



Research paper

# Efficient hydrolysis of hemicellulose to furfural by novel superacid SO<sub>4</sub>H-functionalized ionic liquids

Wei Hui<sup>1</sup>, Yan Zhou<sup>1</sup>, Yan Dong, Zhi-Jun Cao, Fei-Qiang He, Min-Zhong Cai, Duan-Jian Tao\*

College of Chemistry and Chemical Engineering, Institute of Advanced Materials, Jiangxi Normal University, Nanchang, 330022, China

Received 11 February 2018; revised 20 June 2018; accepted 27 June 2018

Available online 2 July 2018

## Abstract

Novel superacid SO<sub>4</sub>H-functionalized ionic liquids (SFILs) were designed and prepared in this work. The catalytic activities of SFILs were evaluated in xylan hydrolysis and xylose dehydration to produce furfural. Combined with the results of acid strength of SFILs characterized by solid-state <sup>31</sup>P MAS NMR, it was found that the catalytic performance of SFILs was positively correlated to their acid strength. The superacid SFIL [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] displayed the best catalytic performance with more than 80% yield of furfural, and it was also obviously superior to usual SO<sub>3</sub>H-functionalized acidic ILs, mineral liquid acids, and acidic resin Amberlyst-15 catalysts in catalytic activity under optimized conditions. In addition, the superacid SFIL [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] could be easily separated from reaction system and reused at least five times without obvious decrease.

© 2018, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

**Keywords:** Superacid; Ionic liquids; Hemicellulose; Hydrolysis; Furfural

## 1. Introduction

The fast exhaustion of fossil resources is a major challenge to be addressed recently [1]. Biomass recognized as the most promising renewable source of organic carbon available is the perfect equivalent of petroleum in the production of fuels and carbon-based materials [2,3]. Therefore, exploring an effective approach to transforming biomass resources into chemicals and fuels has become so popular that it attracts many attentions from scientific research [4–6].

Furfural is a key biomass derivative and it has great platform potential for the manufacture of solvent, fuels, plastic and so on [7,8]. As shown in Scheme 1, the degradation of hemicellulose by acid is the mainstream method for preparation of furfural. Traditionally, several inorganic acids (HCl and

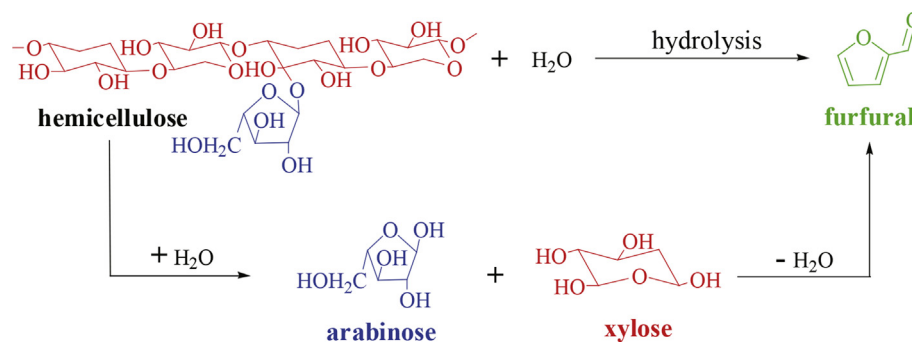
H<sub>2</sub>SO<sub>4</sub>) and solid acids were employed for hydrolysis of hemicellulose to obtain furfural [9–12]. However, these acidic catalysts suffer from many problems such as poor selectivity, tedious separation of product and catalyst, and easy deactivation of solid acids. Thus, it is significant to develop new acid catalysts for efficient degradation of hemicellulose to produce furfural.

Ionic liquids (ILs) are a class of state-of-the-art chemical medium with excellent catalytic activity [13,14]. They have many unique properties including, molecular designability, negligible volatility, and high thermal stability [15,16]. Acidic ILs can provide major benefits in the hydrolysis of hemicellulose to furfural because it can be used not only as a catalyst but also as a solvent [17–20]. For example, Bogel-Lukasik et al. [18] studied the hydrolysis of xylan using [Bmim][HSO<sub>4</sub>] as solvent and catalysts, in which furfural was obtained with a very low yield of 32.2%. Wang et al. [19] employed SO<sub>3</sub>H-functionalized ILs [MimSO<sub>3</sub>H][HSO<sub>4</sub>] as catalyst for efficient xylose dehydration with 78% furfural

\* Corresponding author.

E-mail address: [djtao@jxnu.edu.cn](mailto:djtao@jxnu.edu.cn) (D.-J. Tao).

<sup>1</sup> These authors contributed equally to this work.



Scheme 1. Preparation of furfural by hydrolysis of hemicellulose.

yield, however, only a 29% yield of furfural was obtained in the hydrolysis of xylan. These findings show that the catalytic efficiencies of common acidic ILs for the degradation of xylan are relatively low. It is well known that the acid strength of acidic catalyst plays a key role in the degradation of hemicellulose [20]. The ILs owning strong acid strength would improve the degradation efficiency of hemicellulose. Therefore, it is highly desirable to design and prepare super acidic ILs for efficient degradation of hemicellulose to furfural.

