Microwave-assisted hydrolysis of crystalline cellulose catalyzed by biomass char sulfonic acids†

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The development of an environmentally benign process for the hydrolysis of cellulose into reducing sugars can be one of the key technologies for making full use of cellulosic biomass in the future. Here, a biomass char sulfonic acid (BC-SO_3H)-catalyzed hydrolysis of cellulose in water was achieved under microwave irradiation. The BC-SO_3H catalysts prepared cheaply from natural bamboo, cotton and starch, showed a much higher turnover number (TON, 1.33-1.73) for this reaction compared to a dilute H_2SO_4 solution (TON, 0.02), which was likely due to their strong affinity to β-1,4-glycosidic bonds of cellulose. In addition, microwave irradiation played key roles in activating cellulose molecules and strengthening particle collision, which can lead to a remarkable acceleration effect on this heterogeneously catalytic process.

1. Introduction

Cellulose hydrolysis is a key technology to obtain reducing sugars from vegetation such as grasses, agricultural and wood waste,[1] because the reducing sugars can be converted into a range of important industrial chemicals, including ethanol, hydrocarbons and starting materials for the production of polymers.[2,3] Thus far, available technologies for cellulose transformation into the reducing sugars include enzyme hydrolysis,[4,5] dilute acid hydrolysis,[4,6] concentrated acid hydrolysis,[7] alkaline hydrolysis[8] and supercritical water hydrolysis,[9,10] but none of the known methods are cost-effective for large-scale applications. For example, acid hydrolysis has a long industrial history, but needs high operating costs and leads to various environmental pollutants.[6] Enzymatic hydrolysis is one of the most promising hydrolysis technologies,[11] but suffers the severe controls of enzymes and the troublesome separation processes. Supercritical water hydrolysis has been proven to be very effective owing to its unique physical and chemical effects,[12] but it is carried out in an extremely short residence time (seconds) to avoid further degradation and dehydration of produced reducing sugars,[9,13] which will cause difficulties for developing a commercial reaction system with effective heat recovery. To solve these problems, Suganuma *et al.*,[14] Toda *et al.*[15] and Onda *et al.*[16] have developed the hydrolysis of cellulose catalyzed by solid acids, but this heterogeneously catalytic process shows poor hydrolysis efficiency due to a mass transfer resistance between solid acids and insoluble cellulose in water. Recently, new attention has been focused on the hydrolysis of cellulose in some ionic liquids (ILs)[17,18] because these ILs have good solubility for cellulose.[19] However, the expensive cost and high viscosity of ILs hamper its commercialized application.

In the last decade, the use of microwave irradiation to accelerate organic reactions has been of growing interest as a type of environmentally benign process,[20] in particular it has been successfully applied to promote the dilute alkali[21]—and dilute acid[22]—catalyzed hydrolysis of various lignocellulosic materials, as well as the solid acid-catalyzed hydrolysis of cellulose with the low degree of polymerization (DP, 100-450) in ILs,[23] usually affording a high yield of reducing sugars in a short reaction time. We believe that such technology should be very effective for accelerating the solid acid-catalyzed hydrolysis of cellulose since both thermal effects (rapid heat generation) and non-thermal effects (particle collision) are involved.[24] Here, we report an environmentally benign process for the hydrolysis of cellulose into reducing sugars under microwave irradiation, as shown in scheme 1. The biomass carbon sulfonic acids (BC-SO_3H) derived from bamboo, cotton and starch were used as the catalysts, only a small amount of water was used as the reaction medium, and the separation of products and catalysts was readily carried out by filtration.

2. Results and discussion

2.1. Characterization of BC-SO_3H catalysts

The BC-SO_3H catalysts were characterized *via* X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analyses (TGA), respectively, and the resulting figures are shown in the ESI†. In this, the main results were summarized as follows: (i) The XRD pattern of a typical material BC-SO_3H-1 exhibited a broad but weak diffraction peak at 2θ angles of 10–35° which is attributed to amorphous carbon composed of aromatic carbon

