ORIGINAL PAPER



The synthesis of Fe-containing ionic liquid and its catalytic performance for the dehydration of fructose

Hui Liu¹ · Yue Wang¹ · Wanxia Ma¹ · Hongwei Wang¹ · Deping Wang¹ · Wei Jiang² · Ming Zhang² · Cunshan Zhou³ · Huaming Li¹

Received: 26 August 2016/Accepted: 15 February 2017 © Institute of Chemistry, Slovak Academy of Sciences 2017

Abstract Four Fe-containing ionic liquids (ILs) were synthesized by coupling of conventional imidazole ionic liquids $[C_xmim]Cl (x = 4, 8, 12, 16)$ with FeCl₃ and were characterized by FT-IR, Raman, ESI–MS and TG. All of the Fe-containing ILs were applied to the conversion of fructose into 5-hydroxymethylfurfural (HMF) in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) subsequently and the result showed that $[C_{16}mim]FeCl_4$ exhibited excellent catalytic performance. Then the different reaction parameters with $[C_{16}mim]FeCl_4$ as catalyst were studied in detail. A 92.8% yield of HMF was obtained with 0.03 g $[C_{16}mim]FeCl_4$ and 0.1 g fructose in 1.0050 g [Bmim]Cl at 80 °C for 40 min in fructose/[Bmim]Cl solution.

Keywords HMF · Fe-containing ionic liquid · Dehydration · Fructose

Introduction

Sustainable concerns and the rising of crude oil prices prompted a surge in research for renewable feed-stock. Biomass, as an abundant and sustainable resource, has been

Hui Liu lh7544@ujs.edu.cn

Huaming Li lihm@ujs.edu.cn

- ¹ School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China
- ² Institute for Energy Research, Jiangsu University, Zhenjiang 212013, People's Republic of China
- ³ School of Food and Biological Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China

received particular attention and become the most important renewable resources to replace petroleum feedstock (Rosatella et al. 2011; Melero et al. 2012). It is an important process of preparing 5-hydroxymethylfurfural (HMF) from biomass for this purpose (Takagaki et al. 2012; Van Putten et al. 2013). HMF is well known as "important platform compound" due to its great potential application as a versatile intermediate between biomassbased carbohydrate chemistry and petroleum-based industrial organic chemistry (Gallezot 2012), which can be converted into spices, pharmaceuticals, transportation fuel and fine chemicals (Rosatella et al. 2011; Dutta et al. 2012; Sun et al. 2016). Fructose, an abundant C_6 -sugar molecule, is a potential feedstock for preparing HMF, and the interest in converting it to HMF is increased sharply, recently (Zhao et al. 2016; Zhou et al. 2014).

For the conversion of fructose to HMF was described using different catalysts or reaction mediums. Various catalytic systems including mineral and organic acids (Yang et al. 2011; Harmer et al. 2009), salts (Zhou et al. 2014; Liu et al. 2015), zeolites(Li et al. 2013; Dornath and Fan, 2014), and ion-exchange resin have been broadly studied (Li et al. 2013). However, those catalytic systems usually suffer from some drawbacks, such as long reaction time, the hazard of toxicity, high prices and lower fructose conversion. In our previous works, D001-cc ion-exchange resin is utilized for the dehydration of fructose and indicates excellent catalytic performance (Li et al. 2013). The D001-cc ion-exchange resin is inexpensive, non-poisonous and useable. But the D001-cc ion-exchange resin is easily broken over 100 °C and its channels are easy to be blocked by the formed polymer in the process of fructose dehydration. It restricts its application in the future. Hence, developing an efficient and economic system for fructose dehydration is still essential.