On the basis of our previous work [21], three novel acidic  $\text{SO}_4\text{H}$ -functionalized ionic liquids (SFILs) were designed and prepared in this work. Then the acid strength of as-prepared SFILs  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ ,  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ , and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  were determined by solid-state phosphor-31 magic-angle-spinning nuclear magnetic resonance ( $^{31}\text{P}$  MAS NMR). Their catalytic activities on the yield of furfural by hydrolysis of xylan and dehydration of xylose were further investigated. In addition, the effects of reaction parameters on this hydrolysis reaction and the reusability of SFILs were also studied.

## 2. Experimental

### 2.1. Materials

Choline chloride ( $\geq 99$  wt%), 1,4-dioxane (99 wt%),  $\text{H}_2\text{SO}_4$ , *p*-toluenesulfonic acid (TsOH, 99 wt%), trifluoromethanesulfonic acid (98 wt%), chlorosulfonic acid ( $\geq 99$  wt%), hemicellulose (derived from corn cob, xylan content  $\geq 85$  wt%, molecular weight of 500–12000) were purchased from Aladdin Chemical Reagent Co. Ltd. (Shanghai, China). D-Xylose (98 wt%) was purchased from Macklin Chemical Reagent Co. Ltd. (Shanghai, China). Amberlyst-15 was obtained from Rohm and Haas Co. Ltd. (Shanghai, China). All the chemicals were used as received without further purification.

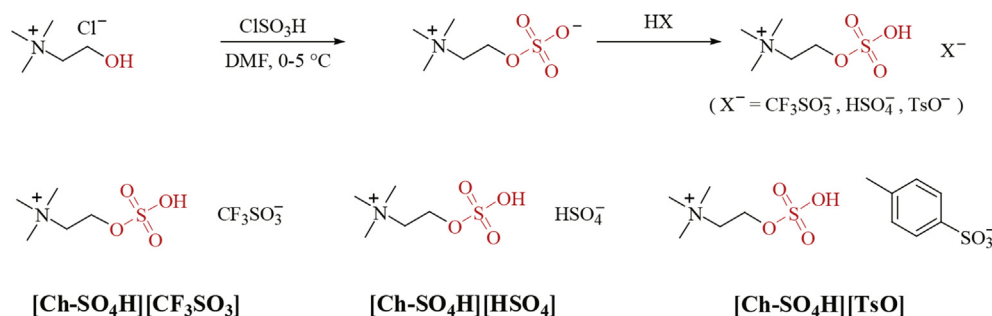
### 2.2. Preparation and characterization of SFILs

Three acidic SFILs  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ ,  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ , and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  (Scheme 2) were prepared according to the previous literature [22]. Taking  $[\text{Ch-SO}_4\text{H}]$

$[\text{CF}_3\text{SO}_3]$  as an example: choline chloride (30 g, 0.21 mol) and DMF (150 mL) were added into a 500 mL round bottom flask followed by a 15 min stirring under the condition of ice bath (below  $5^\circ\text{C}$ ). After that, chlorosulfonic acid (30.05 g, 0.255 mol) was added dropwise with stirring, the reaction was kept at  $0\text{--}5^\circ\text{C}$  for 2 h, during which HCl gas was produced and properly trapped, the solution was controlled to ca.  $\text{pH} = 10$  with aqueous solution of NaOH (20 wt%). The precipitated zwitterion product  $[\text{Ch-SO}_4]$  was filtrated and washed repeatedly with diethyl ether to remove non-ionic residues and further under vacuum at  $80^\circ\text{C}$  for 8 h to eliminate traces of impurities. Then  $[\text{Ch-SO}_4]$  was loaded into a 250 mL round bottom flask followed by dropwise addition of an aqueous solution of trifluoromethanesulfonic acid (60 wt%) with stirring, the reaction was kept at room temperature for 6 h. Then the resulted product,  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ , was washed repeatedly with diethyl ether and dried under vacuum at  $80^\circ\text{C}$  for 12 h. The synthesis processes of  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$  and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  are similar to that of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ . The obtained SFILs were characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra (Bruker Ascend 400), FTIR spectra (Thermo Nicolet 870), and thermal analysis (Netzsch STA 449C).

### 2.3. Acidity characterization by $^{31}\text{P}$ MAS NMR

The solid-state  $^{31}\text{P}$  MAS NMR spectra over  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ ,  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ , and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  were performed as follows: prior to sorption of probe molecule trimethylphosphine oxide (TMPO), the samples were placed in a glass tube and then each sample was subjected to dehydration treatment at  $75^\circ\text{C}$  under vacuum ( $< 10^{-3}$  Pa) over a period of 8 h and then cooled. Detailed procedures involved in introducing the TMPO probe molecule onto the sample can be found elsewhere [23,24]. In brief, a known amount of TMPO adsorbate dissolved in anhydrous  $\text{CH}_2\text{Cl}_2$  was first added into a vessel containing the dehydrated sample in a  $\text{N}_2$  glove box, followed by removal of the  $\text{CH}_2\text{Cl}_2$  solvent by evacuation at room temperature. To ensure a uniform adsorption of adsorbate probe molecules in the acid sites of the SFILs, the sealed sample vessel was further subjected to a thermal treatment at  $100^\circ\text{C}$  for 12 h. Prior to NMR measurements, the sealed