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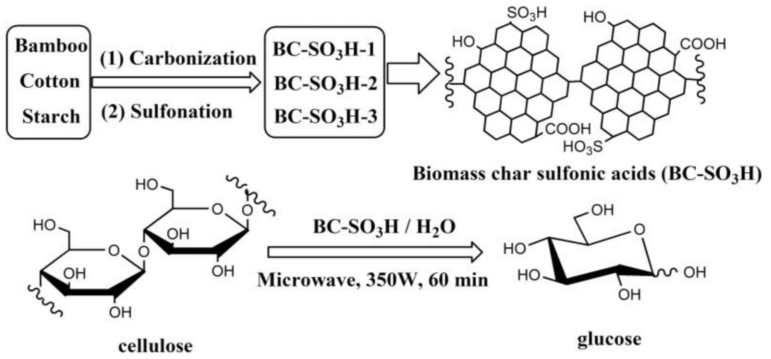
† Electronic supplementary information (ESI) available: Titration method of every functional group over the BC-SO_3H samples; XRD pattern of BC-SO_3H-1 (Fig. S1); FT-IR spectra of BC-SO_3H-1 (Fig. S2); XPS spectra of BC-SO_3H-1 (Fig. S3); TGA curves of the BC-SO_3H samples (Fig. S4). See DOI: 10.1039/b917807d



Scheme 1 Preparation of biomass carbon sulfonic acids and their application in catalytic hydrolysis of cellulose into glucose and cellooligosaccharides under microwave irradiation.

sheets oriented in a considerably random fashion[25] (see the XRD pattern in Fig. S1); (ii) The specific surface area of these BC-SO_3H materials was extremely low (S_g, 2~5 cm^3 g^{-1}) and attributed mostly to the external porosity (97%); (iii) The FT-IR spectrum for the BC-SO_3H-1 exhibited some characteristic stretching vibration bands, consisting of the polycyclic aromatics in 1400-1600 cm^{-1} region, the Ar-OH at 1594 cm^{-1}, the C=O at 1713 cm^{-1} and the S=O at 1032 cm^{-1}.[26] The XPS spectrum for the BC-SO_3H-1 exhibited a single S_{2p} peak at 168 eV, which is assigned to SO_3H groups.[27] These findings confirmed that the surface of BC-SO_3H-1 possessed SO_3H, COOH, and hydrophilic OH groups (see the FTIR and XPS spectra in Fig. S2 and Fig. S3, respectively) and; (iv) The BC-SO_3H materials showed a strong capacity to adsorb water molecules, and the adsorption amount of water measured from their TGA curves (see Fig. S4) followed the sequence BC-SO_3H-1(19.73%) > BC-SO_3H-2(18.38%) > BC-SO_3H-3(13.06%), which basically matched with the content of -SO_3H and -OH groups measured by chemical titration method (see table S1).

Table 1 Comparison of glucose and cellooligosaccharides yields between conventional heating and microwave (MW)-assisted hydrolysis of crystalline cellulose catalyzed by BC-SO_3H-1[a]

		Yield of reducing sugars (%)			
		Conventional heating		MW-assisted	
Temp (°C)	Time (min)	Glucose	COSs[b]	Glucose	COSs
70	30	trace	trace	trace	trace
	60	trace	trace	0.8	1.2
	120	1.5	0.3	2.0	3.3
90	30	trace	trace	7.2	5.6
	60	3.1	2.0	16.7	7.4
	120	5.3	2.7	10.0	8.0
100	30	3.0	0.2	12.5	0
	60	5.0	1.9	10.6	9.0
	120	7.0	2.5	8.0	6.0

[a] BC-SO_3H-1 catalyst, 0.1 g; cellulose, 0.2 g; water, 1.5 ml; microwave power, 350 W. [b] COSs indicated cellooligosaccharides that consisted of reducing sugars except for glucose.

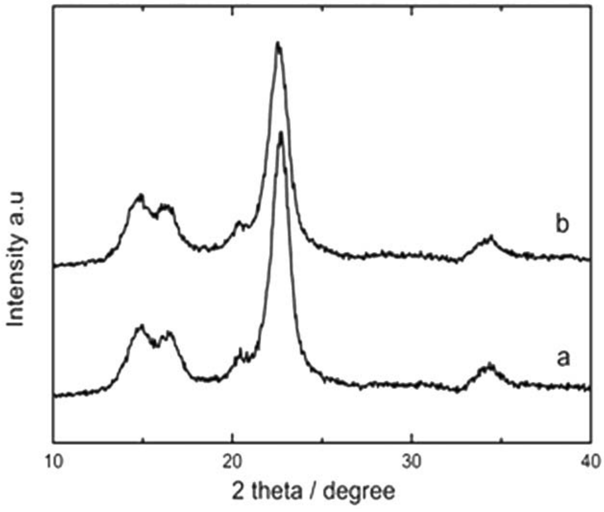


Fig. 1 X-ray diffraction patterns of microcrystalline cellulose (a) before microwave irradiation and (b) after microwave irradiation for 3 h.

