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## 1. Introduction

Biomass derived carbon-based sulfonated catalysts have become a research hotspot recently, and this kind of catalyst has been widely studied in biodiesel production,<sup>1-3</sup> hydrolysis of cellulose,<sup>3-5</sup> and some other applications.<sup>5-9</sup> One of the advantages of this kind of catalyst is that the raw material (biomass) is abundant, widely existent, and renewable. Biomass derived carbon-based sulfonated catalysts can be prepared by sulfonation of a carbon-based precursor with concentrated H<sub>2</sub>SO<sub>4</sub>, while the precursor can be obtained from biomass through carbonization methods, including pyrolysis, gasification, hydrothermal carbonization, and flash carbonization.<sup>10</sup> In summary of the former works, most of the carbonbased sulfonated catalysts were prepared by biomass pyrolysis followed by sulfonation. Hydrothermal carbonization could be a good method to get a carbon-based precursor (hydrochar) due to its relative low temperature<sup>10</sup> and lack of necessity for predrying as water is used as the solvent. However, detailed information on the effects of various biomass hydrochar in preparing carbon-based sulfonated catalyst is very lacking.

5-Hydroxymethylfurfural (HMF) is expected to be a versatile and key precursor for the production of fine chemicals,

# Preparation of biomass hydrochar derived sulfonated catalysts and their catalytic effects for 5-hydroxymethylfurfural production

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Amorphous carbon-based sulfonated catalysts were generated from four kinds of biomass (lignin, cellulose, wood meal and D-xylose) by hydrothermal carbonization at various temperatures (225, 245 and 265 °C) followed by sulfonation, with a yield of 36–56%. All of these catalysts showed aromatic structure, hydroxyl and carboxyl groups, with a density of SO<sub>3</sub>H groups between 0.56 and 0.87 mmol g<sup>-1</sup>. 5-Hydroxymethylfurfural (HMF) was produced from inulin in ionic liquids (ILs) in one step with the addition of carbon-based sulfonated catalysts, with a factual yield of 47–65% at 100 °C, 60 min. Moderate extension of reaction time (from 30 to 90 min) and increase of temperature (from 80 to 120 °C) promoted HMF production. Ethyl acetate was used as extractant, and about 39–55% of HMF can be recovered from ILs. One problem with these carbon-based sulfonated catalysts was that they would be partly deactivated in ILs for separate reuse, however, they can be easily regenerated by dilute sulfuric acid treatment. The carbon-based sulfonated catalysts exhibited good catalytic activity compared with traditional solid acid catalysts, and the carbon-based sulfonated catalyst/ILs reaction system showed high reusability. In consideration of the renewable as well as the high catalytic activity abilities, these biomass derived carbon-based sulfonated catalysts would be promising for industrial application.

polymeric materials, and biofuels.<sup>11,12</sup> In recent years, dehydration of biomass-based carbohydrates for HMF preparation has received much attention, especially in the acid-catalyzed dehydration of fructose by eliminating three moles of water molecules. Moreover, considerable interest has emerged in the application of ionic liquids (ILs) in the field of HMF production, due to the good solubility of carbohydrates in ILs.<sup>11</sup> However, it remains a challenge to develop an efficient and green catalyst to obtain HMF from carbohydrates.<sup>13</sup> Inulin is a natural polysaccharide consisting of linear chains of fructose units linked by a  $\beta$  (2  $\rightarrow$  1) linkage with the polymer chains terminating in a glucose unit, and it exists in many plants, such as chicory, dahlia and jerusalem artichoke, etc. Inulin would be a promising biomass material for HMF production in two steps, hydrolysis for fructose production and then dehydration of fructose for HMF production.

In this paper, wood meal, cellulose, lignin, and D-xylose were first hydrothermally carbonized, and then these hydrothermal carbonization products were sulfonated to obtain four kinds of biomass derived carbon-based sulfonated catalysts; the object was to test and compare the characterization properties and catalytic effects of these four kinds of catalysts. Moreover, in contrast to the typical two step processes, catalytic one step in ILs with these carbon-based sulfonated catalysts was explored to obtain HMF from inulin.

