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ORIGINAL PAPER

Cellulose hydrolysis catalyzed by highly acidic lignin-derived carbonaceous catalyst synthesized via hydrothermal carbonization

Linhuo Gan · Jundong Zhu · Li Lv

Abstract Acidic carbonaceous solids were synthesized from mass pine alkali lignin via hydrothermal carbonization followed by sulfonation. Hydrothermal carbonization of lignin in the presence of acrylic acid (LAHC-SO$_3$H) provided many more carboxylic groups than that in the absence of acrylic acid, allowing subsequent sulfonation to produce a highly active and stable catalyst for cellulose hydrolysis in the [BMIM]Cl-H$_2$O solvent system. The hydrochar and catalyst were characterized using field emission scanning electron microscopy, X-ray diffractometer, X-ray photoelectron spectroscopy, thermal gravimetric analysis, Fourier transform infrared spectrometer, Brunauer–Emmett–Teller and acid–base titration. Results showed that a high acid content of 5.48 mmol/g, including carboxylic group (2.85 mmol/g), phenolic hydroxyl group (1.05 mmol/g) and sulfonic acid group (1.58 mmol/g), contributed significantly to the highly efficient hydrolysis of cellulose. Further, it was found that addition of trace water in [BMIM]Cl was favorable to cellulose hydrolysis. The highest yield (75.4%) of total reducing sugar (TRS) obtained in [BMIM]Cl-H$_2$O at a mass ratio of 100:1 was more than twice that (36.1%) achieved in [BMIM]Cl without water; the corresponding reaction conditions were 50 mg of microcrystalline cellulose, 30 mg of catalyst, 1.0 g of [BMIM]Cl, 10 mg of H$_2$O, reaction temperature of 130 °C and reaction time of 2 h. Furthermore, the TRS yield with 5 cycles for LAHC-SO$_3$H was higher than 68.1%, and the catalytic activity of catalyst could be fully recovered (74.0% of TRS yield) easily by regeneration.

Introduction

Transformation of cellulose into sugar platform chemicals still remains a challenging issue due to the strong intra-and intermolecular hydrogen bonds in its structure and its poor water solubility (Wang et al. 2015; Hara et al. 2015; Hu et al. 2015a, b). Although cellulase and liquid acid have been applied in industrial cellulose hydrolysis (Zhu et al. 2016; Zou et al. 2016), there are several problems in practical application, such as the difficulty of separating sugar from catalyst and poor recycling ability, among others (Wang et al. 2013). Therefore, separable and reusable heterogeneous solid acid catalysts have been developed in the interest of green and sustainable chemistry.

Carbonaceous solid acid catalysts, mainly derived from biomass materials, have been one of the research hotspots in recent years, and they have shown comparable abilities for hydrolyzing cellulose

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to reducing sugar, as listed in Table 1. Traditional biomass-derived solid acids were synthesized by incomplete carbonization at high temperature and followed by sulfonation (Nakhate and Yadav 2016; Qi et al. 2014), such as cellulose-derived solid acids reported by Hara (2010), Fukuhara et al. (2011) and Suganuma et al. (2008). However, due to harsh carbonization conditions and emission of harmful gases, the pyrolysis carbonization process is not environmentally friendly and sustainable (Laginhas et al. 2016). More recently, thermochemical conversion of biomass has been carried out via hydrothermal carbonization at moderate temperature (150–300 °C) under self-generated pressure. The corresponding hydrochar materials have received considerable interest in catalysis studies owing to their various structural morphologies with abundant oxygen-containing functional groups (Jain et al. 2016; Tekin et al. 2014). Furthermore, sulfonated hydrochar has shown a favorable catalytic performance for cellulose hydrolysis in comparison with that prepared by the pyrolysis carbonization method (Kang et al. 2013). Qi et al. (2014) reported that two functional carbon materials were synthesized by hydrothermal carbonization of glucose in the presence of sulfosalicylic acid or acrylic acid. The corresponding catalysts exhibited good catalytic activities for cellulose hydrolysis, and the yields of total reducing sugar (TRS) reached 59.4 and 50.0% in ionic liquid ([BMIM]Cl) at 130 °C for 3 h, respectively.

Many research efforts on hydrothermal carbonization have concentrated on carbohydrates or raw biomass (Liu et al. 2015; Titirici et al. 2015). Compared with carbohydrates, lignin requires higher carbonization temperatures, probably owing to its relatively stable aromatic structure (Kang et al. 2012). Fortunately, this obstacle can be overcome effectively by adjusting hydrothermal conditions, especially for hydrothermal solvents and catalysts. Wikberg et al. (2015) found that kraft lignin structure was altered to a certain extent by hydrothermal treatment when adding catalysts (H_2SO_4, Fe^{2+}), resulting in higher carbon recovery as well as a more stable carbonaceous structure. Thus, lignin could become a high quality source for preparing activated carbon (Fierro et al. 2007) or carbonaceous solid acid via hydrothermal carbonization, owing to its higher carbon content compared to carbohydrates such as cellulose or glucose.

Here, using acrylic acid as a directing agent via hydrothermal carbonization followed by sulfonation, we have developed a novel lignin-derived solid acid (LDSA) from alkali lignin in a black liquor of soda pulping. In comparison with other catalysts shown in Table 1, the optimized LDSA sample prepared in this work exhibited higher catalytic activity for cellulose hydrolysis in a [BMIM]Cl-H_2O solvent system. Characterizations such as field emission scanning electron microscopy (FESEM), X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), Fourier transform infrared spectrometer (FT-IR), Brunauer–Emmett–Teller (BET) and acid–base titration were conducted to better understand the structure–function relationship of LDSA. In addition, we find that full utilization of renewable lignocellulose composed of cellulose, lignin and hemicellulose can be realized

Table 1 Catalytic performances of acidic carbonaceous solids in cellulose hydrolysis

Catalyst	Solvent	Temperature (°C)	Time (h)	TRS yield (%)	References
MCM-41-SO$_3$H	H$_2$O	230	0.25	47.2	Bai et al. (2013)
LPC-SO$_3$H	H$_2$O	180	3	50.8	Zhu et al. (2016)
BC-SO$_3$H-IL-Zn	H$_2$O	90	2	58.7	Zhang et al. (2014)
MLC-SO$_3$H	[BMIM]Cl	140	2.5	69.3	Hu et al. (2016a, b)
SC-SO$_3$H	[BMIM]Cl	110	4	63.0	Liu et al. (2013)
PCM-SO$_3$H	[BMIM]Cl	130	3	68.9	Guo et al. (2013)
Fe$_3$O$_4$@SiO$_2$–SO$_3$H	[BMIM]Cl	130	8	73.2	Xiong et al. (2014)
LHC-SO$_3$H	[BMIM]Cl-H$_2$O	130	2	61.9	This work
LAHC-SO$_3$H-40	[BMIM]Cl-H$_2$O	130	2	75.4	This work

through cellulose hydrolysis when efficiently catalyzed by highly acidic lignin-derived solid acid.