Scheme 2. The preparation procedure and structures of three acidic SFILs.

sample tube was opened and the sample was transferred into a NMR rotor with a Kel-F end cap under a dry  $\text{N}_2$  atmosphere in a glove box. NMR experiments were performed on a Bruker Ascend-500 spectrometer at a resonance frequency of 202.63 MHz for  $^{31}\text{P}$ , with a 4 mm triple-resonance MAS probe at a spinning rate of 10 kHz.  $^{31}\text{P}$  MAS NMR spectra with high power proton decoupling were recorded using a  $\pi/2$  pulse length of 4.1  $\mu\text{s}$  and a recycle delay of 30 s. The chemical shift of  $^{31}\text{P}$  was referenced to 1 M aqueous  $\text{H}_3\text{PO}_4$ .

#### 2.4. Representative procedure for xylan hydrolysis

A certain amount of xylan, distilled water, catalyst, and solvent were sequentially added into a 25 mL reaction kettle. The hydrolysis of xylan was initiated with mechanical agitation at given temperature. After the reaction was done, the reaction system was immediately cooled. Subsequently, the reaction mixture was extracted with ethyl acetate and deionized water (10 mL  $\times$  3), and the system thus forms a liquid–liquid biphasic system, and the aqueous phase containing the IL catalyst could be easily separated by simple decantation. After that, the catalyst IL was further in a vacuum oven at 80  $^\circ\text{C}$  for 12 h to remove water and other solvents and residues prior to reuse in the next run. The procedure for dehydration of xylose is similar to that of xylan.

#### 2.5. Determination of furfural yield

Firstly, the structure of the product furfural was determined and confirmed by GC–MS (Figure S1). According to the previous literature [25], furfural can react with aniline with the aid of concentrated HCl to form a dye, which shows characteristic ultraviolet absorption at 518 nm. The chromogenic reaction of xylose with phloroglucinol, which shows characteristic ultraviolet absorption at 554 nm [26]. Based on these chromogenic reactions, the yield of furfural can be determined according to the absorbance of the characteristic ultraviolet absorption band of the dye. The UV-Vis spectrum of the dye was collected on an ultraviolet visible spectrophotometer (Hitachi Jasco V-750).

To estimate the concentration of furfural produced by hydrolysis of xylan or dehydration of xylose, a standard calibration curve was obtained first by plotting the UV-Vis absorbances of a series of standard furfural solutions against

their corresponding concentrations. The standard calibration curve is given in Figure S2. Then the concentration of furfural of the reaction system can be determined according to its UV-Vis absorbance. Therefore, the yield of furfural can be estimated from the following equation:

$$\text{Furfural yield} = \frac{\text{moles of produced furfural}}{\text{moles of starting xylan (xylose)}} \times 100\% \quad (1)$$

Similarly, the chromogenic reaction of xylose with phloroglucinol can be used for determination of the concentration of xylose. The standard calibration curve for xylose was obtained in a fashion similar to that of furfural, which is shown in Figure S3. Thus, the concentration of the remaining reactant xylose can be determined. Hence, the conversion of xylose and yield of furfural in the reaction of dehydration of xylose can be obtained from the following equation:

$$\text{Xylose conversion} = \left( 1 - \frac{\text{moles of remaining xylose}}{\text{moles of starting xylose}} \right) \times 100\% \quad (2)$$

### 3. Results and discussion

#### 3.1. Acid strength of SFILs

Three novel acidic SFILs [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>], [Ch-SO<sub>4</sub>H][HSO<sub>4</sub>], and [Ch-SO<sub>4</sub>H][TsO] were successfully synthesized and their molecular structures were confirmed by the results of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, and FTIR spectra, as shown in Figures S4–S12. The characterization results of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra showed that there is no trace of impurities in these three SFILs and the purities of these three SFILs are more than 98%. The residual chloride content of these three SFILs was also checked to be less than 500 ppm using the Mohr titration. In addition, the TG analysis further showed that the SFILs [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] and [Ch-SO<sub>4</sub>H][HSO<sub>4</sub>] have very good thermal stability (Figure S13).

Solid-state  $^{31}\text{P}$  MAS with TMPO probe developed by Zheng et al. [23,24] is highly sensitive in terms of characterization of Brønsted acid strengths in acids, in which acid strength can be measured through  $^{31}\text{P}$  chemical shift. They demonstrated that  $^{31}\text{P}$  chemical shift threshold value of super-