At present, Fe-containing ionic liquid is subjected to high attention by researchers (Yao & Chu, 2013; Martinez-Magadan et al. 2012; Wang et al. 2010, 2012). Alexander et al. (2004) reported the sulfonvlation of benzene and its derivatives using [Bmim]Cl·FeCl₃ ionic liquid under mild conditions. Wang et al. (Wang et al. 2010) studied the depolymerization of poly(ethylene terephthalate) in ethylene glycol using [Bmim]FeCl₄ and good conversion was obtained. Due to its excellent performance, it is widely used in different organic reaction, such as the polymerization reaction (Kim et al. 2008; Wei et al. 2010), Friedel-Crafts reaction of aromatic (HoangTran et al. 2014; Csihony et al. 2001), and AryI Grignard cross-coupling reaction (Bica and Gaertner 2006; Xia et al. 2012). In addition, Fe-containing ionic liquid occurs a particular magnetization in the presence of external magnetic field, which makes it possible to be separated from the reaction mixture (Lee et al. 2007). Hence, Fe-containing ionic liquid has more valuable compared to conventional catalysts in catalysis (Nguyen et al. 2008) and synthesis (Shang et al. 2009). However, the application of Fe-containing ionic liquid in the dehydration of fructose has not been reported. It is, therefore, of interest to study the catalytic performance of Fe-Containing ionic liquids for the dehydration of fructose.

In this paper, four Fe-containing ionic liquids $C_x \text{mimFeCl}_4$ (x = 4, 8, 12 and 16) are synthesized and employed for the dehydration of fructose. The catalytic properties of different Fe-containing ionic liquids are studied and the optimum catalyst are screened out by the preparing experiments of 5-hydroxymethylfurfural (HMF) from fructose. Finally, the effect of different reaction parameters to fructose dehydration are investigated for optimized reaction conditions in [Bmim]Cl.

Experiment

HMF (99% purity) was purchased from Wutong Spice Co., Ltd. 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-Octyl-3-methylimidazolium chloride ([C₁₂mim]Cl) and 1-cetyl-3-methylimidazolium chloride ([C₁₆mim]Cl) were obtained from Shanghai Cheng Jie Chemical Co., Ltd. Fructose (B. R. grade), iron chloride (FeCl₃·6H₂O, A.R. grade), DMSO (A. R. grade), methanol alcohol (CH₃OH, L. C. grade) and ethanol (C₂H₅OH, L. C. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. All of them were used without further purification.

Preparation of Fe-containing ionic liquid

Firstly, 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, 0.1 mol) was added in an ethanol solution of iron chloride (0.1 mol) (Warnke et al. 2010). The mixture was stirred at

40 °C for 24 h in the oil bath and a yellow solution was obtained. Then, the solvent (ethanol) in the solution was evaporated. Finally, the residue was washed with ethanol and dried in vacuum at 80 °C for 24 h. Thus, the [Bmim]FeCl₄ catalyst was prepared. According to the same method, $[C_xmim]FeCl_4$ (x = 8, 12, 16) catalysts were prepared by replacing [Bmim]Cl with $[C_xmim]Cl$ (x = 8, 12, 16), respectively. [Bmim]FeCl₄, [Omim]FeCl₄ and $[C_{12}mim]FeCl_4$ existed as liquids, whereas $[C_{16}mim]FeCl_4$ existed as solid at room temperature.

Characterization of catalysts

Raman tests were performed by a Thermo Scientific DXR Smart Raman spectrometer equipped with a 532 nm excitation. The Fourier transform infrared (FT-IR) spectra (KBr disc) were recorded on Nicolet Model Nexus 470 FT-IR instrument in the mid IR region (400–4000 cm⁻¹). Thermogravimetric scanning (TG) analysis was performed in STA-449C Jupiter (NETZSCH Corp) under N₂ atmosphere. The testing process was carried out from 30 to 1000 °C at a heating rate of 10 °C/min with N₂ flow rate of 30 mL/min. The *m/z* parameters of Fe-containing ionic liquid were characterized by Electrospray ionization tandem mass (ESI–MS) (Thermo LXQ, USA).

Typical procedure for fructose dehydration

Fructose (0.1 g) and [Bmim]Cl (1.0 g) were firstly added into the reaction bulb. The mixture was heated to form a clear solution by an oil bath with a magnetic stirrer at a desired reaction temperature. Then, the reaction started after adding a certain amount of Fe-containing ionic liquid into the mixture. After the desired time, the reaction bulb was immediately cooled with cold water. Finally, the reaction mixture was diluted with pure water to a certain concentration and filtered through a syringe filter before the HPLC analysis (Scheme 1).



