize the environmental impact, new green approaches have been developed, such as the use of cellulase enzymes,⁴ hydrolysis in sub- or super-critical water, 5 ionic liquid promoted dissolution and hydrolysis of cellulose, 6,7 hydrogenolysis into polyols $^{8-12}$ as well as hydrolysis into glucose by solid catalysts.^{13–17} Among others, the solid catalysts present the advantages of catalyst recovery, less or even no corrosion, and milder reaction conditions. Various solid acids have been investigated in the hydrolysis of cellulose, including sulfonated carbon materials,13,14 ionexchange resins,15 heteropolyacids,16 and layered transition-metal oxide.¹⁷ A significant challenge associated with the application of solid acids is their much lower efficiency than the mineral liquid acids. Actually, the highest yield of glucose derived from hydrolysis of cellulose over various solid acids was reported to be only about 40%,¹³ which is far less than that on mineral acids. Therefore, it is desirable to develop a highly active and recyclable solid acid catalyst for the hydrolysis of cellulose.

Compared with resin-type or oxide-type solid acids, sulfonated carbons are more robust in hot water besides having preferable textural properties. By sulfonation in appropriate conditions, the surface acidity and hydrophilicity/hydrophobicity may be tuned to best facilitate the hydrolysis of cellulose. Nevertheless, the sulfonation conditions have rarely been optimized towards the hydrolysis of cellulose. Herein we report that by elevating the sulfonation temperature of the active carbon (AC) from 150 °C to 250 °C, the glucose yield in the hydrolysis of cellulose was remarkably enhanced from 7% to 61%. Moreover, when 250 °C-sulfonated CMK-3 (an ordered mesoporous carbon) was used as the catalyst, a glucose yield was attained as high as 74.5%. To our knowledge, this is the highest glucose yield obtained to date over a solid acid catalyst.

The sulfonation of the carbon materials was carried out under nitrogen atmosphere at 150-300 °C for 24 h, using 15 mL concentrated sulfuric acid per gram of carbon. Before the sulfonation, some carbons were pretreated with nitric acid. The samples are designated with functional groups followed by sulfonation temperature; for example, AC-N-SO₃H-250 represents the sample treated with nitric acid and subsequently sulfonated at 250 °C. Table 1 lists the acid densities, specific surface areas, and adsorbed water amount of the sulfonated carbons. It should be pointed out that the acid densities determined by the titration method are 3-5 times larger than those determined by the NH₃-adsorption method. Nevertheless, both the methods show the same trend for samples sulfonated at different conditions. For clarity, we here use the titration-determined acid densities to discuss the influence of sulfonation temperatures. The non-treated AC had an acid density of 0.15 mmol g^{-1} and a specific surface area of 703 m² g^{-1} . After sulfonation treatment, the acid density had a large increase. Moreover, the higher the sulfonation temperature, the higher the acid density of the sulfonated carbon. For example, the AC sulfonated at 300 °C (AC-SO₃H-300) showed an acid density of 2.19 mmol g^{-1} , which was 15-fold that of the untreated AC. Meanwhile, the specific surface areas of the samples were slightly increased when the sulfonation temperature was raised from 150 to 250 °C, but they decreased rapidly with increasing the temperature further. It is interesting to note that the pretreatment with nitric acid prior to the sulfonation led to an additional increase in the acid density because treating the AC with nitric acid alone also introduced some acidic functional groups such as -OH and/or -COOH. On the other hand, the densities of functional group -SO₃H, which were determined by elemental analysis of S, were significantly lower than the acid densities. Moreover, it was found that the AC-N-SO₃H-250 possessed the highest density of -SO₃H groups, whereas a higher temperature (>250 °C) caused the decomposition of sulfonate. Besides the acid density, we also investigated the hydrophilicity of the carbon materials. As shown in Table 1, the adsorbed water amount increased with the sulfonation temperature, indicating the hydrophilicity of the carbon materials is improved by elevating the sulfonation temperature.

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[†] Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c0cc02014a

 Table 1
 The surface properties of AC sulfonated at different temperatures and their catalytic activities for hydrolysis of cellulose^a