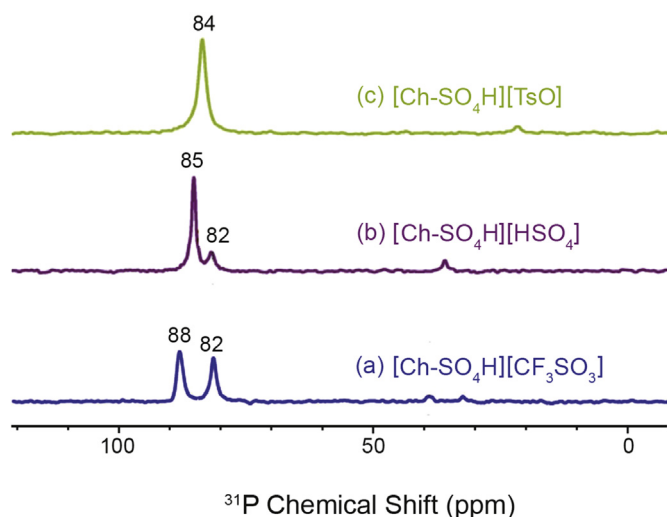


Fig. 1.  $^{31}\text{P}$  MAS NMR spectra of TMPO adsorbed on the SFILs: (a)  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ , (b)  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ , (c)  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$ .

acid was 86 ppm [27–30]. Fig. 1 shows the  $^{31}\text{P}$  MAS NMR spectra of adsorbed trimethylphosphine oxide (TMPO) probe molecules on these three SFILs. A single peak of  $^{31}\text{P}$  MAS NMR spectra was observed for  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$ , while double peaks were noticed for  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  and  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ . This finding implies that  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  has one kind of uniform Brønsted acid strength, whereas  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  and  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$  show two kinds of Brønsted acid strengths because of two different  $\text{TMPOH}^+$  complexes on Brønsted acid sites. Moreover, for  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ ,  $^{31}\text{P}$  chemical shift value was larger than 86 ppm, indicating the presence of super acidity in  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ . For  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$  and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$ , their  $^{31}\text{P}$  chemical shifts had not reach 86 ppm, indicating that neither of them belongs to superacid ILs. Therefore, the order of acid strength of SFILs is  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3] > [\text{Ch-SO}_4\text{H}][\text{HSO}_4] > [\text{Ch-SO}_4\text{H}][\text{TsO}]$ , and  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  is considered to be a superacid IL. In addition, the Hammett acidity of these three SFILs was also evaluated through the determination of the Hammett functions ( $H_0$ ). It is obvious from Table S1 that the Hammett acidity of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  is slightly higher than the acidity of  $\text{H}_2\text{SO}_4$ , further confirming the nature of super acidity in  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ .  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$  and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  are not considered to be superacid because of their relatively weak acidic anions.

### 3.2. Catalytic performance of SFILs

Firstly, the catalytic performance of SFILs for hydrolysis of xylan to produce furfural was screened under various conditions. The results are summarized in Table 1. It was found that under the condition of 1,4-dioxane as solvent at 120 °C for 6 h,  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ ,  $[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$ , and  $[\text{Ch-SO}_4\text{H}][\text{TsO}]$  had high catalytic activity in the hydrolysis of xylan, with the yield of furfural of 82%, 74.8% and 66.5%, respectively. The catalytic activity of these three SFILs was on the order of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3] > [\text{Ch-SO}_4\text{H}][\text{HSO}_4] > [\text{Ch-SO}_4\text{H}][\text{TsO}]$ , which is in consistency with their acid strength.

Table 1

Yields of furfural by catalytic hydrolysis of xylan using different catalysts under various conditions.<sup>a</sup>

Entry	Catalyst	Temperature (°C)	Solvent	Time (h)	Yield (%)
1	$[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$	120	1,4-dioxane	6	82.0
2	$[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$	120	1,4-dioxane	6	74.8
3	$[\text{Ch-SO}_4\text{H}][\text{TsO}]$	120	1,4-dioxane	6	66.5
4	$[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$	140	Toluene	4	46.3
5	$[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$	140	Toluene	4	28.3
6	$[\text{Ch-SO}_4\text{H}][\text{TsO}]$	140	Toluene	4	21.8
7	$[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$	170	$\gamma$ -Valerolactone	1	58.5
8	$[\text{Ch-SO}_4\text{H}][\text{HSO}_4]$	170	$\gamma$ -Valerolactone	1	54.2
9	$[\text{Ch-SO}_4\text{H}][\text{TsO}]$	170	$\gamma$ -Valerolactone	1	41.8
10 <sup>b</sup>	$\text{CH}_3\text{SO}_3\text{H}$	120	1,4-dioxane	6	45.2
11 <sup>b</sup>	TsOH	120	1,4-dioxane	6	39.4
12	Amberlyst-15	120	1,4-dioxane	6	34.0

<sup>a</sup> Reaction conditions: xylan 0.2 g, solvent 5 g, catalyst dosage percentage of 2%, and water percentage of 2%.

<sup>b</sup> The same amount of acidic sites as that of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$ .

This suggests that the SFIL  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  possessing super acid strength displayed the best catalytic activity in hydrolysis of xylan. Further, the yield of furfural by hydrolysis of xylan was also examined using traditional liquid acids ( $\text{CH}_3\text{SO}_3\text{H}$ , TsOH) and solid acid (Amberlyst-15) as catalysts, the results are listed in Table 1. It can be seen that  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  show higher catalytic activity than those of  $\text{CH}_3\text{SO}_3\text{H}$ , TsOH, and Amberlyst-15. It is reasoned that on the basis of the same amount of acidic sites, the acid strength of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  is super than that of these liquid acids. Also, the heterogeneous catalyst Amberlyst-15 has a relatively large mass transfer resistance, thus resulting in a low yield of furfural. Therefore, the above results demonstrated that  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  is considered to be a promising superacid catalyst with high activity for hydrolysis of xylan.

