Production of 5-Hydroxymethylfurfural from Fructose Catalyzed by Sulfonated Bamboo-Derived Carbon Prepared by Simultaneous Carbonization and Sulfonation

Zhongquan Shen, Ximeng Yu, and Jizhong Chen *

A novel sulfonated bamboo-derived carbon (SBC) was prepared through a one-pot simultaneous carbonization and sulfonation method using *p*-toluenesulfonic acid as the sulfonating agent. This method was used in place of the two-step method of high temperature carbonization followed by sulfonation, in order to reduce energy consumption and avoid the use of substantial amounts of strong liquid acid. The as-prepared catalyst bearing SO_3H, COOH, and phenolic OH groups demonstrated efficient catalytic activity in the dehydration of fructose to 5-hydroxymethylfurfural (HMF), achieving 92.1% HMF yield in a mixture of tetrahydrofuran (THF) and dimethylsulfoxiden (DMSO) (volume ratio of THF/DMSO 3/7). The mixture had a fructose concentration of 0.08 $g \cdot mL^{-1}$ with a catalyst amount of 10% weight of fructose at 140 °C in 60 min. No distinct activity drop was observed after the initial deactivation during 5 recycling runs, confirming a good stability of the prepared catalyst. Moreover, kinetic data showed that SBC promoted fructose dehydration to HMF may follow pseudo-first order kinetics with the activation energy of 43.6 $kJ \cdot mol^{-1}$ under investigated conditions. The convenient catalyst preparation method and excellent catalytic performance of the catalyst provide an easy-handling and eco-friendly strategy for crude biomass utilization in catalyst production.

Keywords: Bamboo; Sulfonated carbon; Dehydration; Fructose; 5-Hydroxymethylfurfural

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INTRODUCTION

With the growing consumption of basic chemical raw materials and the increasing depletion of fossil fuels, research into the production of chemicals and fuels from biomass (Shen *et al.* 2014a) has become an attractive solution to the problem of energy and resource scarcity. Furan derivatives obtained from renewable biomass resources have the potential to serve as substitutes for the petroleum-based building blocks that are currently used in the production of plastics and fine chemicals (N-Leshkov *et al.* 2006). Among them, 5-hydroxymethylfurfural (HMF), an acid-catalyzed dehydration product of hexose, is one of the versatile platform chemicals playing an important role in the synthesis of biofuels and other valuable chemical intermediates such as aromatic hydrocarbons (Zhao *et al.* 2013), 2, 5-dimethylfuran (DMF) (Saha *et al.* 2014), and 5-ethoxymethylfurfural (EMF) (Che *et al.* 2012).

Homogeneous catalysts, such as tyrosine, $InCl_3$, and $CrCl_3$ have been demonstrated to be efficient in the catalytic dehydration of hexose to HMF with 72.1%, 79.0%, and 50.3% yields of HMF achieved from fructose in ionic liquid 1-ethyl-3-methylimidazolium bromide, fructose in water, and glucose in the ionic liquid tetrabutylammonium chloride, respectively (Su *et al.* 2013; Shen *et al.* 2014b; Wang *et al.* 2014). However, applications of the above-mentioned homogeneous catalysts are often accompanied by several disadvantages including toxicity, pollution, and separation problems (Hu *et al.* 2013). Due to the increasing demand for green chemistry and sustainable technology, environmentally benign and easily separable solid acidic catalysts are definitely better choices in the synthesis of HMF. Sulfonated carbon materials derived from renewable biomass, in particular, are receiving growing interest owing to such advantages as widely available and low-cost crude biomass materials, high density of acid sites, mechanical stability, and chemical inertness (Liu *et al.* 2010; Geng *et al.* 2012).

A variety of biomass-derived sulfonated carbon materials bearing SO_3H, COOH, and phenolic OH groups (Kitano *et al.* 2009; Kastner *et al.* 2012) have been prepared *via* the similar route first reported by the Hara group (Hara *et al.* 2004; Toda *et al.* 2005; Nakajima *et al.* 2007), *i.e.*, natural organic resources are initially incompletely carbonized to obtain amorphous carbon and then subjected to sulfonation to introduce SO_3H groups. These kinds of catalysts are efficient in the catalytic production of HMF, *e.g.*, sulfonated cellulose-derived carbon, prepared by the incomplete carbonization of cellulose at 400 °C, followed by sulfonation with concentrated sulfuric acid (98%) at 180 °C (10 mL acid$\cdot$g^{-1} carbon) for 5 h. This process achieved 81.4% and 46.4% yields of HMF in ionic liquid 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) from fructose and glucose, respectively (Hu *et al.* 2013), and sulfonated corn stalk-derived carbon achieved 44.1% HMF yield from corn stalk in [BMIM]Cl (Yan *et al.* 2014).

However, the related two-step process of preparing the catalyst involves carbonization under high temperature in the first step and large amounts of acid during sulfonation in the second step. This results in the consumption of substantial amounts of energy and in the tedious separation of the final products from dangerous and corrosive chemicals, which may cause severe environmental problems in the catalyst production process.