2.2. Hydrolysis of cellulose under microwave irradiation

Firstly, we examined the hydrolysis of cellulose catalyzed by a solid acid catalyst BC-SO_3H-1 under microwave irradiation and conventional heating, the results are listed in table 1. As expected, the accelerated effect of temperature on this reaction was evident whether microwave irradiation or conventional heating was used. Also, the yield of reducing sugars (RSs) drastically increased with increasing temperature from 343 to 363 K, but slightly decreased when the temperature further went up (373 K), in consequence of the RSs to be further hydrolyzed into the more small molecules. Notably, the microwave irradiation significantly accelerated the hydrolysis reaction and increased the yield of RSs as compared to the conventional heating method. For example, the yield of RSs under the microwave irradiation was *ca.* 24.1% at 363 K for 60 min, being 3.8-fold higher than that under conventional heating. On the other hand, the composition of RSs showed that cellooligosaccharides (COSs) were much more present in the products obtained by using the conventional heating method, while glucose was mostly obtained by using the microwave method. The promoted effect of microwave irradiation on cellulose hydrolysis is likely because: (i) it may be absorbed deeply into the folding layers of cellulose to destroy the crystal structures, which can be confirmed by XRD characterization. As shown in Fig. 1, the XRD pattern of cellulose before the microwave irradiation showed some characteristic diffraction peaks crystalline cellulose around 16.5, 22.5 and 34.5°. After microwave irradiation of 3 h, the peak

Table 2 Microwave-assisted hydrolysis of crystalline cellulose catalyzed by various catalysts[a]

Catalyst	Functional groups	Density (mmol/g)	Yields of hydrolysis products	TON[b]	Adsorption value (mg/g)[c]
BC-SO_3H-1	SO_3H COOH phenolic OH	1.8750 0.1769 2.5930	glucose: 16.71% COSs: 7.39%	1.59	21.6
BC-SO_3H-2	SO_3H COOH phenolic OH	1.9886 0.1321 3.4317	glucose: 19.8% COSs: 8%	1.73	22.4
BC-SO_3H-3	SO_3H COOH phenolic OH	1.1357 0.2927 1.9818	glucose: 4.6% COSs : 7.5%	1.33	7.6
Amberlyst-15[d]	SO_3H	4.7	glucose: — COSs: —	—	—
H_2SO_4[e]		20.4	glucose: 29.5% COSs: 12.9%	0.02	—

[a] Catalyst: 0.1 g; cellulose: 0.2 g; water: 1.5 ml, reaction time: 1 h; reaction temperature: 363 K. [b] Turnover number was evaluated on the basis of the molar amount of converted substrate per mole effective acid sites (SO_3H) (mol. mol^{-1}). [c] In the adsorption experiments, 0.1 g of solid acid was immerged in a 10 ml of hydrolytic solution (28.7 mg L^{-1}) containing 7.39% of COSs and 16.71% of glucose and then stirred for 12 h at room temperature. Because we had confirmed that the solid acid could not adsorb glucose under the present conditions, the amount of adsorbed COSs could be directly estimated by UV-vis measurement of the supernatant solution. [d] Amberlyst-15 (polystyrene-based cation exchangeable resin with *ca.* 4.7 mmol g^{-1} of SO_3H, 38 m^2 g^{-1} of specific surface area and 30 nm of porous diameter). [e] Using 26% of H_2SO_4 (20 ml) as a catalyst.

intensity at $2\theta = 22.5°$ decreased. By use of a formula suggested by Rebuzzi *et al.*[28] (Crystallinity % = $I_{cr}/(I_{cr} + I_{am}) \times 100$, where I_{cr} and I_{am} are the peak intensities from crystalline and amorphous regions of cellulose, respectively) the cellulose crystallinity calculated from the intensity of XRD peaks was about 75% before irradiation and decreased to 58% after the irradiation of 3 h, clearly indicating partial demolishment of the crystal structure of cellulose; (ii) It probably enhances the collision opportunity between solid cellulose and catalyst particles.