For comparison, the yields of furfural under different reaction conditions according to previous works were also summarized in Table 2 [31–38]. It is obvious that for those reactions in absence of the IL catalyst, either the yields of furfural are relatively low or a higher reaction temperature is needed, while for those reactions using IL as catalyst, the yields of furfural from xylan hydrolysis and xylose dehydration are also low because of their weak acidities. While by using the superacid SFIL  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  catalyst, however, the reaction can be conducted under mild conditions with more than 80% yield of furfural.

### 3.3. Optimization of reaction conditions

To optimize the reaction conditions for  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  in catalytic hydrolysis of xylan to prepare furfural, the effects of solvent, reaction time, reaction temperature, water loading and catalyst dosage on the yield of furfural were investigated. Firstly, the reaction was examined in eight different solvents, as listed in Table 3. It is found that the high furfural yield of 82% was obtained by using 1,4-dioxane as solvent. This is probably due to the fact that 1,4-dioxane can

Table 2  
Comparison of yield of furfural under different reaction conditions.

Entry	Feedstock	Solvent	Catalyst	Temp. (°C)	Time (h)	Yield (%)	Refs.
1	xylan	[Emim]Cl/DMA-LiCl	CrCl <sub>2</sub> +HCl	140	2	25	17
2	xylan	GVL-H <sub>2</sub> O	[MimSO <sub>3</sub> H][HSO <sub>4</sub> ]	140	3	29	19
3	xylan	CPME-NaCl	SSP	190	0.85	37	31
4	xylan	toluene-H <sub>2</sub> O	SAPO-44	170	8	85	32
5	xylan	xylene-H <sub>2</sub> O	HUSY (Si/Al = 15)	170	4	56	33
6	xylan	2-MTHF	SO <sub>4</sub> <sup>2-</sup> /Sn-MMT	160	1.5	77	35
7	xylan	1,4-dioxane	[Ch-SO <sub>4</sub> H][CF <sub>3</sub> SO <sub>3</sub> ]	120	6	82	This work
8	xylose	DMA-LiBr	CrCl <sub>2</sub>	100	4	56	17
9	xylose	GVL-H <sub>2</sub> O	[MimSO <sub>3</sub> H][HSO <sub>4</sub> ]	140	3	78	19
10	xylose	toluene	[Emim][HSO <sub>4</sub> ]	100	6	84	34
11	xylose	DMSO	MCM-41-SO <sub>3</sub> H	140	4	82	36
12	xylose	THF	[N <sub>2224</sub> SO <sub>3</sub> H][CH <sub>3</sub> SO <sub>3</sub> ]	150	1	32	37
13	xylose	GVL-H <sub>2</sub> O	[Bmim]Cl-AlCl <sub>3</sub>	140	4	79	38
14	xylose	1,4-dioxane	[Ch-SO <sub>4</sub> H][CF <sub>3</sub> SO <sub>3</sub> ]	120	10	95.1	This work

form azeotropes with water upon high speed stirring, thus leading to an increased contact area between aqueous phase and organic phase [39]. The hydrolysis product furfural can get away from the acidic environment immediately upon forming, which significantly reduces the occurrence of side reactions and promotes the reaction towards the direction of the furfural product, thus results to the greatly increased yield of furfural. Therefore, 1,4-dioxane was selected as the best solvent for catalytic hydrolysis of xylan.

Then, the reaction time was examined in the range of 2–10 h. The results are shown in Fig. 2a. The yield of furfural gradually increases to 82% in the first 6 h but decreases at longer reaction times, suggesting increased side reactions such as isomerization, condensation, and polymerization of furfural upon extending reaction time [6,11]. Thus, 6 h is chosen as the optimal reaction time. Further, the effect of reaction temperature was investigated in the range of 100–130 °C. Fig. 2b shows that as the reaction temperature increases from 100 to 120 °C, the yield of furfural increases from 13.9% to 82%, however, as reaction temperature increases further, the yield of furfural decreases, which is probably due to carbonization of xylan upon high reaction temperature on one hand, and side reactions of furfural on the other [36]. As a result, 120 °C is regarded as the optimal reaction temperature for catalytic hydrolysis of xylan.

Table 3  
Hydrolysis of xylan using various solvents.<sup>a</sup>

Entry	Solvent	Yield (%)
1	toluene	67.3
2	DMSO	33.1
3	THF	54.1
4	2-MTHF	30.3
5	acetone	43.9
6	acetonitrile	25.5
7	DEC	67.2
8	1, 4-dioxane	82.0

<sup>a</sup> Reaction conditions: reaction temperature 120 °C, reaction time 6 h, xylan 0.2 g, solvent 5 g, [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] catalyst percentage of 2%, and water percentage of 2%.