Recently, *p*-toluenesulfonic acid (PTSA) was found to be an efficient sulfonating agent (mass ratio of PTSA/carbon source ≤ 1) in the one-pot synthesis of sulfonated carbon material from glucose or furaldehyde under mild conditions (Xiao *et al.* 2010; Zhang *et al.* 2010). This may provide an environmentally benign solution to the problems mentioned above. Moreover, the PTSA-sulfonated carbon material was rather active in the dehydration of fructose into HMF, achieving 91.2% yield of HMF in DMSO (Wang *et al.* 2011). Nevertheless, crude biomass materials such as bamboo, wood, rice husk, and corn stalk, each composed of carbohydrate polymers with different sugar monomers (cellulose, hemicellulose), as well as aromatic polymers (lignin), could be used to produce sulfonated carbon materials directly using PTSA as sulfonating agent in the one-pot method instead of glucose or furaldehyde. This would be a more environmentally benign approach for agricultural waste treatment and reduce the production cost of the catalyst as well. This is all challenging, and more work is needed with respect to the properties and application of the PTSA-sulfonated carbon materials derived from crude biomass in the synthesis of HMF.

In the present work, sulfonated carbon was prepared from bamboo waste by one-pot simultaneous carbonization and sulfonation using PTSA as the sulfonating agent. The catalyst was fully characterized by X-ray diffraction (XRD) spectroscopy, scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) analysis, thermogravimetric analysis (TGA), elemental analysis, as well as inverse titration, and applied in the catalytic dehydration of fructose to HMF. The influences of reaction conditions including solvent, reaction time, temperature, catalyst dosage, and initial fructose concentration on HMF yield were investigated systematically. Additionally, the reusability test of the catalyst was conducted, and its initial deactivation cause has been clarified. Moreover, the reaction kinetic of fructose dehydration to HMF was studied as well.

EXPERIMENTAL

Materials

HMF (99 %), *p*-toluenesulfonic acid monohydrate ($PTSA{\cdot}H_2O$) (98.5%), Amberlyst-15 and fructose (99%) were purchased from Aladdin Industrial Co., Ltd. (Shanghai, China). Dimethylsulfoxide (DMSO), tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All chemicals were used as received without further purification. Bamboo powder from a local bamboo fabrication plant was screened to pass 40 mesh and dried at 80 °C for 24 h before use.

Catalyst Preparation

The sulfonated carbon was prepared by simultaneous carbonization and sulfonation of bamboo waste powder, using PTSA as the sulfonating agent. The preparation method was based on the literature (Xiao *et al.* 2010; Zhang *et al.* 2010) with modification. Typically, 8.0 g $PTSA{\cdot}H_2O$ and 10.0 g bamboo powder were mixed in a 100 mL Teflon-sealed autoclave and treated at 180 °C for 18 h. The resulting solid material was subjected to heat treatment at 180 °C in air for 6 h to remove low molecular weight compounds in the material and then washed with hot water (~80 °C) under agitation until the wash water showed a neutral pH value. The obtained sample was dried at 120 °C for 4 h and ground into powder, which is denoted as SBC. SBC-1 and SBC+1, using 4.0 g and 12.0 g $PTSA{\cdot}H_2O$, respectively, were also prepared accordingly. For comparison study, another catalyst was also prepared as follows: 10 g bamboo was put in a 100 mL Teflon-sealed autoclave and treated at 180 °C for 18 h, after which the residue was soaked in 8 mL PTSA solvent (1g $PTSA{\cdot}H_2O{\cdot}mL^{-1}$ H_2O). The mixture was stirred at 25 °C for 2 h and then dried at 120 °C for 6 h. After washing with hot water (~80 °C) and drying at 120 °C for 4 h, the obtained solid was grounded into powder and denoted as Supported-PTSAC.

Catalyst Characterization

X-ray diffraction (XRD) patterns of the samples were observed on a Shimadzu LabX XRD-6000 diffractometer. The morphologies of catalysts were observed using a Hitachi TM-1000 SEM at 15 kV. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet Magna 560 IR spectrometer. The sulfur and carbon content of catalysts were determined using a SE-IASII sulfur elemental analyzer and an E-CHN2000 elemental analyzer, respectively. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Scientific Escalab 250Xi instrument using an Al Kα source to excite the photoelectrons from the sample. The densities of every functional group were measured by a titration method according to literature (Wu *et al.* 2010). The Brunauer-Emmett-Teller (BET) specific surface areas of catalysts were determined by N_2 adsorption at 77 K using a Micromeritics ASAP2020M+C instrument. Thermogravimetric analysis (TGA) was carried out using Mettler Toledo TGA/SDTA851e equipment at a heating rate of 10 °C·min^{-1} in flowing N_2.

Production of HMF from Fructose

In a typical experiment, 6 mL DMSO, 0.5 g fructose and 0.1 g catalyst SBC were successively charged into a round-bottom flask mounted in an oil bath with a reflux condenser and a magnetic stirrer. Catalytic dehydration reactions of fructose by SBC were carried out under flowing N_2 and the given reaction conditions. After the reaction proceeded for a given reaction time, the flask was cooled in an ice-water bath to stop the reaction. The post-reaction liquid was obtained by filtration and the concentration of HMF in the liquid product was determined by a UV-Visible spectrophotometric technique (De *et al.* 2011). Particularly, the UV-Visible spectrum of HMF solution has a distinct peak at 284 nm and the absorbance of the solution is proportional to the concentration of HMF, based on which a standard curve with regard to the absorbance and the concentration of HMF can be obtained. Thus the concentration of HMF in product could be calculated from the absorbance of the solution using the standard curve. The concentration of fructose was determined on an Agilent 1200 HPLC system with a Bio-Rad Aminex HPX-87H analytical column and a refractive index detector based on the external standard. The eluent was 0.005 M sulfuric acid solution, and the volumetric flow rate was 0.5 mL·min^{-1}. Triplicate measurements were performed on each sample, with results agreeing to within 1.5%. The HMF yield and fructose concentration were defined as follows:

$$HMF\ yield\ (mol\ \%) = \frac{HMF\ conc.\ in\ product}{Fructose\ conc.\ in\ loaded\ sample} \times 100\% \tag{1}$$

$$Fructose\ conver.(mol\ \%) = [1 - \frac{Fructose\ conc.\ in\ product}{Fructose\ conc.\ in\ loaded\ sample}] \times 100\% \tag{2}$$

RESULTS AND DISCUSSION

Catalyst Characterization

The XRD patterns of bamboo and SBC are presented in Fig.1a. The XRD pattern of bamboo displayed diffraction peaks at 16° and 22°, which were attributed to the crystalline region of the cellulose in bamboo (Li *et al.* 2015). By contrast, the XRD pattern of SBC exhibited a weak and broad C (002) diffraction peak at 2θ=10 to 30°, attributable to amorphous carbon composed of aromatic carbon sheets oriented in a considerably random fashion (Okamura *et al.* 2006).

The SEM images (Fig. 2) show that bamboo mainly consisted of netted fibers with a porous structure. On the other hand, SBC, the solid material obtained from the simultaneous carbonization and sulfonation of bamboo, exhibited an irregular morphology with a few enlarged pores distributed randomly on the surface.

Compared with bamboo, the FT-IR spectrum of SBC (Fig. 1b) demonstrates bands at 1008 cm^{-1}, 1033 cm^{-1}, and 1173 cm^{-1}, which are consistent with SO_3H groups (Zhang *et al.* 2010; Geng *et al.* 2011). In addition, phenolic C-OH, C=C, C=O, OH stretching vibration, and carboxylic C-OH bending vibration bands appear at 1225 cm^{-1}, 1618 cm^{-1}, 1733 cm^{-1}, 2995 cm^{-1}, and 1430 cm^{-1}, respectively, demonstrating the presence of COOH and phenolic OH groups on the surface of the catalyst (Weng 2010; Fu *et al.* 2012; Qi *et al.* 2012).