In the following experiments, we checked the effect of microwave power on the hydrolysis of cellulose catalyzed by the BC-SO_3H-1 under the optimum temperature (363 K). As shown in Fig. 2, an increase in microwave power resulted in an enhanced hydrolysis rate and a shortened reaction time to achieve the highest yield of RSs. The best result was obtained using the microwave power of 350 W and the irradiation time of 60 min. Any attempt to increase microwave power or to prolong irradiation time actually resulted in a decreased yield of RSs, which was due to the accelerated degradation of RSs.

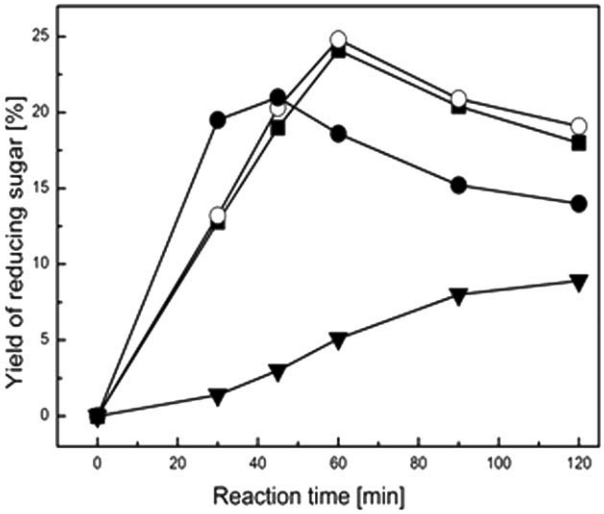


Fig. 2 Effect of microwave power on the BC-SO_3H-1-catalyzed hydrolysis of celllulose. (▼) oil bath, (■) 250 W, (○) 350 W, (●) 450 W.

The catalytic performance of various BC-SO_3H was examined by the microwave-assisted hydrolysis of cellulose under the optimum conditions, and compared with that of a commercial Amberlyst-15 with single -SO_3H group and a dilute H_2SO_4 solution. As shown in table 2, all the BC-SO_3H catalysts were active for the reaction, and the yield of RSs was proportional to the density of SO_3H groups of these catalysts. Moreover, the turnover number (TON), and especially the glucose yield, increased with the densities of the -SO_3H and -OH groups. Evidently, the high activity of the BC-SO_3H catalysts can not be adequately explained as being due solely to factors such as acid property or surface hydrophilicity, because an Amberlyst-15 catalyst with a higher acid density could not hydrolyze cellulose at all (see table 2), and a dilute H_2SO_4 solution which owns a stronger acidity and is close to cellulose more easily, gave an abnormal low TON (*ca.*0.02) for this reaction. Suganuma and co-workers[14] have reported that a similar carbon material bearing -SO_3H, -COOH and -OH groups had a stronger affinity for β-1,4-glycosidic bonds of cellulose than the other solid acids with only -SO_3H groups. In the experiments of using the BC-SO_3H to absorb a hydrolytic solution containing 7.39% of COSs and 16.71% of glucose, we also found that all the BC-SO_3H samples could selectively adsorb COSs rather than glucose as a monomer of cellulose, and the adsorption ability was basically proportional to the density of phenolic OH groups. But Amberlyst-15 with only SO_3H groups could not adsorb the hydrolytic solution at all. These findings undoubtedly indicate that the phenolic OH groups should be responsible for the adsorption ability, which is probably due to the strong hydrogen bond interaction between the phenolic OH groups of BC-SO_3H and the oxygen atoms in β-1,4-glycosidic bonds of COSs.