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# 2. Materials and methods

#### 2.1. Materials

1-Allyl-3-methylimidazolium chloride ([AMIM]Cl, >99%) was obtained from The Chinese Academy of Sciences Lanzhou Institute of Chemical Physics. Inulin (Biochemical) was obtained from Aladdin-reagent Co., Ltd. Lignin (dealkali) was obtained from Tokyo Chemical Industry Co., Ltd., and cellulose (microcrystalline) was obtained from Sinopharm Chemical Reagent Co., Ltd., China. D-Xylose was obtained from Aladdin Chemistry Co., Ltd. Wood meal (Pine) was obtained from Guangdong province, China, and which was about 3  $\times$  1  $\times$  0.5 mm<sup>3</sup> in size, consisting of 26.1% lignin, 50.3% cellulose, and 22.3% hemicellulose on a dry basis. The moisture contents in lignin, cellulose, wood meal, and D-xylose were 10.3, 2.6, 4.6, and 0%, respectively. HZSM-5 molecular sieve was obtained from Tianjin Kaimeisite Technology Co., Ltd. Strong-acid 732 cation resin was obtained from Shanghai Lingfeng Chemical Reagent Co., Ltd. Amberlyst-15 resin was obtained from Aladdin Chemical Co., Ltd. Sulfated zirconia was synthesized according to Yee et al.14

#### 2.2. Preparation of carbon-based catalyst

Wood meal, cellulose, lignin and D-xylose were first hydrothermally carbonized at various temperatures (225, 245, 265 °C) to get corresponding hydrochars (carbon-based precursor) according to Kang et al.,15 then these hydrochars were sulfonated according to Suganuma et al.4 Briefly, these hydrochars were sulfonated by concentrated  $H_2SO_4$  at 150  $^\circ C$ for 12 h, followed by a washing process with excess hot water (>80  $^{\circ}$ C). The washed sulfonated solid products were dried at 105 °C to constant weight in a vacuum drying oven to form the carbon-based sulfonated catalysts. The yield of catalyst was calculated as (weight of catalyst)/(weight of biomass raw material). The lignin, cellulose, wood meal, and D-xylose derived hydrochar are labeled as LX, CX, WX, DX, respectively, where X (X = 225, 245, 265 °C) is the hydrothermal carbonization temperature. The lignin, cellulose, wood meal, and D-xylose derived carbon-based sulfonated catalysts are labeled as LX-SO<sub>3</sub>H, CX-SO<sub>3</sub>H, WX-SO<sub>3</sub>H, DX-SO<sub>3</sub>H, respectively. For example, L225-SO<sub>3</sub>H means the lignin derived carbon-based sulfonated catalyst, and the carbon-based precursor (lignin hydrochar) was produced at 225 °C.

#### 2.3. Characterization

The obtained sulfonated carbon catalyst was characterized by X-ray diffraction (XRD) (D8 Advance, Bruker), thermogravimetric (TG) and derivative thermogravimetric (DTG) (TGAQ 5000), Fourier transform infrared spectroscopy (FTIR) (Nexus 670, Nicolet), scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) (S-3700N, Hitachi), X-ray photoelectron spectroscopy (XPS) (Kratos AXis Ultra), elemental analyzer (Vario EL III) and Brunauer-Emmett-Teller (BET) surface area analyzer (ASAP 2020 V3.03 H, Micromeritics).

The hydrogen ion exchange capacity was estimated from the exchange of  $Na^+$  in aqueous NaCl solution. The densities of  $SO_3H$  groups were estimated based on XPS analysis and the sulfur content determined by elemental analysis.

#### 2.4. Catalytic reaction procedure

In a typical run, 0.1 g of inulin, 0.1 g of water and 2 g of [AMIM]Cl were added into the reactor with or without 0.1 g of catalyst. Before the addition, the catalysts were ground and filtered by a 200 mesh strainer. The reaction mixture was agitated with electromagnetic stirring at the desired temperature and desired time in an oil bath. All experiments were conducted in duplicate.

#### 2.5. Separation and analyses

After reaction, two methods were used to detect the content of the products. Method 1: the products were extracted by 30 mL (4  $\times$  7.5 mL) of ethyl acetate, then the content of HMF was detected by GC (Shimadzu QP 2010), and the yield of HMF was defined as the ethyl acetate extracted yield.