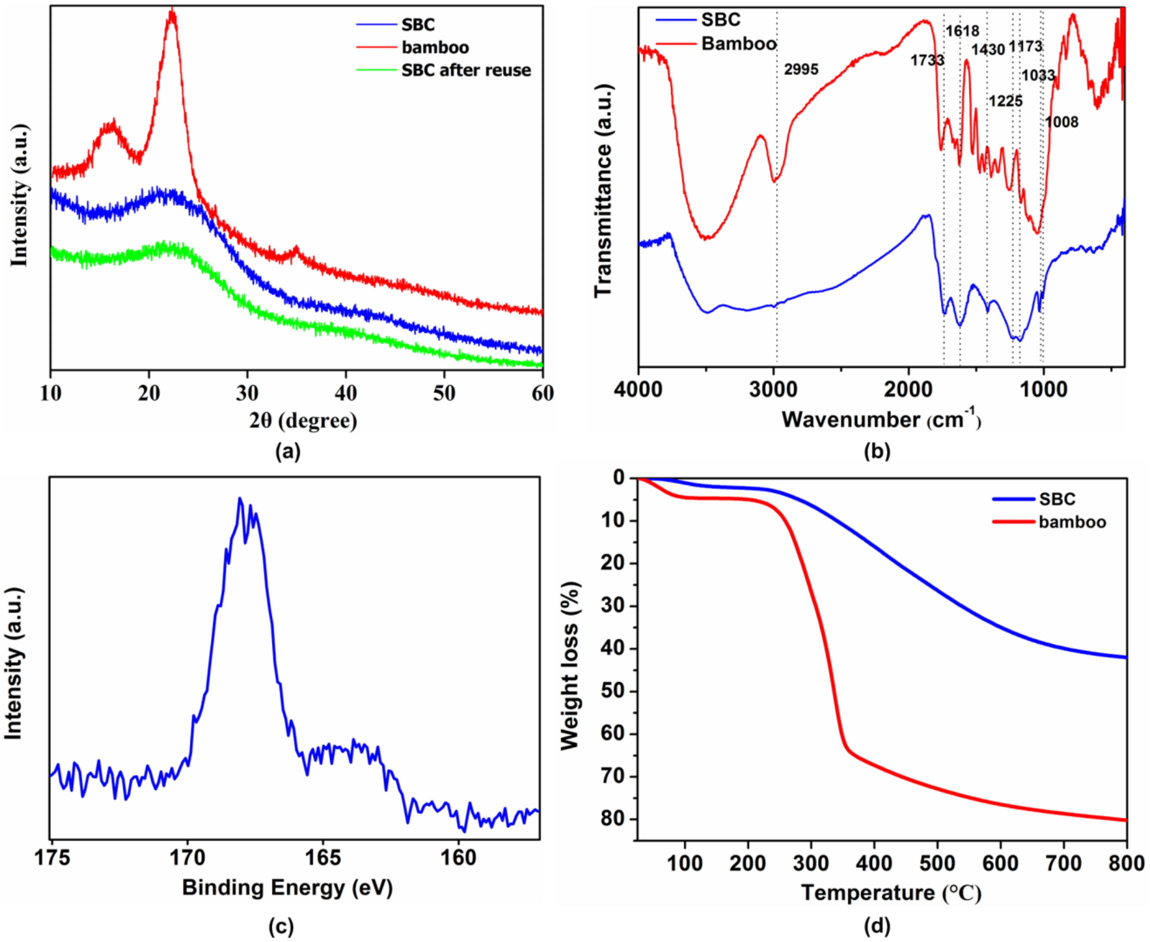


Fig. 1. XRD patterns (a), FT-IR spectra (b), XPS pattern (c), and TGA curves (d)

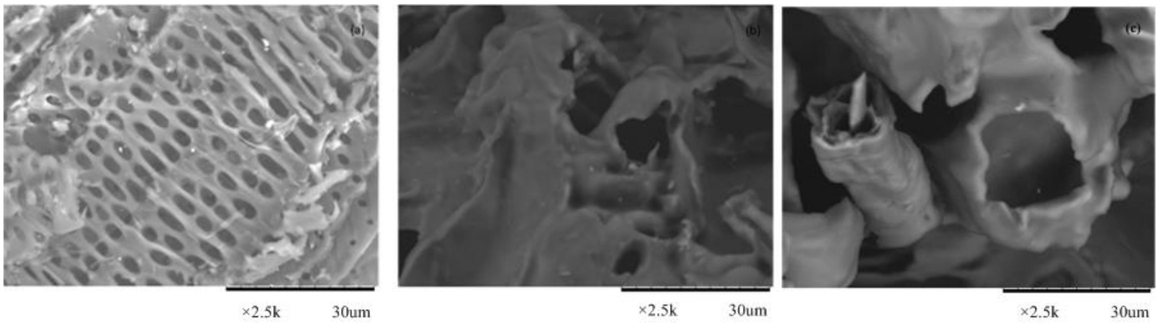


Fig. 2. SEM images of bamboo (a), catalyst SBC (b), and catalyst SBC after fifth runs (c)

XPS analysis (Fig. 1c) confirms that most sulfur elements of SBC can be assigned to SO_3H groups with an S_{2p} binding energy of 168.0 eV (Okamura *et al.* 2006), further indicating the successful incorporation of SO_3H groups into the amorphous carbon structure. It should be pointed out that no sulfur content is detected in the raw bamboo material.

The sulfur, carbon content, total acid density, density of every functional group, and surface area of SBC are listed in Table 1. This is compared with sulfonated carbon derived from various biomasses prepared by a method of carbonization and subsequent sulfonation. In spite of having a lower surface area, the catalyst SBC had a higher density of SO_3H groups compared with other catalysts, something that favors its catalytic acid activity. Moreover, the carbon content of SBC approached other catalysts (entry 2 and 4), suggesting that simultaneous carbonization and sulfonation of crude biomass using PTSA is an efficient method for the preparation of sulfonated carbon materials.

Table 1. Properties of Sulfonated Biomass Carbon Materials

Entry	Catalyst	SO_3H density (mmol·g^{-1})	Total acid density (mmol H^{+}·g^{-1})	Surface area (m^{2}·g^{-1})	Carbon content (%)
1	Sulfonated carbon derived from cellulose (Hu *et al.* 2013)	0.59	2.72	24.9	-
2	Sulfonated carbon derived from de-oiled canola meal (Rao *et al.* 2011)	1.38	2.16	4	58
3	Sulfonated carbon derived from sugar cane bagasse (Gonçalves *et al.* 2013)	0.53	6.2	<10	-
4	Sulfonated carbon derived from bamboo (Bai *et al.* 2014)	0.56	2.52	328.6	57.8
5	SBC	1.9	3.2[a]	1.2	60.8
6	SBC-1	1.2	2.6[b]	0.5	58.1
7	SBC+1	2.2	3.3[c]	1.4	61.0

[a] consists of 1.9 mmol·g^{-1} SO_3H, 1.0 mmol·g^{-1} COOH and 0.3 mmol·g^{-1} OH; [b] consists of 1.2 mmol·g^{-1} SO_3H, 1.1 mmol·g^{-1} COOH and 0.3 mmol·g^{-1} OH; [c] consists of 2.2 mmol·g^{-1} SO_3H, 0.9 mmol·g^{-1} COOH and 0.2 mmol·g^{-1} OH.

Thermal stabilities of both SBC and bamboo were investigated by TGA (Fig. 1d). The slight weight loss of bamboo below 220 °C is attributable to the vaporization of moisture and volatile content of the sample. The major weight loss from 220 to 380 °C resulted from the pyrolysis of hemicellulose and cellulose. After 380 °C the decomposition of lignin is the main reason for the weight loss of the sample (Muhammad *et al.* 2015). The weight of SBC decreased with increasing temperature in the range 50 to 140 °C, resulting from the removal of water present and/or trapped in the sample, but it maintained stability within the range 140 to 220 °C, suggesting that SBC is also stable below 220 °C. The weight decreased further, but much more slowly than that of bamboo, to *ca.* 60% of the initial weight, as temperature reached 800 °C, which may have resulted from the fact that most of the hemicellulose, cellulose, and lignin had been carbonized in SBC.