Catalyst	$-\mathrm{SO_3H}^b$ / mmol g ⁻¹	Acid density ^{c} / mmol g ⁻¹	Acid density ^{d} / mmol g ⁻¹	$\frac{S_{\mathrm{BET}}}{\mathrm{m}^2 \mathrm{g}^{-1}}^{e/}$	Adsorbed water ^f /%	$\begin{array}{c} Y_{\mathrm{Glu}}{}^{g}\\ \mathrm{C} \ (\%) \end{array}$	$\begin{array}{c} \operatorname{Conv}^h \\ \operatorname{C}(\%) \end{array}$
AC		0.15	0.05	703	8.8	0	10.0
AC-NO ₃	0.02	1.49	0.36	762	10.7	9.7	31.5
AC-SO ₃ H-150	0.19	0.80	0.22	709	13.8	7.1	25.1
AC-SO ₃ H-200	0.24	1.03	0.42	728	15.4	17.9	43.4
AC-SO ₃ H-250	0.24	1.58	0.47	945	17.9	61.0	70.4
AC-SO ₃ H-280	0.23	2.03	0.59	462	18.3	56.0	66.6
AC-SO ₃ H-300	0.20	2.19	0.54	278	19.6	36.7	63.1
AC-N-SO ₃ H-150	0.12	2.15	0.37	723	14.1	19.0	42.1
AC-N-SO ₃ H-200	0.34	2.18	0.43	741	15.4	56.1	64.3
AC-N-SO ₃ H-250	0.44	2.23	0.50	762	19.6	62.6	74.3
AC-N-SO ₃ H-280	0.27	2.38	0.70	362	20.8	58.4	66.3
AC-N-SO ₃ H-300	0.27	2.39	0.78	30	21.3	54.2	68.6

^{*a*} The hydrolysis reaction was conducted at 150 °C for 24 h, with 0.27 g of cellulose, 0.3 g of catalyst and 27 mL water in a 50 mL autoclave. ^{*b*} The density of $-SO_3H$ groups was measured by ICP-AES. ^{*c*} The acid density was determined by a titration method. ^{*d*} The acid density was determined by an NH₃-adsorption method. ^{*e*} Specific surface area was measured by N₂ adsorption at -196 °C according to the Brunauer–Emmett–Teller (BET) method. ^{*f*} The amount of adsorbed water was measured with a static adsorption method. ^{*g*} Y_{Glu} was the carbon-based yield of glucose. ^{*h*} Conv. was the carbon-based conversion of cellulose determined by analysis of total organic carbon (TOC) of the liquid product.

The above samples obtained at different sulfonation temperatures were investigated for hydrolysis of cellulose. Prior to the catalytic reaction, the cellulose was pretreated by ball-milling for 48 h in order to decrease the crystallinity (Fig. S1), as reported in the literature.^{13–17} The hydrolysis reaction was conducted at 150 °C for 24 h, with 0.27 g of cellulose, 0.3 g of catalyst and 27 mL water in a 50 mL autoclave. The conversion of cellulose was determined by measuring the soluble carbon content in the liquid product using a TOC (total organic carbon) analyzer, while the glucose yield was calculated by the ratio of carbon amount in glucose product (determined by HPLC) to that in cellulose (determined by a CHNS analyzer). Table 1 shows the conversions of cellulose and the yields of glucose produced over different sulfonated carbons. The nontreated AC was poorly active for degradation of cellulose; only 10% of cellulose was depolymerized and no glucose was detected in the product. In contrast, over sulfonated carbons, both the conversion of cellulose and the production of glucose were enhanced. Moreover, they were strongly dependent on the sulfonation temperature. When the sulfonation temperature of AC was increased from 150 to 250 °C, the glucose yield was increased from 7.1% to 61.0% and the cellulose conversion was increased from 25.1% to 70.4%. However, further elevation of the sulfonation temperature brought about a decrease in both the cellulose conversion and glucose yield, although the sulfonated carbons have a higher acid density in this case. It was found that the trend of cellulose conversion and glucose yield was in good agreement with the density of sulfonate groups, indicating that the acid sites associated with the SO₃H functional groups act as the active sites for the selective hydrolysis of cellulose into glucose. For the AC-N-SO₃H series catalysts, the activity and selectivity were even higher, attributed to the further increased densities of sulfonate groups in comparison with the AC-SO₃H series catalysts. Among the AC-based catalysts, the best result was achieved on the AC-N-SO₃H-250 catalyst which gave the glucose yield of 62.6% and the cellulose conversion of 74.3%. Previously, Suganuma *et al.*¹⁴ reported a carbon material bearing SO_3H , COOH, and OH groups which exhibited a high efficiency for

hydrolysis of cellulose into saccharides; but the glucose yield was very low (4%). Onda *et al.*¹³ also used a sulfonated carbon for hydrolysis of cellulose, and they obtained a much higher yield of glucose (40.5%) than Suganuma *et al.* In comparison with the results reported in the literature, the AC-N-SO₃H-250 catalyst we report here gave a significantly increased glucose yield attributed to a higher sulfonation temperature used.

The kinetic study for cellulose conversion over the AC-N-SO₃H-250 catalyst revealed that the cellulose was hydrolyzed fast and selectively into glucose at the initial stage (from 0 to 4 h), followed by a slow hydrolysis process until 20 h (Fig. S2). However, even on prolonging the reaction time to 48 h, the cellulose could not be fully hydrolyzed. Meanwhile, the decomposition of glucose took place on extending the reaction time longer than 24 h. This result may imply that the degradation of cellulose follows an inhomogeneous process from the most easily attacked part to the part most difficult to attack.