Furthermore, the effect of water percentage was explored in the range of 1%–10% (based on the total mass of reaction mixture). Fig. 2c shows that as water consumption increased from 1% to 2%, the furfural yield improved from 51.4% to 82%, while as the water percentage increases further, the yield of furfural decreases. This is not hard to understand because at lower water percentage, the [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] catalyst is not completely dissolved in water, which results to a limited contact chance of xylan and the catalyst, while at higher water percentage, however, the increase of water loading may lead to a decreased concentration of catalyst, which eventually affect the hydrolysis process of xylan and results to a lowered yield of furfural. Hence, the optimal water dosage for this reaction is 2%. Finally, the effect of catalyst loading was investigated in the range of 1%–3%. The results are shown in Fig. 2d. As the catalyst percentage increases from 1% to 2%, the yield of furfural increased gradually from 35% to 82%, because the acidity of the reaction system simultaneously enhanced as the loading of the acidic catalyst increased, which results to improve the yield of furfural. As the catalyst percentage increases further, however, the side reactions such as isomerization and polymerization of the product furfural may occur, thus leading to a lowered yield of furfural at higher catalyst loading conditions [19]. Therefore, the optimal reaction conditions for [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] in catalytic hydrolysis of xylan to prepare furfural is determined to be: reaction time of 6 h, reaction temperature of 120 °C, water dosage of 2%, and catalyst loading of 2%.

### 3.4. Preparation of furfural by catalytic dehydration of xylose

To extend the applications of SFILs in preparation of furfural, the catalytic performance of [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] in the dehydration of xylose was also investigated. The results are summarized in Table 4. It was indicated that [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] also showed excellent performance with 99.2% conversion of xylose and 95.1% yield of furfural. However,

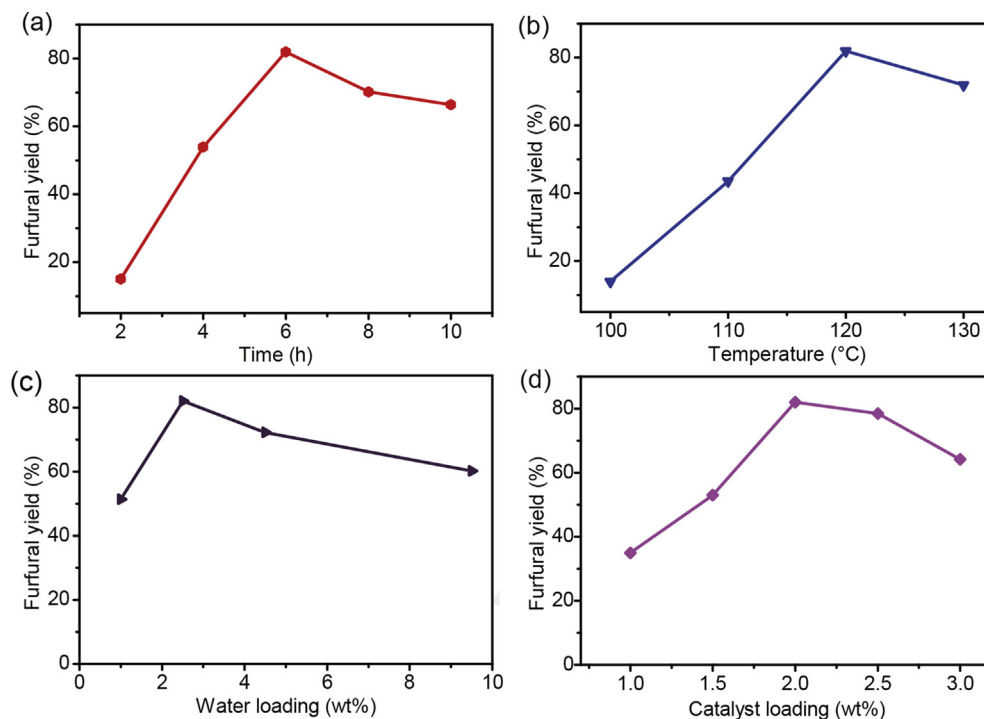


Fig. 2. Effect of reaction time (a), reaction temperature (b), water percentage (c), and catalyst loading percentage (d) on the yield of furfural using [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] as catalyst.

Table 4  
Dehydration of xylose catalyzed by [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>].<sup>a</sup>

Entry	Catalyst percentage (wt%)	Time (h)	Xylose conversion (%)	Furfural yield (%)
1	1	6	40.3	38.4
2	1.5	3	32.6	32.0
3	1.5	6	64.0	62.4
4	1.5	10	99.2	95.1
5	2	3	46.8	45.7
6	2	6	84.0	81.5

<sup>a</sup> Reaction conditions: reaction temperature 120 °C, xylose 0.2 g, 1,4-dioxane 5 g, and water percentage of 2%.