Experimental

Materials

Masson pine alkali lignin (MAL), which was separated and purified from Masson pine pulping black liquor using an acidic treatment, was supplied by Nanping Paper-making Co. Ltd. (Nanping, China), 1-Butyl-3-methyl imidazolium chloride (99%) was purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). Microcrystalline cellulose (MCC, 25 μm), glucose, 3,5-dinitrosalicylic acid (DNS), Amberlyst-15 were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). γ-Al$_2$O$_3$ and HZSM-5 were purchased from Nankai University Catalyst Co. (Tianjin, China). H$_2$SO$_4$ (≥ 98%) and acrylic acid (> 99%) were obtained from Xilong Chemical Factory Co., Ltd. (Shantou, China).

LDSA preparation

To prepare the LDSA, 4.0 g of MAL and acrylic acid (10–50 wt%) were mixed into 40 mL deionized water and then ultrasonicated for 20 min. Subsequently, the suspension was loaded into a 100 mL Teflon-lined stainless steel autoclave and heated at 240 °C for 10 h under self-generated pressure. The generating hydrochar was washed several times with deionized water followed by ethanol, and was dried in an oven at 80 °C. Then, the hydrochar was sulfonated with concentrated sulfuric acid (m/v, 1 g/20 mL) at 180 °C for 12 h. After cooling at room temperature, the resulting black product was washed with hot deionized water (> 80 °C) until no sulfate ions could be detected in the filtrate by the barium sulfate gravimetric method. Eventually, the sulfonated hydrochar was dried in a vacuum oven at 105 °C for 12 h and labeled as LAHC-SO$_3$H-X, where X (X = 10, 20, 30, 40, 50) is the mass concentration of acrylic acid with respect to lignin. For example, LAHC-SO$_3$H-10 means the sulfonated lignin-derived carbonaceous
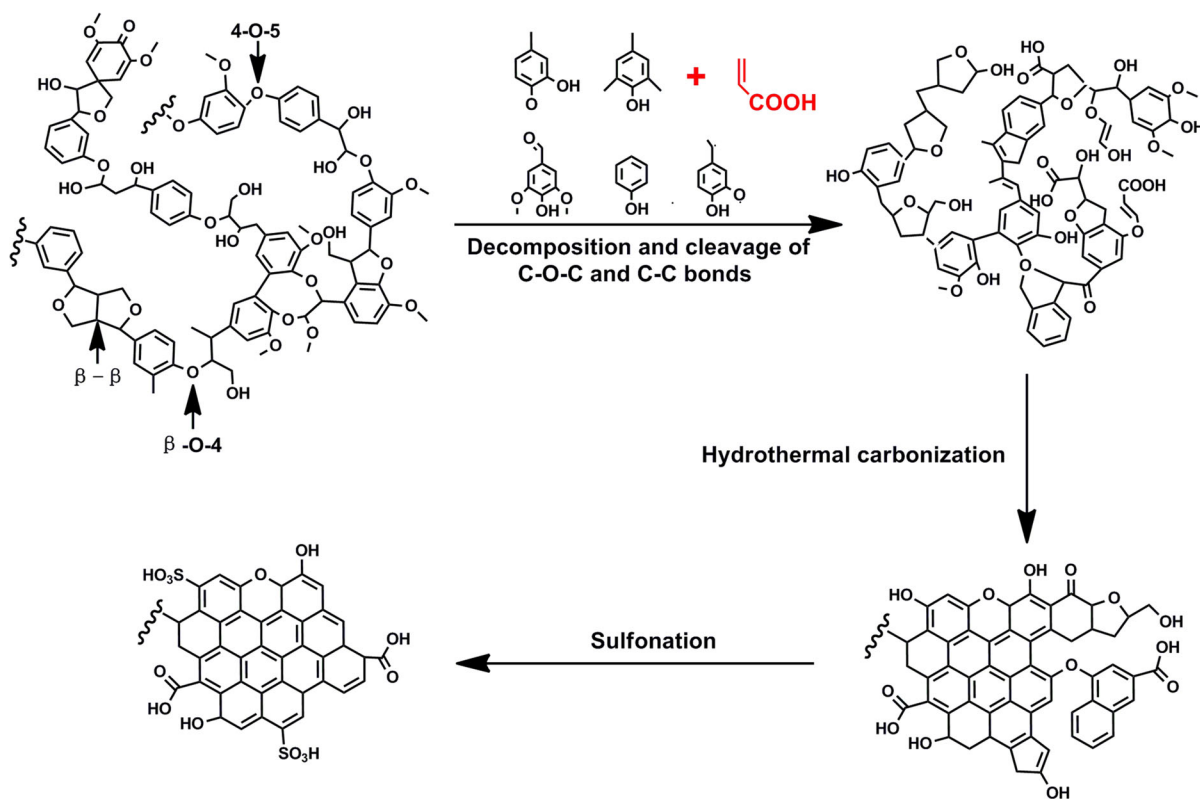
Scheme 1 Plausible formation pathway of lignin-derived solid acid via hydrothermal carbonization with acrylic acid

solid acid was prepared by adding 10 wt% acrylic acid during the hydrothermal carbonization process. For comparison, a lignin-derived solid acid was prepared by hydrothermal carbonization of lignin without acrylic acid at 240 °C for 20 h and followed by sulfonation. The corresponding sulfonated hydrochar was labeled as LHC-SO$_3$H. Scheme 1 shows a schematic diagram of preparation of LHAC-SO$_3$H in this work.