Production of HMF from Fructose

The reaction solvent is vital for HMF production; therefore, a survey of fructose dehydration to HMF in various solvents including DMSO, DMF and NMP was carried out, and the results are given in Table 2 (entries 1 to 3). It can be seen that DMSO was the most effective solvent among the three. However, the high boiling point of DMSO makes the separation of HMF from the reaction mixture challenging. The addition of a low boiling point solvent of THF into DMSO not only can increase the selectivity to HMF, but it also improves the separation efficiency (Wang *et al.* 2013). On the one hand, in THF, fructose is very favorable to be converted into the furanoid form, which is much easier to generate HMF (West *et al.* 2008; Zhu *et al.* 2011; Wang *et al.* 2013), and on the other hand, miscibility of THF with water can take the generated water away from liquid phase, preventing the side reactions due to the presence of water molecules (Chan and Zhang 2009; Cao *et al.* 2011; Wang *et al.* 2013). The influence of the volume ratio of THF/DMSO on fructose dehydration to HMF is shown in Table 2 (entries 4 to 8). The HMF yield exhibited a slight increase from 88.3 % to 89.2 % as the volume ratio of THF/DMSO increased from 1/9 to 3/7, while no obvious change of fructose conversion occurred. However, HMF yield as well as fructose conversion decreased with further increase in the volume ratio of THF/DMSO, due to the decreased solubility of fructose as the volume ratio of THF/DMSO increases (Wang *et al.* 2013). Therefore, THF/DMSO mixture in volume ratio of 3/7 was used as the suitable solvent for further investigation.

Table 2. Effect of Solvents on Fructose Dehydration to HMF

Entry	Solvent	HMF yield (%)	Fructose conversion (%)
1	DMSO	87.8	97.9
2	NMP	71.4	95.8
3	DMF	59.1	94.2
4	THF/DMSO volume ratio 1/9	88.3	98.2
5	THF/DMSO volume ratio 2/8	88.5	98.5
6	THF/DMSO volume ratio 3/7	89.2	98.4
7	THF/DMSO volume ratio 4/6	83.8	97.6
8	THF/DMSO volume ratio 5/5	79.9	97.1

* Reaction conditions: 0.1 g SBC, 0.5 g fructose, 6 mL different solvent, 130 °C, 60 min

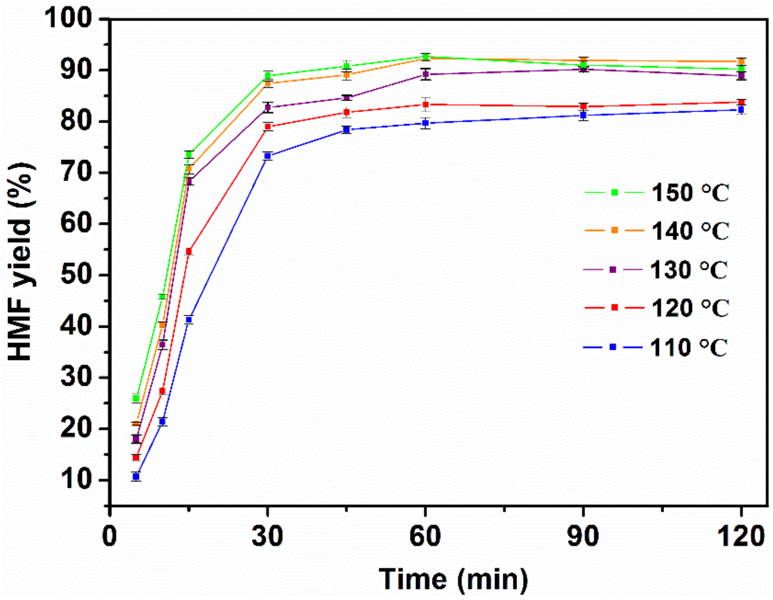


Fig. 3. Effects of reaction time and temperature on HMF yield catalyzed by SBC. Reaction conditions: 0.1 g SBC, 0.5 g fructose, and 6 mL THF-DMSO in volume ratio of 3/7

Figure 3 shows that reaction time and temperature had significant effects on HMF yield. As can be seen, HMF yield increased rapidly during the initial 30 min, with a slight increase subsequently. It may decrease at a later stage, indicating that HMF is an intermediate product of fructose dehydration reaction and can convert into other undesired byproducts, resulting in a maximum value of HMF yield at different temperatures. Higher temperature favored the generation of HMF and its yield increased from 82.3 % in 120 min at 110 °C to 92.7 % in 60 min at 150 °C. However, it also promoted the conversion of HMF to byproducts. At 150 °C, its yield decreased after 60 min, probably due to HMF decomposition to levulinic acid and HMF self-polymerization or cross-polymerization at high temperature (Wang *et al.* 2013). It should be noted that no obvious increase of HMF yield was observed when the temperature was raised from 140 °C (92.3 % HMF yield in 60 min) to 150 °C. Thus the proper reaction temperature and time for HMF production were considered to be 140 °C and 60 min, respectively. The maximum HMF yield obtained was higher than the 87.8 % achieved in a THF-aqueous mixture at 180 °C for 60 min using $InCl_3$ as a catalyst (Shen *et al.* 2014c).