Method 2: the products after reaction was diluted with 30 mL of ultra pure water, then the product contents were analyzed with Ion Chromatography (Dionex, ICS-3000). The yield of HMF detected by method 2 was defined as the factual yield.

### 3. Results and discussion

#### 3.1. Yields of carbon-based sulfonated catalysts

As shown in Fig. 1, the yield of these carbon-based sulfonated catalysts is among 36–56%, and with a trend of lignin derived catalyst > wood meal derived catalyst  $\geq$  cellulose derived catalyst > D-xylose derived catalyst at the same preparation temperature. The catalyst yield got a maximum value at 245 °C, which was an integrated result of both hydrothermal carbonization (hydrochar preparation from biomass) and sulfonation (catalyst preparation from hydrochar) processes. The yield of carbon-based precursor (hydrochar) prepared from the raw materials decreased as temperature increased from 225 to 265 °C, while the hydrochar produced at a low temperature resulted in a low yield of carbon-based sulfonated



Fig. 1 Yield of carbon-based sulfonated catalysts. The values are averages of two duplicate experiments.



Fig. 2 SEM spectra of hydrochars and the corresponding carbon-based sulfonated catalysts.

catalysts during the sulfonation process. This is probably because the low temperature results in high hydrochar yield but a relatively soft and loose structure of the hydrochar, and some of the relatively soft and loose hydrochar particles would be easily lost during the sulfonation and washing process.

# 3.2. Characterization and properties of the carbon-based catalysts

The SEM spectra of carbon-based sulfonated catalysts are compared with those of the corresponding hydrochars in Fig. 2. The surface topography of cellulose and wood meal derived hydrochars (C245, W245) have changed a lot after sulfonation, and the fiber skeletons are destroyed in both C245–SO<sub>3</sub>H and W245–SO<sub>3</sub>H. The D245–SO<sub>3</sub>H keeps the accumulation status of microspheres, however, these microspheres in D245–SO<sub>3</sub>H are accumulated much closer than the corresponding hydrochar D245. Compared with the corresponding hydrochar L245, there are obvious cracks and holes in the surface of L245–SO<sub>3</sub>H, which meant that sulfonation has destroyed the polymeric surface of lignin derived hydrochar. All of the above results indicated that sulfonation reaction has occurred on all of the biomass derived hydrochars.



Fig. 3 XRD spectra of carbon-based sulfonated catalysts.

As shown in Fig. 3, broad peaks are located between 10 and  $30^{\circ}(2\theta)$  for D245–SO<sub>3</sub>H, L245–SO<sub>3</sub>H, C245–SO<sub>3</sub>H and WM245–SO<sub>3</sub>H, which can be ascribed to the diffraction of amorphous carbon,<sup>4,16</sup> indicating that all of these biomass feedstock have become corresponding amorphous carbon catalysts after the hydrothermal carbonization and sulfonation processes.

The TG/DTG curves are shown in Fig. 4, a weight loss in the TG curve occurs before 100  $^{\circ}$ C, which should be caused by the loss of water adsorbed on the catalysts. The catalysts seem somewhat stable between 100–200  $^{\circ}$ C, and the weight decreased obviously with increasing temperature from 250  $^{\circ}$ C. Moreover, according to the DTG curve peak and TG remaining weight, the thermal stability of these catalysts increases with increased carbon-based precursor preparation temperature.

The functional groups are shown in Fig. 5, the FTIR spectra of the catalysts produced by the same feedstock are similar and they differ only in the intensity of some peaks, indicating that hydrothermal carbonization at various temperatures (225, 245 and 265 °C) followed by sulfonation did not change the functional group composition. The FT-IR spectrum shows that all of these catalysts have aromatic structure (around 1600 cm<sup>-1</sup>), OH groups (around 3400 cm<sup>-1</sup>), SO<sub>3</sub>H groups (around 1190 and 1040 cm<sup>-1</sup>) and C=O groups (around 1720 cm<sup>-1</sup>).