Characterization

Thermal gravimetric analysis of MAL, LHC-SO$_3$H and LAHC-SO$_3$H were carried out on a Shimadzu DTG-60H thermogravimetric analyzer in a temperature range of 30–800 °C under N$_2$ at a constant heating rate of 10 °C/min. Fourier transform infrared spectroscopy spectra of hydrochar and catalysts were recorded on a Nicolet iS50 FT-IR spectrometer for KBr pellets in a range of 4000–400 cm^{-1} and 32 scans per sample. The morphologies of the hydrochar and the catalysts were observed by Hitachi SU8000 field emission scanning electron microscopy operated at 3 kV. X-ray diffraction patterns were recorded on a Rigaku/SmartLa X-ray diffractometer with Cu Kα radiation source at 40 kV and 30 mA from 10° to 80° (2θ) at a scanning speed of 4°/min. X-ray photoelectron spectroscopy was performed on a Thermo Escalab 250xi spectrometer with an Al Kα radiation source (hv = 1486.6 eV). The binding energies were calibrated using the C1s peak at 284.9 eV, while high-resolution scans of the O 1s, C 1s and S 2p regions were acquired with a pass energy of 20 eV. Nitrogen adsorption–desorption isotherms of LAHC-SO$_3$H-40 were determined on Quantachrome Autosorb-IQ gas adsorption analyzer at −196 °C, and its specific surface area calculated according to the Brunauer–Emmett–Teller method was 0.8 m^2/g, which could be negligible as described in literature (Kang et al. 2013). In addition, according to the method described by Braghiroli et al. (2015), a krypton adsorption study of LAHC-SO$_3$H-40 was also carried out. The surface area obtained was only 1.6 m^2/g, which was not similar to the result of carbon derived from hydrothermally treated tannin described in the literature (Braghiroli et al. 2015).

The loading amounts (mmol/g) of sulfonic acid group (–SO$_3$H), carboxylic group (–COOH), phenolic hydroxyl group (Ar–OH) and total acids in catalyst were estimated using acid base back titration according to our previous work (Zhu et al. 2017).

Cellulose hydrolysis and TRS determination

In a typical run, 0.05 g of cellulose was dissolved into 1.0 g of [BMIM]Cl at 100 °C, then 0.03 g of catalyst and 0.01 g of deionized water were added. The reaction mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and kept at a certain temperature for a given time. After reaction, the reactor was cooled to room temperature immediately. Hydrolysate was diluted with 10 g of deionized water and the suspension was filtered using 0.22 μm filter membrane for further TRS analysis.

TRS yield was determined by the DNS method according to previous reports (Hu et al. 2016a, b). The concentration of TRS was determined by employing a standard curve prepared using glucose. TRS yield was calculated as follows:

$$\text{TRS yield } (\%) = \frac{C \times V}{50} \times 100 \tag{1}$$

where C is the concentration of reducing sugar (mg/mL) and V is the volume of hydrolysate (mL).

Catalyst cycles and regeneration

Catalyst cycles were conducted by running MCC hydrolysis successively 5 times under optimized hydrolysis conditions. Hydrolysis was first run with fresh catalyst to complete conversion, then catalyst was filtered and washed with hot deionized water; the cleaned catalyst was dried in oven at 110 °C and reused. Regeneration of catalyst was carried out via resulfonation in concentrated sulfuric acid.

Results and discussion

Characterization of hydrochar and sulfonated catalyst

It has been found that certain acidic oxygen-containing groups of carbon-based solid acid catalyst, such as carboxylic groups, acting as the cellulose-binding group for adsorbing β-1, 4-glucans of cellulose, as well as the cellulose-hydrolytic group serving as main active catalytic center, play an important role in the

efficient hydrolysis of cellulose (Hu et al. 2016a, b; Yang and Pan 2015; Zhou et al. 2015). Thus for better catalytic performance during the cellulose hydrolysis process, it is necessary to increase the amount of –COOH in the sulfonated lignin-derived hydrochar. In this work, with the addition of acrylic acid, carboxylic groups were grafted onto the carbonaceous material formed by the hydrothermal carbonization of lignin. The effects of adding various amounts of acrylic acid on the densities of the acidic oxygen-containing groups of LDSA and TRS yield in MCC hydrolysis were investigated under fixed conditions (50 mg MCC, 30 mg catalyst, 1.0 g [BMIM]Cl, 10 mg H_2O, reaction temperature 130 °C and reaction time 2 h). The experimental results are given in Table 2.

As shown in Table 2, without adding acrylic acid during hydrothermal carbonization process, –COOH content was only 1.56 mmol/g, and there was an obvious increase in –COOH content (from 1.67 to 2.88 mmol/g) when the dosage of acrylic acid increased (from 10 to 50 wt%). As the amount of acrylic acid increased, variation trends of total acidic functional group concentration and TRS yield were the same as that of the –COOH content. It should be noted that sulfonated lignin-derived hydrochars of LAHC-SO$_3$H-40 and LAHC-SO$_3$H-50 (Table 2) had total acid contents of 5.48 and 5.54 mmol/g, respectively, which were much larger than those by NaOH titration reported in previous literature (Wang et al. 2013; Zhang et al. 2013). However, the contents of both –SO$_3$H and Ar–OH varied in non-monotonic ways. For example, LAHC-SO$_3$H-20 contained the largest density of –SO$_3$H (1.60 mmol/g) and more Ar–OH content (1.12 mmol/g) among all of the catalyst samples listed in Table 2. This suggests that besides –SO$_3$H groups as the main catalytic domain, –COOH groups probably play a vital role in the enhancement of

catalytic activity of LDSA applied in cellulose hydrolysis.

FT-IR spectra of lignin-derived hydrochars before (LHC, LAHC) and after sulfonation (LHC-SO$_3$H, LAHC-SO$_3$H-40) are presented in Fig. 1. As depicted in Fig. 1, the absorption bands at around 3400 and 2900 cm^{-1} were attributed to O–H and –CH$_3$/–CH$_2$ stretching vibration, respectively (Shen et al. 2014a, b). The band at 1714 cm^{-1} was due to C=O bending vibration in –COOH groups (Lou et al. 2014). More significantly, LAHC had a stronger absorption peak in comparison with LHC at 1714 cm^{-1}, highlighting a higher content of –COOH groups on the hydrochar surface. The absorption peaks at around 1600 and 1535 cm^{-1} were assigned to C=C vibration absorptions in the aromatic skeleton, suggesting that the lignin maintained its basic structure to a certain extent. Adsorptions originating from O=S=O symmetric and asymmetric stretching vibrations in –SO$_3$H (1190 and 1032 cm^{-1}) for LHC-SO$_3$H and LAHC-SO$_3$H-40 increased, proving –SO$_3$H groups were successfully loaded onto the surface of the lignin-derived hydrochar (Kang et al. 2013).