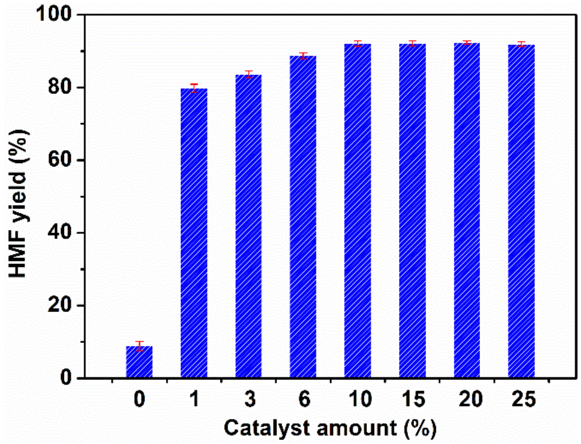


Fig. 4. Effect of catalyst dosage on HMF yield catalyzed by SBC. Reaction conditions: 0.5 g fructose, 6 mL THF-DMSO in volume ratio of 3/7, 140 °C and 60 min

The effect of catalyst dosage on HMF yield was studied, and the results are shown in Fig. 4. It was found that the catalyst SBC had high catalytic efficiency for the dehydration of fructose to HMF. Without the catalyst, an 8.9% yield of HMF was achieved; by comparison, a 79.8% yield of HMF was obtained with a catalyst dosage of only 1% of the weight of fructose. Increasing the catalyst dosage from 1% to 10% of the weight of fructose resulted in an increase in HMF yield from 79.8% to 92.1%. This could be ascribed to the increased amount of available acid sites, and no obvious increase of HMF yield occurred with a further increase in catalyst dosage from 10% to 25% weight of fructose. Thus, the optimum catalyst dosage was 10% weight of fructose. Additionally, the effect of SO_3H density was also investigated (Fig. 5). HMF yield increased from 81.4% to 92.1% with the increasing SO_3H densities from 1.2 $mmol{\cdot}g^{-1}$ (SBC-1, Table 1 entry 6) to 1.9 $mmol{\cdot}g^{-1}$ (SBC-1, Table 1, entry 5). No obvious increase of HMF yield was observed with further increasing in SO_3H densities from 1.9 $mmol{\cdot}g^{-1}$ (SBC-1, Table 1, entry 5) to 2.2 $mmol{\cdot}g^{-1}$ (SBC-1, Table 1, entry 7), evidently implying that SBC has the optimum SO_3H density for the dehydration of fructose to HMF. Moreover, the HMF yield catalyzed by SBC was much higher than that catalyzed by $PTSA{\cdot}H_2O$, further demonstrated the catalytic efficiency of SBC.

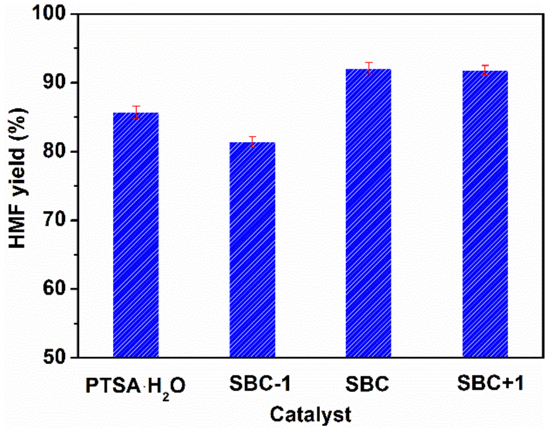


Fig. 5. Effect of SO_3H density on HMF yield. Reaction conditions: 0.5 g fructose, 0.05 g catalyst, 6 mL THF-DMSO in volume ratio of 3/7, 140 °C and 60 min

In the acid catalytic production of HMF, the formed HMF tends to react with carbohydrates and cross-polymerizes to generate humins (Yan *et al.* 2014). Therefore, the effect of the initial fructose concentration on HMF yield was investigated (Fig. 6). The HMF yield increased from 88.7% to 92.1% with increasing fructose concentration from 0.04 $g\cdot mL^{-1}$ to 0.08 $g\cdot mL^{-1}$, due to the increased probability of the collision of fructose with acid sites. Yield decreased to 84.7% with the further increase of fructose concentration to 0.15 $g\cdot mL^{-1}$, something that may result from the cross-polymerization of HMF with a high concentration of fructose to form humins (Qi *et al.* 2008). Therefore, the suitable initial fructose concentration was determined to be 0.08 $g\cdot mL^{-1}$.