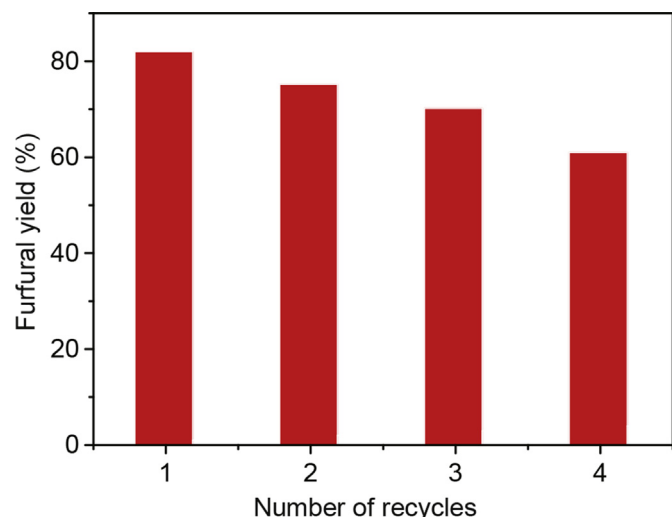


Fig. 3. Recycling test of [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] for catalytic hydrolysis of xylan.

many previous studies induced low yields of furfural in the presence of usual acidic ILs as catalysts (Table 2). Our results indicated great potential of superacid SFILs in catalytic dehydration of xylose to produce furfural.

### 3.5. Reusability of SFILs

The reusability of ILs is very important for their applications. Hence, the reusability of [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] in catalytic hydrolysis of xylan was examined. [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] was reused for four times and the results are illustrated in Fig. 3. As can be seen from the figure, the yield of furfural slightly decreased from ca. 80% to ca. 60% after reused for four times, which is probably due to the inevitable loss of partial catalyst during experimental operations, and may also due to the accumulation of by-products such as monosaccharides and humin in ILs. The reusability of [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] in catalytic dehydration of xylose was also investigated. The catalyst was reused for five times and the results are shown in Fig. 4. The results showed that both the conversion of xylose and the yield of furfural remained ca. 90% after five times, indicating good reusability of [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] in catalytic dehydration of xylose. It was also found that the FTIR spectra (Figure S14) of reused [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] after five runs were nearly the same as those of a fresh sample. This finding demonstrates that the IL [Ch-SO<sub>4</sub>H][CF<sub>3</sub>SO<sub>3</sub>] can be recovered and reused very well in the hydrolysis of xylose.

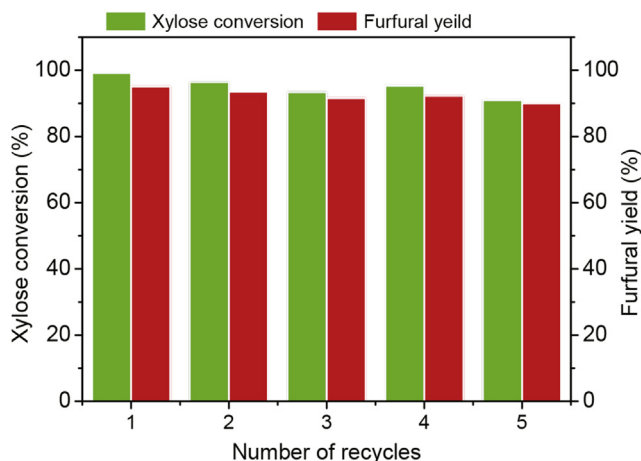


Fig. 4. Recycling test of  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  for catalytic dehydration of xylose.

#### 4. Conclusions

In summary, three new acidic SFILs with  $-\text{SO}_4\text{H}$  group had been synthesized, characterized and employed as highly efficient catalysts for xylan hydrolysis and xylose dehydration to produce furfural under mild reaction conditions. It was found that the catalytic activities of SFILs were positively correlated to their acid strength. The super acid SFIL  $[\text{Ch-SO}_4\text{H}][\text{CF}_3\text{SO}_3]$  displayed the best catalytic performance with more than 80% yield of furfural and it was also superior to usual  $\text{SO}_3\text{H}$ -functionalized acidic ILs. We believe that the design and utilization of superacid SFILs provides a promising strategy for improving the yield of furfural from hemicellulose, thus facilitating their potential applications in biomass conversion.

#### Conflict of interest

There is no conflict of interest.

#### Acknowledgments

We thank the National Natural Science Foundations of China (Nos. 21566011, 31570560), the Jiangxi Province Sponsored Programs for Distinguished Young Scholars (No. 20162BCB23026), and the Science & Technology Programs of Jiangxi Province Department of Education (No. GJJ160272) for financial support.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.gee.2018.06.002>.

#### References

[1] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.