Scheme 1 The dehydration of fructose to HMF

Analysis of product

Quantitative analysis of HMF was performed by high performance liquid chromatography (HPLC), which was equipped with a Varian ProStar325 UV–Vis detector, an Agilent TC-C (18) column and two Varian ProStar210 pumps. The using ultraviolet wavelength was 283 nm. All the measured parameter and the calculated formula of HMF yield were consistent with the literature (Li et al. 2013).

Results and discussion

Characterization of catalysts

Temperature-responsive behavior

Compared with other Fe-containing catalysts, $[C_{16}-mim]FeCl_4$ exists as solid under room temperature, which is due to the long carbon chain in $[C_{16}mim]FeCl_4$. The temperature-responsive behavior of $[C_{16}mim]FeCl_4$ is shown in Fig. 1. $[C_{16}mim]FeCl_4$ is in solid state at room temperature and starts to melt at 38.8 °C. When the temperature rises to 40 °C, high-viscosity liquid is observed. Similarly, the ionic liquid changes into solid state with the decrease of temperature. The temperature-control effect of $[C_{16}mim]FeCl_4$ can make it spontaneously separated from the reaction system.

FT-IR spectroscopy

The FT-IR spectra of different Fe-containing ionic liquids are presented in Fig. 2. As can be seen from the spectra, the bands in all of the catalysts within the range from 4000 to 500 cm^{-1} are similar, indicating that the catalysts have a similar structure. The bands at 3130 and 3082 cm⁻¹ come from the stretch vibration of heterocyclic C-H. The adsorption at 2960 and 2874 cm⁻¹ are assigned to the stretch vibration of C–H of substituent on the imidazole



Fig. 1 Reversible melting and solidifying behavior of $[C_{16}mim][FeCl_4]$



Fig. 2 FT-IR spectra of different form Fe-containing ionic liquids

ring. The characteristic peaks at 1569 and 1463 cm⁻¹ can be attributed to the stretch vibration of C=N on the imidazole ring. The characteristic peak at 1488 cm⁻¹ is attributed to the bending vibration of C–H. The strong peak at 1164 cm⁻¹ belongs to the stretch vibration of imidazole ring (Bahr et al. 2001). According to the results, it is found that the structures of imidazole ring is not destroyed in the preparing process of catalysts, which may be attributed that the cationic $[C_x mim]^+$ in $[C_x mim]Cl$ is not involved in the preparing process of catalysts.

FT-Raman spectroscopy

The Raman spectrum of Fe-containing catalysts is shown in Fig. 3. Only an identical peak at 330 cm⁻¹ is observed in all of the Fe-containing catalysts. According to the literature, the identical peaks at 330 and 370 cm⁻¹ in Raman spectrum were, respectively, represented the totally symmetric Fe–Cl stretch vibration of FeCl₄⁻ and Fe₂Cl₇⁻ (Del Sesto et al. 2008; Pei et al. 2010). The result of Fig. 3 shows that only FeCl₄⁻ is existed in all of Fe-containing catalysts, which is due to the mole ratio of 1:1 between FeCl₃ and [C_xmim]Cl (x = 4, 8, 12, 16).

ESI-MS analysis

To analyze the structures and purities of the synthesized Fecontaining ionic liquids, ESI–MS spectra were carried out and the results are shown in Fig. 4. It can be seen from the positive ESI–MS of catalysts (Fig. 4a) that the characteristic ionic peaks at m/z: 139.1, 195.2, 251.3 and 307.4 are found, respectively, which correspond to the [Bmim]⁺, [Omim]⁺, [C₁₂mim]⁺ and[C₁₆mim]⁺ in the Fe-containing ILs, respectively. Hence, the cationic structures of Fe-containing ILs have been determined. The negative spectra of Fe-