To further verify the variations in structural properties of the char and sulfonated char, XPS spectra of LHC-SO$_3$H (a) and LAHC-SO$_3$H (b) are given in Fig. 2. As shown in Fig. 2, the peak of S 2p spectrum was fitted into S 2p 3/2 and S 2p 1/2 peaks at 168.6 and 169.8 eV, which were assigned to –SO$_3$H groups, indicating the introduction of –SO$_3$H groups onto the lignin-derived hydrochars (Liu et al. 2013; Lou et al. 2012). In addition, polyaromatic carbon was indicated, consisting of C–C or C–H bonds (about 284.2 eV), C–OH or C–O–C bonds (about 286.1 eV) and C=O (about 288.1 eV). The O 1s peak was resolved into two separate peaks at 533.1 and 531.3 eV, which were associated with C–OH and C=O, respectively (Sun et al. 2015). Based on the analysis above, it was

Table 2 Measurements of acidic group content and catalytic performance of LDSAs

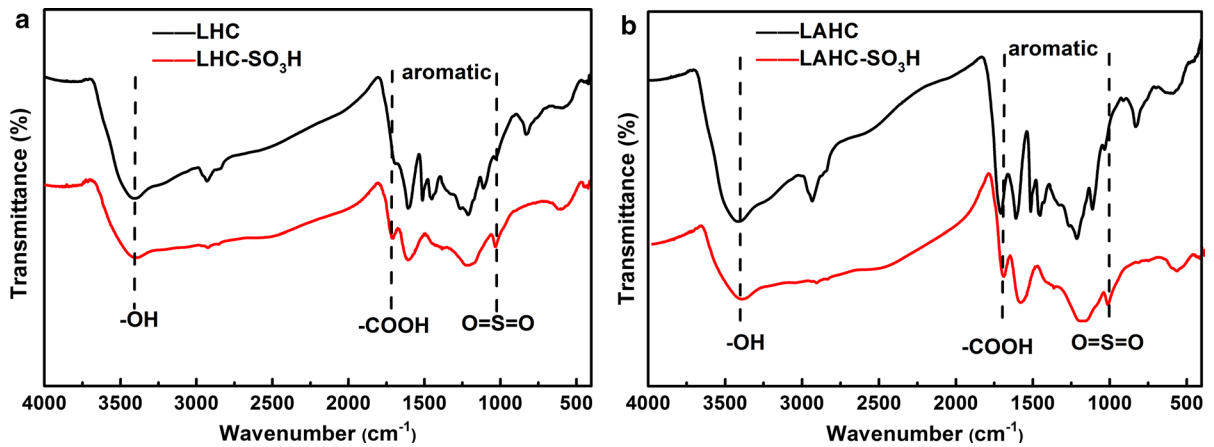| Catalyst	Total acid (mmol/g)	Ar–OH (mmol/g)	–COOH (mmol/g)	–SO$_3$H (mmol/g)	TRS yield (%)
LHC-SO$_3$H	3.68	0.92	1.56	1.20	59.1
LAHC-SO$_3$H-10	4.01	0.84	1.67	1.50	59.5
LAHC-SO$_3$H-20	4.86	1.12	2.14	1.60	64.5
LAHC-SO$_3$H-30	4.94	0.87	2.62	1.45	67.3
LAHC-SO$_3$H-40	5.48	1.05	2.85	1.58	75.4
LAHC-SO$_3$H-50	5.54	1.13	2.88	1.53	72.1

Fig. 1 FT-IR spectra of hydrochars and sulfonated hydrochars prepared without acrylic acid (**a**) and with acrylic acid (**b**)
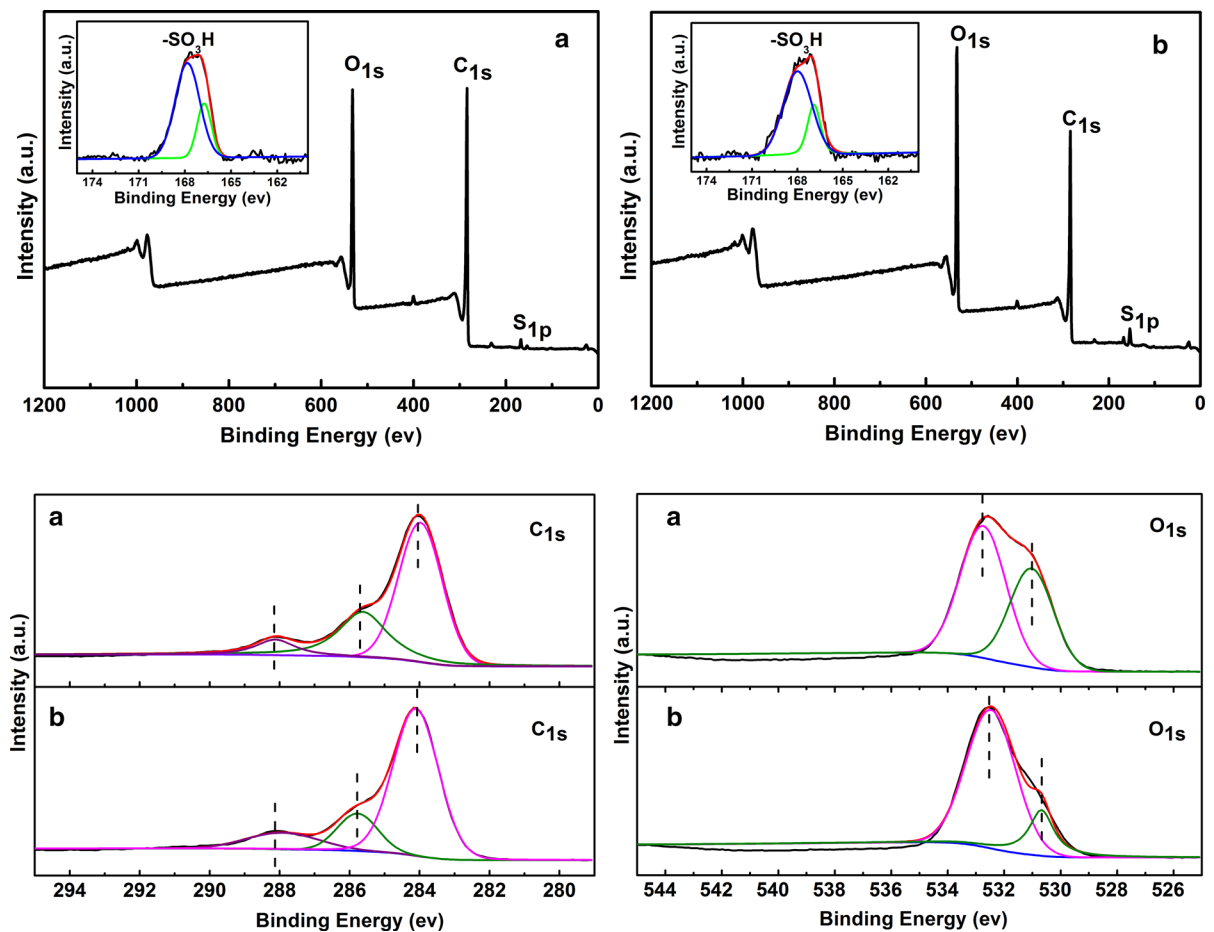