- [2] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 2411–2502.
- [3] P. Gallezot, *Chem. Soc. Rev.* 41 (2012) 1538–1558.
- [4] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* 114 (2014) 1827–1870.
- [5] S. Van den Bosch, W. Schutyser, S.F. Koelewijn, T. Renders, C.M. Courtin, B.F. Sels, *Chem. Commun.* 51 (2015) 13158–13161.
- [6] L.S. Ribeiro, J.J. de Melo Órfão, M.F.R. Pereira, *Bioresour. Technol.* 244 (2017) 1173–1177.
- [7] D.S. Naidu, S.P. Hlangothi, M.J. John, *Carbohydr. Polym.* 179 (2018) 28–41.
- [8] M. Besson, P. Gallezot, C. Pinel, *Chem. Rev.* 114 (2013) 1827–1870.
- [9] S.H. Zhu, Y.F. Xue, J. Guo, Y.L. Cen, J.G. Wang, W.B. Fan, *ACS Catal.* 6 (2016) 2035–2042.
- [10] M.B. Fusaro, V. Chagnault, D. Postel, *Carbohydr. Res.* 409 (2015) 9–19.
- [11] B. Danon, G. Marcotullio, W. de Jong, *Green Chem.* 16 (2014) 39–54.
- [12] P.L. Dhepe, R. Sahu, *Green Chem.* 12 (2010) 2153–2156.
- [13] D.J. Tao, Y. Dong, Z.J. Cao, F.F. Chen, X.S. Chen, K. Huang, *J. Ind. Eng. Chem.* 41 (2016) 122–129.
- [14] A.S. Amarasekara, *Chem. Rev.* 116 (2016) 6133–6183.
- [15] S. Zhang, Y. Wang, H. He, F. Huo, Y. Lu, X. Zhang, K. Dong, *Green Energy Environ* 2 (2017) 329–330.
- [16] K. Dong, X. Liu, H. Dong, X. Zhang, S. Zhang, *Chem. Rev.* 117 (2017) 6636–6695.
- [17] J.B. Binder, J.J. Blank, A.V. Cefali, R.T. Raines, *ChemSusChem* 3 (2010) 1268–1272.
- [18] A.V. Carvalho, A.M. Costa, L.R. Bogel-Lukasik, *RSC Adv.* 5 (2015) 47153–47164.
- [19] H.Z. Lin, J.P. Chen, Y. Zhao, S.R. Wang, *Energy Fuels* 31 (2017) 3929–3934.
- [20] E. Henon, F. Bohr, N. Sokolowski-Gomez, F. Caralpb, *Phys. Chem. Chem. Phys.* 34 (2003) 5431–5437.
- [21] D.J. Tao, Z. Cheng, F.F. Chen, Z.M. Li, N. Hu, X.S. Chen, *J. Chem. Eng. Data* 58 (2013) 1542–1548.
- [22] F. Liu, A. Zheng, I. Noshadi, F.S. Xiao, *Appl. Catal. B Environ.* 136 (2013) 193–201.
- [23] A.M. Zheng, S.J. Huang, S.B. Liu, F. Deng, *Phys. Chem. Chem. Phys.* 13 (2011) 14889–14901.
- [24] A.M. Zheng, H.L. Zhang, X. Lu, S.B. Liu, F. Deng, *J. Phys. Chem. B* 112 (2008) 4496–4505.
- [25] C.C. Loi, H.C. Boo, A.S. Mohamed, A.A. Ariffin, *J. Am. Oil Chem. Soc.* 87 (2010) 607–613.
- [26] R.E. Doerfler, L.D. Cain, F.W. Edens, C.R. Parkhurst, M.A. Qureshi, G.B. Havenstein, *Poultry Sci.* 79 (2000) 656–660.
- [27] A.M. Zheng, S.B. Liu, F. Deng, *Chem. Rev.* 117 (2017) 12475–12531.
- [28] A.M. Zheng, G.Y. Gao, H. Huang, J.H. Gao, K.L. Yao, *Phys. Chem. Chem. Phys.* 19 (2017) 13650–13657.
- [29] N.D. Feng, A.M. Zheng, S.J. Huang, H.L. Zhang, N.Y. Yu, C.Y. Yang, S.B. Liu, F. Deng, *J. Phys. Chem. C* 114 (2010) 15464–15472.
- [30] J. Zhang, B. Xie, L. Wang, X.F. Yi, C.T. Wang, G.X. Wang, Z.F. Dai, A.M. Zheng, F.S. Xiao, *ChemCatChem* 9 (2017) 2661–2667.
- [31] Y.T. Wang, T. Len, Y.K. Huang, A.D. Taboada, A.N. Boa, C. Ceballos, F. Delbecq, G. Mackenzie, C. Len, *ACS Sustain. Chem. Eng.* 5 (2017) 392–398.
- [32] P. Bhaumik, P. LaxmikantáDhepe, *RSC Adv.* 4 (2014) 26215–26221.
- [33] R. Sahu, P.L. Dhepe, *ChemSusChem* 5 (2012) 751–761.
- [34] S. Lima, P. Neves, M.M. Antunes, M. Pillinger, N. Ignatyev, A.A. Valente, *Appl. Catal. Gen.* 363 (2009) 93–99.
- [35] Q.X. Lin, H.L. Li, X.H. Wang, L.F. Jian, J.L. Ren, C.F. Liu, R.C. Sun, *Catalysts* 7 (2017) 118–132.
- [36] A.S. Dias, M. Pillinger, A.A. Valente, *J. Catal.* 229 (2005) 414–423.
- [37] J.C. Serrano-Ruiz, J.M. Campelo, M. Francavilla, A.A. Romero, R. Luque, C. Menéndez-Vázquez, A.B. García, E.J. García-Suárez, *Catal. Sci. Technol.* 2 (2012) 1828–1832.
- [38] S.R. Wang, Y. Zhao, H.Z. Lin, J.P. Chen, L.J. Zhu, Z.Y. Luo, *Green Chem.* 19 (2017) 3869–3879.
- [39] W. Mamo, Y. Chebude, C. Márquez-Álvarez, I. Diaza, E. Sastre, *Catal. Sci. Technol.* 6 (2016) 2766–2774.