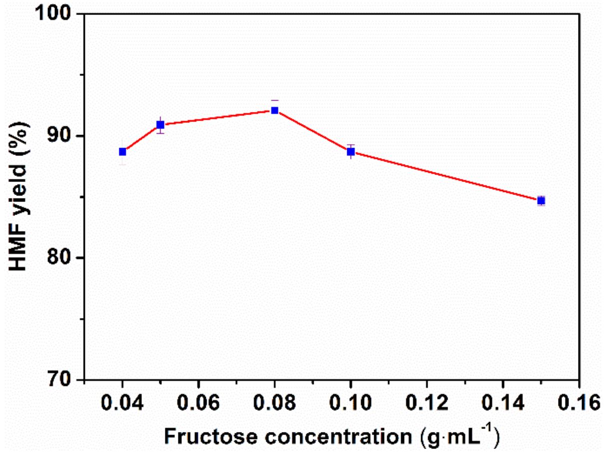


Fig. 6. Effect of initial fructose concentration on HMF yield catalyzed by SBC. Reaction conditions: 0.5 g fructose, 0.05 g SBC, THF-DMSO in volume ratio of 3/7 as solvent, 140 °C and 60 min

Reusability of Catalyst

The reusability of the catalyst is of importance for practical applications, so a recycling test of SBC was conducted. After each test cycle, the recovered catalyst was washed with ethanol and dried at 100 °C for 6 h before the next run. As is shown in Fig.7, a 92.1% HMF yield was achieved in the first run, demonstrating that SBC is more efficient than sulfonated carbon derived from cellulose with an 83% HMF yield in [BMIM][Cl] (Qi *et al.* 2012), sulfonated carbon derived from lignin with an 84% HMF yield in DMSO-[BMIM][Cl] mixture (Guo *et al.* 2012) and graphite oxide (GO) with a 60.8% HMF yield in DMSO (Nie *et al.* 2014). It is also comparable with macroporous strong-acid resin D001-cc with a 93.0% HMF yield in [BMIM][Cl] (Li *et al.* 2013). However, only 70.5% HMF yield was achieved under the same reaction condition using Supported-PTSAC as catalyst resulted from lower sulfur content of Supported-PTSAC (0.3 $\text{mmol}\cdot\text{g}^{-1}$). Besides, remarkable deactivation in the second usage of Supported-PTSAC (50.2% HMF yield) did occur, may have been due to considerable loss of sulfur content (sulfur content of reused Supported-PTSAC 0.1 $\text{mmol}\cdot\text{g}^{-1}$). This suggested that simultaneous carbonization and sulfonation is a more efficient method for the preparation of sulfonated carbon material. Additionally, the activity of SBC remained stable after initial deactivation with an 84.3% HMF yield achieved in the fifth run, which is still higher than the initial catalytic activity of Amberlyst-15 with an 81.6% HMF yield at the same reaction conditions, demonstrating the high stability of the catalyst. Moreover, the elemental sulfur analysis results of the fresh catalyst, as well as the catalysts after the first and fifth runs were 1.89, 1.59, and 1.55 $\text{mmol}\cdot\text{g}^{-1}$, respectively. This implies that most of the SO_3H groups were tightly bonded to the aromatic carbon sheets during the reaction, with a slight loss of sulfur containing groups in the first run. The XRD pattern (Fig. 1a) and SEM image (Fig. 2c) of the catalyst after fifth runs showed no obvious difference with those of the fresh one, and the BET surface area of the catalyst after fifth runs (1.5 $\text{m}^2\cdot\text{g}^{-1}$) was close to that of the fresh one (1.2 $\text{m}^2\cdot\text{g}^{-1}$) as well. These results demonstrate that SBC is stable and can be reused in the production of HMF.