Fig. 2 XPS spectra of LHC-SO₃H (**a**) and LAHC-SO₃H (**b**)

estimated that the oxygen content of LAHC-SO₃H was higher than that of LHC-SO₃H due to the increase in content of –COOH groups, which was in good accord with the results seen from the full-scan XPS spectrum shown in Fig. 2. Hence, the results further confirmed that the existence of acrylic acid in the hydrothermal carbonization process was beneficial to introducing more –COOH groups onto the surface of the lignin-derived hydrochar.

Considering the high temperature (110–150 °C) needed for TRS production from cellulose, sulfonated lignin-derived hydrochars (LHC-SO₃H and LAHC-SO₃H) need thermal stabilization. TGA curves for MAL, LHC-SO₃H and LAHC-SO₃H-40 were detected in Fig. 3. According to the TGA curve of MAL shown in Fig. 3, it was found that MAL structure started to degrade significantly at 240 °C. Therefore, the proper temperature of thermal carbonization for MAL was determined to be 240 °C. As seen from Fig. 3, there was a slight loss in weight at around 100 °C which could be attributed to the evaporation of adsorbed water (Li et al. 2013). It was also observed that LHC-SO₃H and LAHC-SO₃H-40 tended to be stable as MAL in a temperature range from 100 to 220 °C, illustrating good thermal stability of LDSA within this temperature interval, which was beneficial for cellulose hydrolysis. However, when temperature exceeded 220 °C, the weight loss of sulfonated lignin-derived hydrochar was gradually apparent, although a little smaller than that of MAL, which was probably attributable to the decompositions of –SO₃H groups and amorphous carbon.

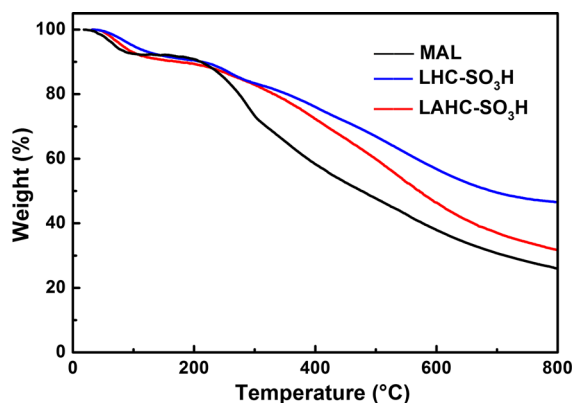Figure 4 depicts the XRD patterns of hydrochars and sulfonated hydrochars prepared without acrylic
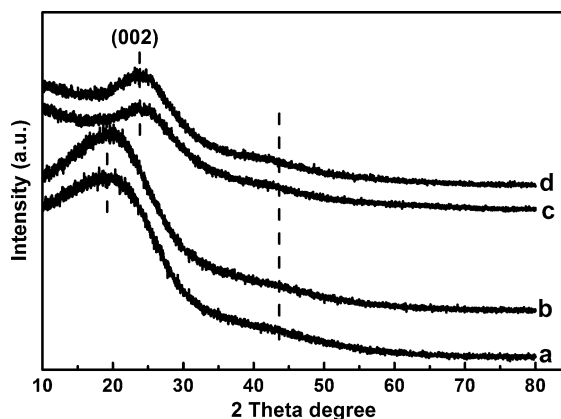

Fig. 4 XRD patterns of LHC (**a**), LAHC (**b**), LHC-SO₃H (**c**) and LAHC-SO₃H (**d**)

acid (LHC and LHC-SO₃H) and with acrylic acid (LAHC and LAHC-SO₃H). The broad diffraction peaks at around 10°–30° were ascribed to amorphous carbon sheets oriented in random fashion (Hu et al. 2016a; Hu et al. 2015a, b). Compared with the diffraction patterns of lignin-derived hydrochars, the diffraction peaks of sulfonated hydrochars had some slight right-shift, which was probably due to the strong oxidized characteristic caused by the reaction between sulfuric acid and hydrochar. Hence, LDSA was a kind of polycyclic aromatic compound with an amorphous carbon structure.

Furthermore, the morphologies of lignin-derived hydrochars (LHC and LAHC) and their corresponding catalysts (LHC-SO₃H and LAHC-SO₃H) were characterized by FESEM (Fig. 5).