Finally, the reuse of BC-SO_3H catalysts was checked by using the BC-SO_3H-1 as an example. After the first reaction run at 363 K for 60 min under microwave irradiation, the solid residue containing the catalyst and cellulose was recovered from the hydrolytic solution by filtering and washing with water. After drying and supplementing some fresh cellulose, the ground residue was directly used for the 2nd hydrolytic reaction under the same conditions. This recycling process proceeded repeatedly for three times, and the results showed that the catalyst was still active in each recycling run, although the yield of RSs gradually decreased from 18.1 (the 2nd run), 16.4 (the 3rd run) to 15.0% (the 4th run). In order to explore the factor that leads to the decrease in activity, we measured the content of -SO_3H groups on the catalyst after the 4th run, and found that the content (*ca.* 1.12 mmol g^{-1}) obviously lowered compared with that of the fresh catalyst (*ca.* 1.87 mmol g^{-1}), which indicated that a part of SO_3H groups has been shed from the catalyst's surface under microwave irradiation.

3. Experimental

3.1. Preparation of BC-SO_3H catalysts

The BC-SO_3H catalysts were prepared following a published procedure with a little modification.[29] In a typical procedure, 20 g of bamboo powder was treated with 80% sulfuric acid (100 ml) at 353 K for 3 h to obtain a carbonized solid. Then, the ground solid (10.5 g) was immersed in a 150 mL of oleum (50 wt% SO_3) and heated to 353 K for 2 h under N_2. After sulfonation, the cooling suspension was filtered to yield a black precipitate. Finally, the resulting black solid was washed repeatedly with hot distilled water (>353 K, 1000 mL) until impurities such as sulfate ions were no longer detected in the wash water, and then dried at 423 K for 4 h to obtain a bamboo carbonized material bearing -SO_3H, -OH and -COOH groups (denoted as BC-SO_3H-1). By using this method, the other two BC-SO_3H catalysts were prepared using cotton and starch as the starting materials, and coded as BC-SO_3H-2 and BC-SO_3H-3, respectively.

3.2 Hydrolysis of cellulose under microwave irradiation

In a typical experimental run, 0.2 g pure microcrystalline cellulose (particle size, 20-100 μm; degree of polymerization, 200-1000) and 0.1 g BC-SO_3H-1 catalyst were milled for 30 min in an agate bow, and then the ground solid mixture was removed to a Pyrex reactor, followed by adding the distilled water (1.5 mL). The reactor was sealed and placed in a special microwave oven with a frequency of 2.45 GHz, power from 0 to 100% of a maximum 1000 W and temperature controller. In the reaction process, the distilled water was successively added to the reactor through a microfeeder to compensate for water consumed. After the desired reaction time had elapsed, the reaction mixture was diluted with cold water, neutralized with 0.5 mol L^{-1} NaOH solution and filtered. The aqueous solution was collected and subjected to the analysis of reducing sugars (RSs) using an established method with 3, 5-dinitrosalicylic acid (DNS method).[30,31] The mixture of DNS reagent[31] (0.15 mL) and reaction sample (0.2 mL) was heated 5 min at 373 K, then cooled to room temperature, and diluted to 50 mL. The absorbance of the diluted solution was measured on an Agilent 8453 spectrophotometer at 520 nm, and the concentration of RSs was calculated based on a standard curve obtained with glucose. The estimated experimental error in the concentration of RSs was *ca.* 5%. The amount of glucose was conveniently analyzed on a Shimazu 20AT HPLC equipped with ODS C18 column (Spherigel) and refractive index detector (ERC-7571A), each sample was diluted with ultra pure water before analysis to prevent the overloading of the column with organic solvents. The yield of COSs were calculated as follows: COSs yield (%) = yield of RSs (%) – yield of glucose (%).

4. Conclusion

To aim at the general problems encountered in cellulose hydrolysis, such as insolubility and inaccessibility of cellulose in many reaction media, corrosivity of liquid acid catalysis and low efficiency of solid acid catalysis, we have developed a simple and efficient method for the solid acid-catalyzed cellulose hydrolysis under microwave irradiation. Such a method has the following advantages: (i) utilization of more available and cost-effective biomass carbon sulfonic acids as catalysts; (ii) by means of microwave irradiation to simultaneously achieve the activation and acceleration effects for hydrolysis of insoluble cellulose catalyzed by solid acids in the presence of small amounts of water; (iii) high catalytic efficiency and good stability; (iv) saving time and energy, and; (v) facile operation and environmentally friendly process. The method may also be exploited in the future for direct hydrolysis of lignocellulosic biomass into useful sugars and other chemicals.

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