The whole element contents, and C, O and S contents on and near the surface were detected by elemental analysis and EDS, respectively, as shown in Table 1. It shows that the C content on and near the surface was lower than that in the whole body of these catalysts, while the O and S contents on and near the surface were higher than those in the whole body of these catalysts. The results indicated that sulfonation mainly acted on the surface of these hydrochars. While the added O and S contents on and near the surface should be due to the SO<sub>3</sub>H groups. As shown in Fig. 6, the results of XPS analysis show that the S exists in the forms of SO<sub>3</sub>H groups (168 eV). According to the S content in the whole body of the catalyst and the XPS analysis results, the SO<sub>3</sub>H group contents were calculated and shown in Table 2 to be between 0.56 and 0.87 mmol g<sup>-1</sup>. Besides, the H<sup>+</sup> exchange value (from 1.11 to

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Fig. 4 TG/DTG curves of carbon-based sulfonated catalysts.

1.44 mmol  $g^{-1}$ , Table 2) was more than the SO<sub>3</sub>H group content in all of the carbon-based sulfonated catalysts, and according to the above FTIR spectra analysis, there should be some other acid groups in these catalysts, *e.g.* carboxyl groups.

As shown in Table 1, the whole carbon content increased as the hydrochar preparation temperature increased for all of the catalysts. The sulfur content in cellulose, wood meal and Dxylose derived catalysts become lower at a lower hydrochar preparation temperature. The possible reason is that these hydrochars produced at a relatively low temperature would possess a relatively soft but loose structure. Though the soft structure is of benefit to sulfonation, many sulfonated carbon particles on the surface of the catalyst would be run off in the sulfonation and excess hot water washing process due to its loose structure. In contrast, the sulfur content in lignin derived catalysts becomes higher at a lower hydrochar preparation temperature. This phenomenon maybe explained by the phenolic polymeric surface structure of lignin derived hydrochar,<sup>15</sup> which should be relative stable in the sulfonation process and hard to be washed off. While the relatively soft structure of lignin derived hydrochar produced at relatively low temperatures would generate more SO<sub>3</sub>H groups during the sulfonation process.

#### 3.3. Catalytic reactions

HMF can be obtained from inulin by a possible two-step reaction pathway: hydrolysis of inulin to fructose followed by dehydration of fructose (Fig. 7). Both of the two steps can be catalyzed by acid catalysts, so it seems promising for the production of HMF from inulin by an acid-catalysed one pot reaction, however, details of the one pot reaction process with various solid acid catalysts are very limited. In this work, [AMIM]Cl was used as the solvent for the hydrolysis of inulin and for dehydration of fructose. All of these cellulose, lignin, wood meal and D-xylose derived carbon-based catalysts, as well as four traditional solid acid catalysts (HZSM-5, amberlyst-15 resin, 732 cation resin, sulfated zirconia) were tested in the one pot reactions (Fig. 7).

**3.3.1. Catalytic activities of carbon-based catalysts.** As shown in Fig. 8, all of the carbon-based catalysts showed effective catalytic effects in the HMF production compared with the control experiment, with a factual yield of 47–65% at 100 °C, 60 min. It was surprising that fructose was not found in the reaction system, one possible reason is that hydrolysis of inulin to fructose is a rate-determining step, while dehydration of fructose is fast in the ionic liquid of [AMIM]Cl. Comparing Fig. 8 with Table 2, there seems certain relationship between SO<sub>3</sub>H content and catalytic effects for the same biomass



Fig. 5 FTIR spectra of carbon-based sulfonated catalysts.

derived carbon catalysts (*e.g.* D225–SO<sub>3</sub>H, D245–SO<sub>3</sub>H and D265–SO<sub>3</sub>H), the high SO<sub>3</sub>H content would result in high factual yield of HMF, while for the carbon-based catalysts derived from different biomass there seems no obvious correlation between SO<sub>3</sub>H content and the factual yield of