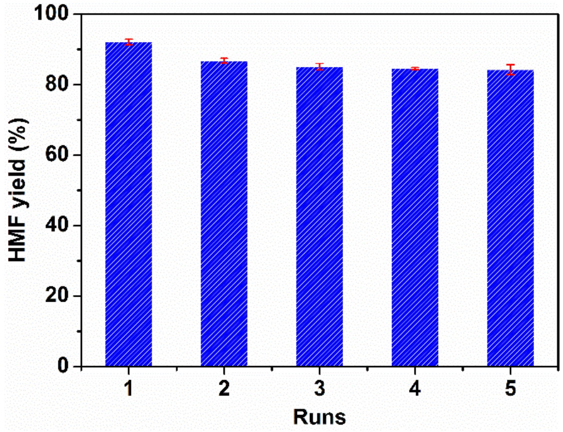


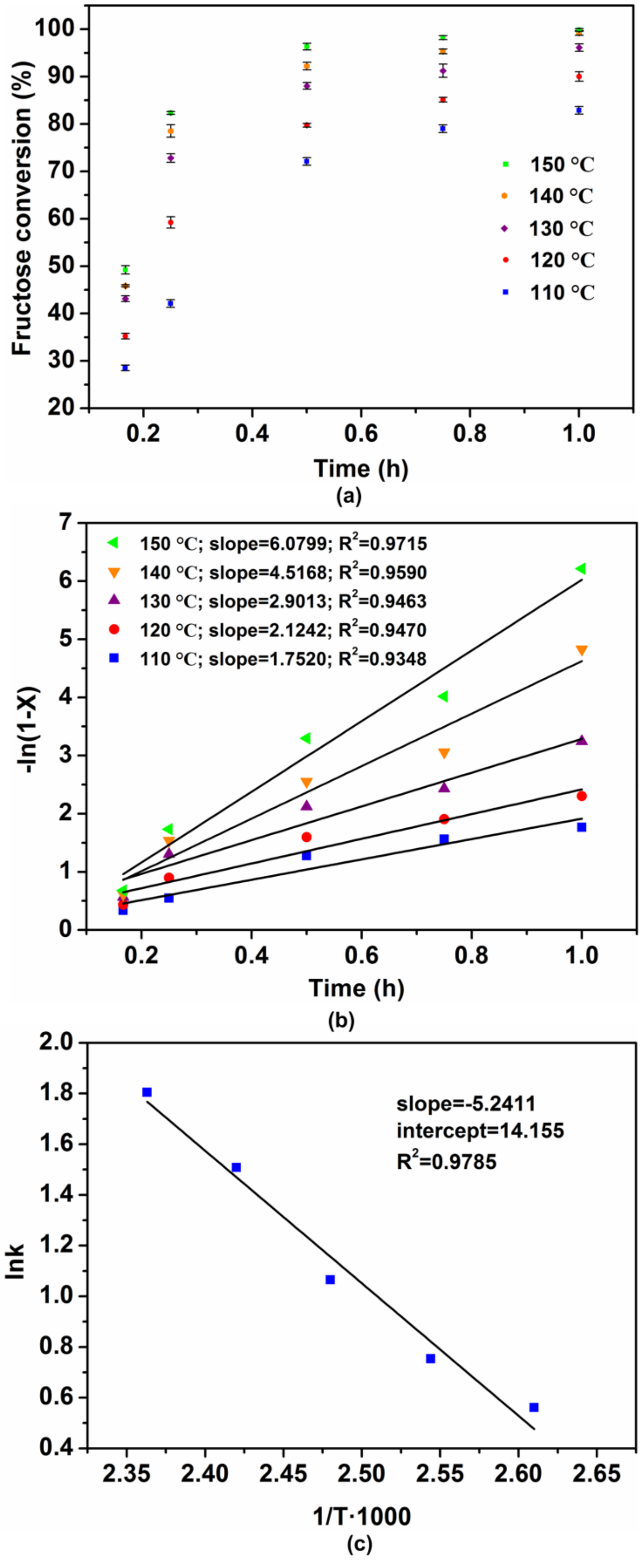
Fig. 7. Reusability of catalyst SBC. Reaction conditions: 0.5 g fructose, 0.05 g SBC, 6 mL THF-DMSO in volume ratio of 3/7, 140 °C, and 60 min

Kinetic Study

A kinetic study of fructose dehydration to HMF was carried out with SBC as catalyst. According to ongoing studies, fructose dehydration to HMF obeys a pseudo-first order process (Chen *et al.* 2014). Thus the fructose transformation rate (r[fructose]) can be expressed as the following equation,

$$-r[\text{fructose}]=-\frac{d[\text{fructose}]}{dt}=k[\text{fructose}] \tag{3}$$

where [fructose] is the molar concentration of fructose and k is the rate constant of fructose transformation at a certain reaction temperature.



(a)

(b)

(c)

Fig. 8. (a) The conversions of fructose at different temperatures using SBC as catalyst, **(b)** the kinetic profiles of fructose dehydration to HMF fitted by first order assumption, and **(c)** Arrhenius plot for fructose dehydration to HMF. Reaction conditions: 0.5 g fructose, 0.05 g SBC, 6 mL THF-DMSO in volume ratio of 3/7.

According to the Arrhenius equation ($\ln k = -\frac{E_a}{RT} + \ln A$), Eq. 3 can be transformed into Eq. 4 with the [fructose] in terms of conversion X. Herein, *t* and *C* are the reaction time and the arbitrary constant, respectively:

$$-\ln(1-X) = kt + C \qquad (4)$$

The conversion of fructose at different temperatures is displayed in Fig. 8a. After data fitting, the linear relationship between ln(1-*X*) and *t* is obtained in Fig. 8b, which evidently implies that fructose transformation to HMF obeys a pseudo-first order process. The reaction rate constants at different temperatures can be derived from the linear slopes and were used to prepare an Arrhenius plot (Fig. 7c), resulting in the activation energy and pre-exponential factor of 43.6 $kJ \cdot mol^{-1}$ and 1.4×10^6 h^{-1}. The calculated activation energy was much lower than that reported by Qi *et al.* (103.4 $kJ \cdot mol^{-1}$) in acetone-water catalyzed by ion exchange resin Dowex 50wx8-10 (Qi *et al.* 2008), and slightly lower than that reported by Chen *et al.* (55 $kJ \cdot mol^{-1}$) in DMSO catalyzed by sulfonic acid-functionalized metal-organic framework (Chen *et al.* 2014), indicating that SBC catalyst can effectively lower the activation energy and lead to a higher reaction rate.

CONCLUSIONS

1. Sulfonated carbon bearing SO_3H, COOH, and phenolic OH groups was prepared by the simultaneous carbonization and sulfonation of bamboo waste using *p*-toluenesulfonic acid (PTSA) as the sulfonating agent under mild conditions, instead of the traditional heat treatment followed by a sulfonation route.
2. The catalyst demonstrated efficient catalytic performance in the synthesis of 5-hydroxymethylfurfural (HMF) from fructose with a 92.1% HMF yield obtained at 140 °C for 60 min in THF/DMSO. It displayed a good reusability as well.
3. Kinetic studies reveal that the SBC promoted fructose dehydration to HMF obeyed pseudo-first order process with an activation energy of 43.6 $kJ \cdot mol^{-1}$.
4. The present study introduced an easy-handling and environmentally benign strategy for a comprehensive utilization of crude biomass with a sulfonated carbon catalyst preparation and application in the synthesis of HMF.

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