Fig. 3 Raman spectrum of different Fe-containing ionic liquids

containing ILs are quite similar and a characteristic ionic peak at m/z: 197.7 belonging to FeCl₄⁻⁻⁻ is observed (Fig. 4b) in all of Fe-containing ILs. The intensity of the characteristic ionic peak is nearly 100%, indicating that Fe-containing ILs have been synthesized with high purities. Test results are as follows: Electrospray MS⁺m/z: 139.1 [Bmim]⁺; MS⁻m/z: 197.7 [FeCl₄]⁻; Electrospray MS⁺m/z: 195.2 [Omim]⁺; MS⁻m/z: 197.7 [FeCl₄]⁻; Electrospray MS⁺m/z: 251.3 [C₁₂mim]⁺; MS⁻m/z: 197.7 [FeCl₄]⁻; Electrospray MS⁺m/z: 251.3 [C₁₂mim]⁺; MS⁻m/z: 197.7 [FeCl₄]⁻; Electrospray MS⁺m/z: 207.06 [C₁₆mim]⁺; MS⁻m/z: 197.7 [FeCl₄]⁻.

The TG curves

To carefully explore the thermal properties of Fe-containing ILs, the TG analysis were investigated by using thermal gravimetric scanning technology and the results are shown in Fig. 5. Compared with $[C_x mim]Cl (x = 4, 8, 12, 16)$, the thermal stability of Fe-containing ILs is improved after the combination of $[C_x mim]Cl (x = 4, 8, 12, 16)$ with FeCl₃. There is no obvious mass loss before 340 °C under nitrogen atmosphere for all of Fe-containing ILs. The significant weight loss is observed with temperature from 341.0 to 510.5 °C, which can be attributed to the decomposition of imidazole ring substituent and iron chlorides. According to the DSC results (data not shown), the corresponding endothermic peak in the region of 310–320 k can be attribute to the melting point of Fe-containing ILs. The results illustrate that Fe-containing ILs are almost in the form of liquid at room temperature.

The hydrophobic property

The hydrophobic property of Fe-containing ILs is shown in Fig. 6. It is obvious that the hydrophobic property of Fe-containing ILs increases with the increasing length of carbon chain on imidazole ring.

Catalytic performance of Fe-containing ILs for the dehydration of fructose

Effect of different cation in Fe-containing ILs on the dehydration of fructose

In order to investigate the effect of different cation in Fecontaining ILs on the dehydration of frucose, a series of experiments were carried out under the same conditions using four different Fe-containing ionic liquids including [Bmim]FeCl₄, [Omim]FeCl₄, [C₁₂mim]FeCl₄ and [C₁₆mim]FeCl₄. As shown in Table 1, only 4.3% Yield of HMF



Fig. 4 ESI-MS spectrum of Fe-containing ionic liquids. **a** and **b** The negative and positive EMI-MS spectrum, respectively. *a-1* and *b-1* $[C_{16}mim]FeCl_4$, *a-2* and *b-2* $[C_{12}mim]FeCl_4$, *a-3* and *b-3* $[Omim]FeCl_4$, *a-4* and *b-4* $[Bmim]FeCl_4$







Fig. 6 The hydrophobic property of Fe-containing ILs

can be observed in the blank experiment (without catalyst), showing a negligible catalytic activity of [Bmim]Cl. When the Fe-containing ILs are applied as catalyst in [Bmim]Cl (entry 2, entry 3, entry 4, entry 5), the HMF yield are improved and ranges from 70.6 to 86.7%, indicating that the catalytic activity of Fe-containing ILs is excellent. Moreover, the catalyst activity of Fe-containing ILs increases with the increasing of carbon chain length on imidazole ring. This may be attributed that the hydrophobic property and the carbon chain are beneficial to the conversion of fructose (Zhao et al. 2007). The longer carbon

 Table 1
 The effects of different catalysts on the dehydration of fructose

Entry	Catalyst	HMF yield/%	
1 ^a	No catalyst	4.3	
2^{a}	[Bmim]FeCl ₄	70.6	
3 ^a	[Omim]FeCl ₄	75.1	
4 ^a	[C ₁₂ mim]FeCl ₄	78.5	
5 ^a	[C ₁₆ mim]FeCl ₄	86.7	
6 ^b	[Bmim]FeCl ₄	65.8	
7 ^b	[Omim]FeCl ₄	66.2	
8 ^b	[C ₁₂ mim]FeCl ₄	66.9	
9 ^b	[C ₁₆ mim]FeCl ₄	72.7	
$10^{\rm a}$	FeCl ₃ ·6H ₂ O	68.4	
11 ^a	[C ₁₆ mim]Cl	5.6	
12 ^a	$[C_{16}mim]Cl + FeCl_3 \cdot 6H_2O$	79.0	
13 ^c	HCl	81.9	