As shown in Fig. 5a, LHC was composed of many larger spherical particles covered by some other smaller irregular particles. It was suggested that the formation of this structure from lignin was not the same as that from carbohydrate under hydrothermal conditions, which was just as reported by Kang et al. (2012). After sulfonation, the LHC-SO₃H surface was covered by more carbon microspheres than LHC (Fig. 5c), which was mainly due to the further carbonization of hydrochar in concentrated sulfuric acid with strong oxidizability. It was also found that the addition of acrylic acid had a dramatic influence on the morphology of the hydrochar during the hydrothermal carbonization process of MAL. Figure 5b illustrates that lignin-derived hydrochar prepared in the presence of acrylic acid (LAHC) had an anomalous pore or alveolate structure with pore diameter of less
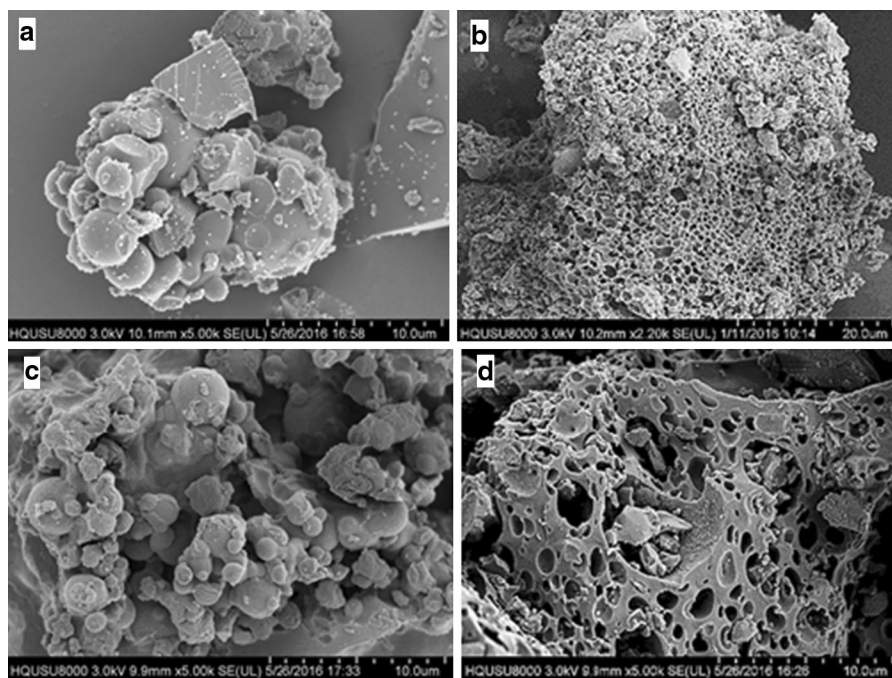

Fig. 3 TGA curves of MAL, LHC-SO₃H and LAHC-SO₃H

Fig. 5 FESEM images of LHC (**a**), LAHC (**b**), LHC-SO$_3$H (**c**) and LAHC-SO$_3$H (**d**)

than 2 μm, which was a completely different morphology in comparison with LHC. After sulfonation, although the majority of the alveolate structure could be maintained, the LAHC-SO$_3$H surface was etched to be rougher, with some pores shrinking or even collapsing (Fig. 5d) due to strong acid attack. Therefore, besides abundant oxygen-containing functional groups (especially –COOH groups) on the catalyst surface produced by the addition of acrylic acid during the hydrothermal carbonization process, the rich surface structure developed by the severe condensation reaction of acrylic acid on the hydrochar surface could also facilitate cellulose hydrolysis.

Catalytic hydrolysis of MCC with LAHC-SO$_3$H-40

Owing to the high content of acidic oxygen-containing groups on its surface (5.48 mmol/g), sulfonated hydrochar prepared in the presence of an acrylic acid dosage of 40 wt% (LAHC-SO$_3$H-40) was selected as an efficient solid acid catalyst to apply for reducing sugar production from microcrystalline cellulose (structural model of cellulose) in a Teflon-lined stainless steel autoclave according to single-factor design. Referring to previous literature (Shen et al.

2014a, b), influences of variables including reaction temperature and time, catalyst loading, water content in solvent system, catalyst type and recycling on TRS yield were investigated, respectively. The results are shown in Fig. 6 and Table 3.