Taking the AC-N-SO₃H-250 catalyst as an example, we then investigated the recovery and reusability of the sulfonated carbons. As shown in Fig. S3, the catalyst presented excellent stability and reusability; the glucose yield still reached 59% over the fourth-recycled catalyst and the cellulose conversion remained the same as that over fresh catalyst. The analysis of the reused catalyst after the fourth recycling test revealed that neither the sulfonate groups nor the acid densities were lost during the repetitive reactions (Table S1). Further experiment by putting the fresh cellulose into the filtrate solution after the first run revealed that the glucose yield did not increase after the reaction at 150 °C for 24 h; instead, it had a decrease of about 10% due to the degradation of glucose. These results provide strong evidence that the hydrolysis reaction takes place solely on the solid catalyst surface.

Apart from the sulfonation conditions, the carbon sources and the carbonization procedures may also affect, even dominate the functional groups on the carbon surface, which will then influence the catalytic activity. As shown in Fig. 1, the six sulfonated carbons¹⁸ behaved remarkably differently in the hydrolysis of cellulose, following the order of ACB < MWCNT < Cell-Carbon < CSAC < Resin-Carbon < CMK-3 in terms of glucose yield. Especially interesting, the sulfonated CMK-3,



Fig. 1 Hydrolysis of cellulose over different carbons sulfonated at 250 °C. The yield of water soluble by-products was calculated from the difference between the conversion of cellulose and the yield of glucose according to ref. 13.

a type of ordered mesoporous material, gave a conversion of cellulose of 94.4% and a glucose yield of 74.5%, which almost doubles that reported by Onda et al.13 This is also the highest glucose yield achieved on solid acids to date. Correlating with the acid densities of the samples in Table 2, one can find that the catalytic performance is well consistent with the acid densities of the carbon materials except for the Cell-Carbon (cellulose-derived carbon). Although possessing a high acid density, the Cell-Carbon has a very low specific surface area which significantly decreases the available active sites for the hydrolysis of cellulose. On the other hand, the sulfonated CMK-3 has a high acid density and a reasonably large surface area (412 m² g⁻¹), both of which are required for the hydrolysis of cellulose into glucose. In addition, the mesoporous structure also facilitates the transportation of large molecules (such as glucose, cellobiose, cellotriose) in comparison with microporous carbons. The advantages of mesoporous carbons as the catalyst supports have recently been demonstrated in hydrogenolysis of cellulose as well as hydrolysis of cellulose.12,19

In summary, we have developed a highly active and selective solid acid catalyst for the hydrolysis of cellulose into glucose. The best result was obtained by using 250 °C-sulfonated CMK-3 as the catalyst, with the cellulose conversion of 94.4% and glucose yield of 74.5% which is the highest value obtained so far on solid acids. The acid density required for

Table 2 The surface properties of different carbons sulfonated at 250 $^\circ\mathrm{C}$

Cat.	$-\mathrm{SO_3H}^a/$ mmol g ⁻¹	Acid density ^{b/} mmol g ⁻¹	Acid density ^{c/} mmol g ⁻¹	$rac{S_{ m BET}/}{ m m^2~g^{-1}}$
ACB	0.02	0.24	0.07	89
MWCNT	0.02	0.26	0.05	96
CMK-3	0.63	2.39	0.88	412
Cell-Carbon ^d	2.01	3.96	1.22	6
Resin-Carbon	0.28	2.08	0.45	834
CSAC	0.33	1.10	0.28	981

^{*a*} The content of –SO₃H was measured by ICP-AES. ^{*b*} Acid density was determined by a titration method. ^{*c*} Acid density was measured by NH₃-adsorption. ^{*d*} Cell-Carbon was sulfonated at 200 °C.

the hydrolysis of cellulose is strongly dependent on the sulfonation temperature of the carbon materials; 250 °C-sulfonation was proved to generate a high acid density and meanwhile did not cause a severe decrease in the specific surface area. In addition, the carbon source also has a great impact on the acid density of the sulfonated carbons. The correlation between the acid density and the catalytic performance established here will guide the design of new solid acids for a variety of acid-catalyzed reactions.

Support from the Natural Science Foundation of China (NSFC Nos. 20773124, 20903089) and from the 973 Program of China (2009CB226102) are gratefully acknowledged

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- 18 ACB refers to acetylene carbon black, MWCNT refers to multiwall carbon nanotube, Cell-Carbon was prepared by pyrolysis of cellulose at 400 °C according to ref. 14, Resin-Carbon was prepared by pyrolysis of resin at 800 °C, and CSAC refers to coconut shell active carbon. For preparation details see supporting information.
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