Table 1 Elemental content of the carbon-based sulfonated catalysts								
	Detected by elemental analyzer				Detected by EDS			
	C (%)	Н (%)	S (%)	$O^{a}$ (%)	C (%)	O (%)	S (%)	
C225-SO <sub>3</sub> H	51.29	3.44	2.17	43.10	42.07	55.43	2.50	
C245-SO <sub>3</sub> H	52.65	3.46	2.22	41.67	41.99	55.47	2.54	
C265-SO <sub>3</sub> H	52.99	3.57	2.27	41.17	42.22	55.00	2.78	
W225-SO <sub>3</sub> H	54.89	3.29	1.79	40.03	41.50	56.15	2.35	
W245-SO <sub>3</sub> H	54.89	3.22	1.91	39.98	41.70	55.72	2.58	
W265-SO <sub>3</sub> H	54.92	3.13	1.98	39.97	41.87	55.51	2.62	
D225-SO <sub>3</sub> H	49.70	3.47	1.81	45.02	41.59	56.25	2.15	
D245-SO <sub>3</sub> H	49.95	3.70	1.94	44.41	42.25	55.47	2.28	
D265-SO <sub>3</sub> H	50.01	3.60	2.02	44.37	42.06	55.37	2.56	
L225-SO <sub>3</sub> H	52.19	3.44	2.79	41.65	41.47	54.88	3.65	
L245-SO <sub>3</sub> H	52.07	3.56	2.72	41.58	42.19	54.7	3.11	
L265–SO <sub>3</sub> H	53.15	3.49	2.37	40.99	43.08	54.02	2.90	

<sup>*a*</sup> O content was calculated by difference.

HMF. These results indicated that  $SO_3H$  content should not be the only factor affecting the reactions. The BET surface area values of all of these biomass derived carbon catalysts were low (<2 m<sup>2</sup> g<sup>-1</sup>), and there was no obvious difference among these



Fig. 6 XPS spectra of D245–SO<sub>3</sub>H.

ſ <b>able 2</b> SO <sub>3</sub> H content and H⁺	exchange value of the	carbon-based sulfonated car	talysts. The values are	averages of two	duplicate experiments
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Catalyst	$SO_3H$ content (mmol g <sup>-1</sup> )	$H^+$ exchange value (mmol $g^{-1}$ )	Catalyst	$SO_3H$ content (mmol g <sup>-1</sup> )	$H^+$ exchange value (mmol $g^{-1}$ )
C225-SO <sub>3</sub> H	0.68	1.41	D265-SO <sub>3</sub> H	0.63	1.43
C245-SO <sub>3</sub> H	0.69	1.42	L225-SO <sub>3</sub> H	0.87	1.21
C265-SO <sub>3</sub> H	0.71	1.44	L245-SO <sub>3</sub> H	0.82	1.21
W225-SO <sub>3</sub> H	0.56	1.11	L265-SO <sub>3</sub> H	0.74	1.15
W245-SO <sub>3</sub> H	0.60	1.20	732 Resin	_	2.06
W265-SO <sub>3</sub> H	0.62	1.25	HZSM-5	_	0.61
D225-SO <sub>3</sub> H	0.57	1.42	Amberlyst-15	_	4.20
D245–SO <sub>3</sub> H	0.61	1.42	Sulfated zirconia	—	2.20

values. So there may be some other factors in influencing the catalytic ability of these biomass derived carbon catalysts, possibly such as the dispersibility in ILs, affinity of these catalysts with reactants, *etc.*; further work on these fields is needed. Compared with amberlyst-15 resin and 732 cation resin (the best two of the four traditional solid acid catalysts), the D265–SO<sub>3</sub>H, L225–SO<sub>3</sub>H, and W265–SO<sub>3</sub>H *etc.* showed a comparative factual yield of HMF.

**3.3.2. Effects of temperature and reaction time.** D265–SO<sub>3</sub>H was selected to test the effects of reaction time and temperature for HMF production. As shown in Fig. 9, the HMF yield increases as reaction time increases from 30 to 90 min, and the yield remains stable as the reaction time increases from 90 to 120 min. This is similar to the former results that the HMF yield could be sustained at a level with prolonged reaction time.<sup>17</sup> High temperature is of benefit to the HMF production; the factual yield increases from 47% to 66% as the temperature increases from 80 to 120 °C.