Effect of reaction temperature and time

First of all, the combined effects of reaction temperature and time on TRS yield were investigated under fixed conditions (50 mg of MCC, 1.0 g of [BMIM]Cl, 10 mg of H$_2$O and 0.03 g (60 wt%) of LAHC-SO$_3$H-40); the results are shown in Fig. 6a. As seen from Fig. 6a, TRS yield increased obviously with elevating reaction temperature from 110 to 150 °C within the initial period of time (180 min for 110 °C, 150 min for 120 °C, 120 min for 130 °C and 60 min for 150 °C), and then decreased gradually with further prolonged reaction time. The maximum TRS yields at different temperatures (69.8% at 110 °C, 65.3% at 120 °C, 75.4% at 130 °C and 65.8% at 150 °C) were obtained. Figure 6a depicts that an appropriate increase in reaction temperature could be beneficial to enhancing the hydrolysis efficiency from cellulose to reducing sugar due to the promotion of mass transfer or diffusion of cellulose onto the catalyst surface, thus
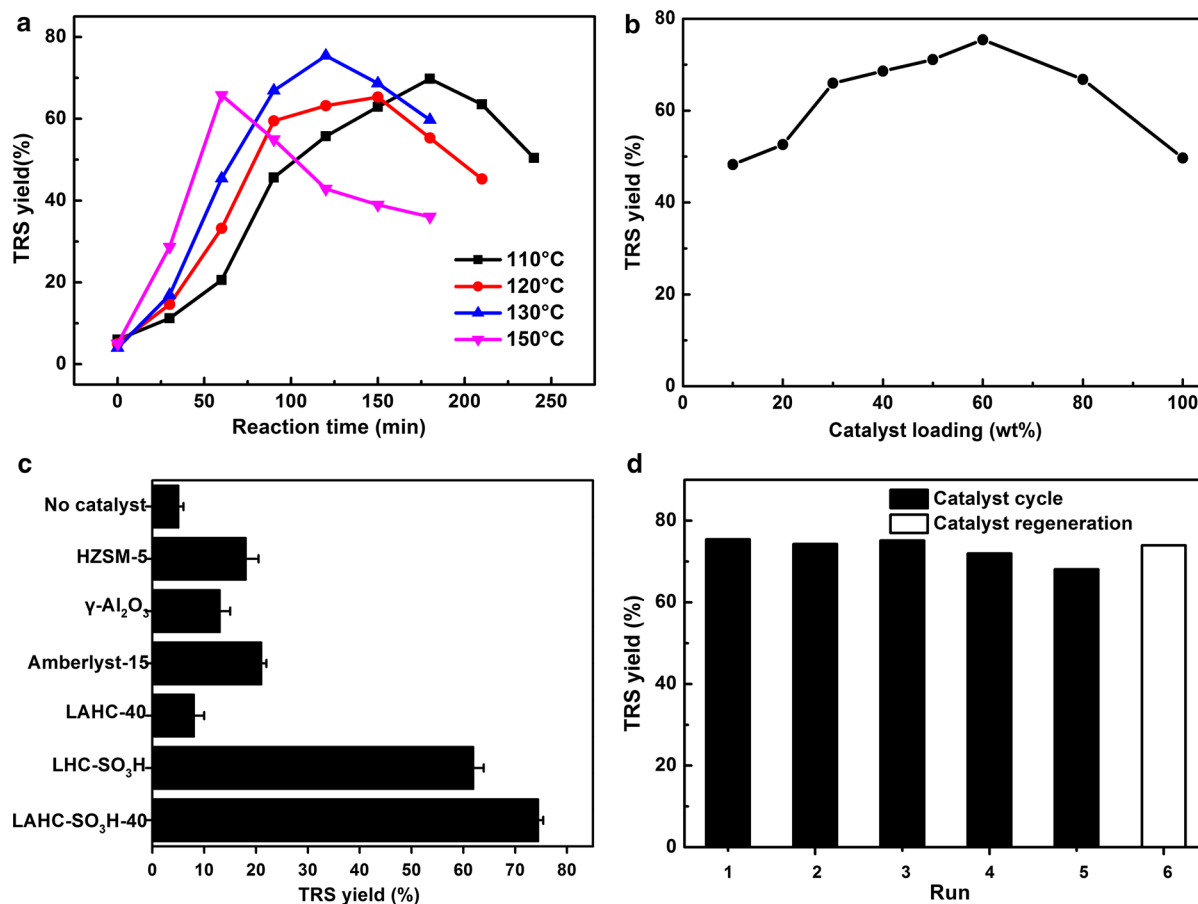
Fig. 6 **a** Effects of reaction temperature and time on TRS yield [MCC: 50 mg, [BMIM]Cl: 1.0 g, H₂O: 10 mg and LAHC-SO₃H-40 loading: 60 wt% (0.03 g)]; **b** effect of LAHC-SO₃H-40 loading on TRS yield (MCC: 50 mg, [BMIM]Cl: 1.0 g, H₂O: 10 mg, reaction temperature: 130 °C and reaction time: 2 h); **c** comparison of catalytic performance between various solid acid catalysts for MCC hydrolysis (MCC: 50 mg, LAHC-SO₃H-40: 30 mg, [BMIM]Cl: 1.0 g, water: 10 mg, reaction temperature: 130 °C and reaction time: 2 h); **d** catalyst recycles for MCC hydrolysis (MCC: 50 mg, LAHC-SO₃H-40: 30 mg, [BMIM]Cl: 1.0 g, H₂O: 10 mg, reaction temperature: 130 °C and reaction time: 2 h)

Table 3 Effect of water content on TRS yield

Entry	Solvent	TRS yield (%)
1	1.0 g [BMIM]Cl	36.1
2	1.0 g [BMIM]Cl + 10 mg H₂O	75.4
3	1.0 g [BMIM]Cl + 20 mg H₂O	67.2
4	1.0 g [BMIM]Cl + 50 mg H₂O	60.6
5	1.0 g [BMIM]Cl + 80 mg H₂O	54.4
6	1.0 g [BMIM]Cl + 100 mg H₂O	47.0

leading to a higher TRS yield in a shorter reaction time (Guo et al. 2012, 2013; Shen et al. 2014a, b). Nevertheless, high reaction temperature would result in a further degradation of TRS into other products

such as 5-hydroxymethyl furfurol (Lai et al. 2011). According to the results mentioned above, reaction temperature and time of 130 °C and 2 h were suitable, and so were selected for MCC hydrolysis.

Effect of catalyst loading

Figure 6b illustrates the effect of catalyst loading on TRS yield under fixed conditions (50 mg of MCC, 1.0 g of [BMIM]Cl, 10 mg of H₂O, 130 °C of reaction temperature and 2 h of reaction time). As is known, the catalyst plays a vital role in cellulose hydrolysis. As shown in Fig. 6b, TRS yield increased gradually from 48.3% to the maximum yield of 75.4% with the loading of LAHC-SO₃H varying from 10 to 60 wt%,

which was attributed to more active catalytic sites for cellulose hydrolysis (Hu et al. 2016a, b). However, when the dosage of LAHC-SO$_3$H-40 was more than 60 wt%, TRS yield decreased sharply to 49.7% (100 wt% of catalyst loading). Because cellulose hydrolysis was a tandem reaction, more catalyst improved the transformation rate of cellulose to TRS at the first stage, but also facilitated the further degradation of TRS to other products in the second stage (Negahdar et al. 2016; Yang et al. 2015). Thus, excessive active catalytic sites accelerated the decomposition of reducing sugar, resulting in an observable reduction in TRS yield with catalyst loading over 60 wt%. Therefore, for best TRS accumulation, the optimum catalyst dosage of 60 wt% was selected in experiments.

Effect of water content

Ionic liquid is considered a favorable solvent for cellulose hydrolysis, owing to its preferable ability to dissolve cellulose via decreasing crystallinity (Xiong et al. 2014), as depicted in Fig. 7. However, it was also necessary to investigate the influence of water content in the solvent system on TRS yield in cellulose hydrolysis due to the strong hygroscopicity of ionic liquids, such as [BMIM]Cl, used in this work (Hu et al. 2016a, b). Therefore, the correlation between TRS yield and water content in the solvent system was studied under fixed conditions (50 mg of MCC, 1.0 g of [BMIM]Cl, 30 mg of LAHC-SO$_3$H-40, 130 °C of reaction temperature and 2 h of reaction time); the corresponding results are shown in Table 3.
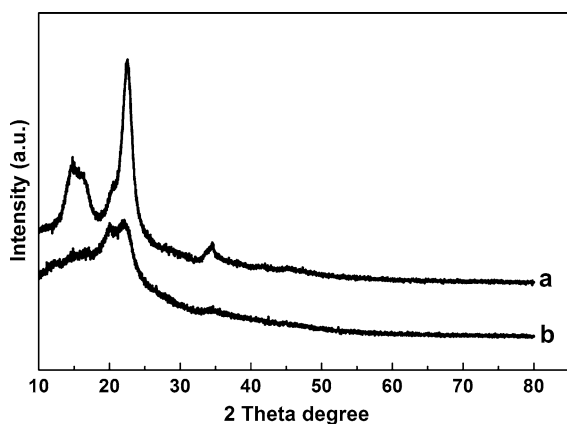