**3.3.3. Extraction effects of ethyl acetate.** Some publications have reported that HMF could be separated from ILs by extraction through some special organic solvents, including ethyl acetate, toluene, *etc.*<sup>11</sup> Ethyl acetate is a potential extracting solvent due to its immiscibility with the ILs but good solvency for HMF, as well as its low boiling point which is hopefully *via* evaporation. In this work, ethyl acetate ( $4 \times 7.5$  mL) was used to extract HMF from [AMIM]Cl. As shown in Fig. 8 and 9, the ethyl acetate extracted yield was much lower than the factual yield, with 39–55% of the HMF being extracted



Fig. 7 The pathways for acid-catalyzed hydrolysis and dehydration of inulin to  $\ensuremath{\mathsf{HMF}}$  .

by ethyl acetate. Further work on the improvement of the extraction efficiency seems necessary.

3.3.4. Reusability. Reuse of D265-SO<sub>3</sub>H in [AMIM]Cl was tested at a reaction condition of 100 °C, 60 min as following steps.<sup>17,18</sup> After a typical reaction, the [AMIM]Cl solution was extracted by excess ethyl acetate until the extracting ethyl acetate looks like the fresh ethyl acetate. The remaining sublayer products (mainly [AMIM]Cl and D265-SO3H) after extraction were distilled at 70 °C in a rotary evaporator to remove the remaining water and ethyl acetate, and little HMF was found in the distilled fraction (mainly water and ethyl acetate). The remaining [AMIM]Cl and D265-SO<sub>3</sub>H were added into weighed fresh inulin to start a reuse reaction. The result was that the [AMIM]Cl and D265-SO<sub>3</sub>H system kept good reusability for HMF production, the factual yield remained at 61% even after being used five times. Impurities, if present in the reaction mixture, did not seem to have any significant effect on the HMF yields in the recycling of the D265-SO<sub>3</sub>H/ [AMIM]Cl mixture. Thus, this recycled catalyst/ILs mixture system retained good activity for conversion of inulin to HMF. However, for some real biomass in the catalyst/ILs mixture, the



Fig. 8 The yield of HMF with the addition of various catalysts in a reaction condition of 100  $^{\circ}$ C, 60 min. The values are averages of two duplicate experiments.



Fig. 9 The effects of reaction time and temperature for HMF production with D265–SO<sub>3</sub>H addition. The values are averages of two duplicate experiments.

impurities maybe a problem for recycling, and further work need to be done.

As a heterogeneous catalyst, D265-SO<sub>3</sub>H was separately investigated for the reusability. After reaction, the D265-SO<sub>3</sub>H was successively separated from the ILs through filtration, washed by water, and dried. The recovered D265-SO<sub>3</sub>H was added into a fresh [AMIM]Cl and inulin system to start a reuse reaction. The results showed that the HMF factual yield was decreased to 44%, indicating that the catalyst was partly deactivated. According to the previous report published by Rinaldi et al.,<sup>19</sup> the inactivation should be caused by loss of acidic sites during the ion-exchange process between the solid catalyst and ILs. Furthermore, regeneration of the partly inactivated D265-SO<sub>3</sub>H was conducted by dipping into 10% H<sub>2</sub>SO<sub>4</sub> solution for about 10 h, and then being washed by pure water. Subsequently, the regenerated catalyst was dried and resupplied for the next reaction. The results showed that with the addition of regenerated D265-SO<sub>3</sub>H, the HMF factual yield reached 63%, which was nearly the same to the HMF factual yield with the addition of fresh D265-SO<sub>3</sub>H.

# 4. Conclusions

Four kinds of hydrochars were successfully sulfonated, yielding carbon-based sulfonated catalysts catalytically active for HMF preparation from inulin in one step in [AMIM]Cl. The carbon-based sulfonated catalysts, including D265–SO<sub>3</sub>H, L225–SO<sub>3</sub>H and W265–SO<sub>3</sub>H, have showed competitive catalytic activities over four traditional solid acid catalysts (HZSM-5, amberlyst-15 resin, 732 cation resin, sulfated zirconia), and the

D265–SO<sub>3</sub>H/ILs reaction system showed good effects in the reusability study. Considering its renewable property, high catalytic activity, as well as good reusability in the ILs mixture system, this biomass derived carbon-based catalyst would have great potential in industry applications.

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