Fig. 7 XRD patters of microcrystalline cellulose (**a**) and microcrystalline cellulose pretreated by [BMIM]Cl solvent (**b**)

As seen from Table 3, when MCC was hydrolyzed in a [BMIM]Cl solvent system without adding water, a low TRS yield of only 36.1% was obtained. However, it was found from Table 3 that TRS yield obtained from MCC hydrolysis in a [BMIM]Cl-H$_2$O solvent system became higher than that achieved in a single ionic liquid solvent system. As listed in Table 3, when [BMIM]Cl dosage was fixed at 1.0 g, the maximum TRS yield of 75.4% was achieved when water content was 10 mg (100:1 of [BMIM]Cl/H$_2$O mass ratio) (Entry 2 in Table 3), and then it quickly decreased to 47.0% with further increasing water amount from 20 mg (50:1 of [BMIM]Cl/H$_2$O mass ratio) to 100 mg (10:1 of [BMIM]Cl/H$_2$O mass ratio) (Entry 3–6 in Table 3). It was suggested that adding a very small amount of water into [BMIM]Cl could achieve a more appropriate viscosity of the solvent system for cellulose hydrolysis rather than pure [BMIM]Cl itself, which was probably more conducive to decreased cellulose crystallinity and insolubility, as well as stimulating its mass transfer or diffusion. However, too much water would decrease acid density and the catalytic properties of the catalyst due to the hydration of oxygen-containing functional groups. Moreover, excessive water could decrease MCC solubility in the solvent system. As a result, a high TRS yield for cellulose hydrolysis would be obtained in a [BMIM]Cl-H$_2$O solvent system at a certain mass ratio (100:1 of [BMIM]Cl/H$_2$O mass ratio in this work).

Comparative study of various catalysts

To investigate the catalytic performances of LDSAs prepared in this work (LHC-SO$_3$H and LAHC-SO$_3$H-40), the effects of various solid acid catalysts on TRS yield obtained from MCC hydrolysis in [BMIM]Cl-H$_2$O solvent system were studied under fixed conditions (50 mg of MCC, 30 mg of LAHC-SO$_3$H-40, 1.0 g of [BMIM]Cl, 10 mg of water, 130 °C of reaction temperature and 2 h of reaction time); the results are shown in Fig. 6c. As seen from Fig. 6c, only 4.8% of TRS yield was obtained without adding catalyst, which proved the importance of the catalyst for transformation of cellulose to platform chemical compounds. Among catalysts tested in this work, traditional solid acids (HZSM-5, γ-Al$_2$O$_3$, Amberlyst-15) displayed poorer catalytic performances (about 15–25% of TRS yield obtained) in comparison with LHC-SO$_3$H (61.9%) and LAHC-SO$_3$H-40 (75.4%). In

the meanwhile, it was observed that the catalytic performance (8.0%) of lignin-derived hydrochar with acrylic acid dosage of 40 wt% (LAHC-40) was less than those of traditional solid acids, and could even be neglected compared to its corresponding sulfonated hydrochar (LAHC-SO$_3$H-40). It was suggested that although –SO$_3$H groups were mainly responsible for catalyzing cellulose hydrolysis, the presentation of more –COOH groups was beneficial tosignificantly improving catalytic performance (increasing TRS yield from 61.9 to 75.4%). In a word, the sulfonated hydrochar catalyst (LAHC-SO$_3$H-40) prepared in this work was much more efficient for cellulose hydrolysis than other solid acid catalysts, which was mainly attributed to the specific synergistic effect of high-density Ar–OH, –COOH and –SO$_3$H groups as cellulose-binding domains and catalytic domains on the catalyst surface.

Recycling of catalyst

Catalyst recycling is essential for practical applications of cellulose hydrolysis. To evaluate the catalytic stability of sulfonated lignin-derived hydrochar for cellulose hydrolysis, catalyst cycles were performed under the conditions of 130 °C, 2 h, 50 mg MCC, 60 wt% catalyst loading, 1.0 g [BMIM]Cl, 10 mg H$_2$O for LAHC-SO$_3$H-40 (Runs 1–5 shown in Fig. 6d). Figure 6d illustrates that the TRS yield with 5 cycles for LAHC-SO$_3$H-40 was still higher than 68.1%, and there was no remarkable difference in catalytic activity between fresh catalyst (75.4% of TRS yield for Run 1) and regenerated catalyst (74.0% of TRS yield for Run 6) via resulfonation in concentrated sulfuric acid. Furthermore, it was observed that there was no obvious decrease in TRS yield for the first 3 cycles, and then the catalytic performance of LAHC-SO$_3$H-40 declined slightly for the fourth and fifth runs, which was probably due to the loss of –SO$_3$H groups in hydrolysis as well as some active sites covered by by-products generated during MCC hydrolysis process (Hu et al. 2016a, b; Lian et al. 2014).

Conclusions

A highly acidic lignin-derived carbonaceous catalyst was synthesized using Masson pine alkaline lignin via hydrothermal carbonization in the presence of acrylic acid and followed by sulfonation in concentrated sulfuric acid. This kind of SO$_3$H-functionalized lignin-derived solid acid proved to be highly efficient for the catalytic hydrolysis of cellulose to reducing sugar in a [BMIM]Cl-H$_2$O solvent system. LHAC-SO$_3$H-40 prepared by adding 40 wt% acrylic acid showed competitive catalytic activity for cellulose hydrolysis (75.4% of TRS yield) in a [BMIM]Cl-H$_2$O solvent system at a mass ratio of 100:1 over traditional solid acid catalysts. It was proposed that more –COOH groups (2.85 mmol/g) contributed to the synergistic effect of surface oxygen-containing functional groups including –SO$_3$H groups (1.58 mmol/g) as main catalytic sites. It was proved that LHAC-SO$_3$H-40 could be recycled 5 times without noticeable loss of catalytic activity. In addition, full utilization of renewable lignocellulose was realized through cellulose hydrolysis efficiently catalyzed by highly acidic lignin-derived solid acid.

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