Conditions a: catalyst 0.1 g, fructose 0.1 g, [Bmim]Cl 1.0050 g, 80 °C, 20 min

Conditions b: catalyst 0.1 g, fructose 0.1 g, DMSO 1.0050 g, 120 °C, 20 min

Conditions c: catalyst 2 $\mu L,$ fructose 0.1 g, [Bmim]Cl 1.0050 g, 80 °C, 20 min

chain is, the more easily the enolization carries out and the stronger hydrophobic property is, the higher the catalyst activity.

Similar results are observed when DMSO is used as solvent (entry 6, entry 7, entry 8, entry 9), indicating that

the sequence of catalytic activity for different Fe-containing ILs is not affected by the solvent.

From the results of entry 5, entry 10, entry 11 entry 12 and entry 13, Only 5.6% yield of HMF can be obtained when $[C_{16}mim]Cl$ was used as catalyst(entry 11). The HMF yield increases to 68.4% when FeCl₃ (entry 10) is used as catalyst. This may be due to FeCl₃ owns Lewis acidity and a new catalyst ([Bmim]FeCl₄) is formed through the interaction of FeCl₃ and [Bmim]Cl in the process of fructose dehydration. When the mixture of $FeCl_3$ and $[C_{16}mim]Cl$ with the mole ratio of 1:1 is added as catalyst(entry 12), the yield of HMF increases to 79.0%. A 81.9% yield of HMF was obtained when HCl was used as catalyst(entry 13). It proves that Brønsted acid exhibites good catalytic activity for the dehydration of fructose. However, compared with the above catalysts, $[C_{16}]$ mim]FeCl₄ (entry 5) has the best catalytic performance and HMF yield reaches 86.7%. It proves that the existence of FeCl_4^- is in favor of the dehydration of fructose to HMF. This may be due to the spatial structure of $FeCl_4^-$ is different from FeCl₃ (Martinez-Magadan et al. 2012).

According to all above results, $[C_{16}mim]FeCl_4$ has the best catalytic activity compared to other Fe-containing ionic liquids. Therefore, $[C_{16}mim]FeCl_4$ as an acid catalyst was chosen in all the following experiments.

Effect of catalyst dosage on the dehydration of fructose

The dehydration reaction of fructose with different catalyst dosage was carried out and the results are presented in Table 2. Only 4.3% yield of 5-HMF is observed without [C₁₆mim]FeCl₄ at 80 °C for 20 min; however, the 5-HMF yield reaches to 51.5% when 0.02 g [C₁₆mim]FeCl₄ is added in the same conditions. It confirmedly proved that $[C_{16}mim]$ FeCl₄ shows remarkable catalytic activity for the dehydration reaction of fructose. It can be observed that 88.5% yield was obtained when the catalyst dosage increased to 0.03 g, which stems from the fact that the catalytic sites increase with the increase of the amount of catalyst. Therefore, the catalytic performance is improved. However, the HMF yield decreases gradually with continuous increasing the dosage of $[C_{16}mim]$ FeCl₄ to 0.15 g, which may be attributed that the over-using of catalysts also accelerates the side reaction.

The effect of different temperatures on the dehydration of fructose

The influence of different reaction temperatures, including 60, 70, 80, 90 and 100 °C, respectively, on the dehydration of fructose is depicted in Fig. 7. It is obvious that different temperature and time had a significant influence on the dehydration reaction. A similar tendency of HMF yield is

Table 2 The effect of the dosages of $[C_{16}mim]FeCl_4$ on the dehydration of fructose

Entry	[C ₁₆ mim]FeCl ₄	HMF yield/%	
1	0	4.3	
2	0.02	51.5	
3	0.03	88.5	
4	0.05	85.2	
5	0.09	80.7	
6	0.12	78.2	
7	0.15	76.9	

Conditions: fructose 0.1 g, [Bmim]Cl 1.0050 g, 80 °C, 20 min



Fig. 7 Temporal HMF as a function of the reaction time at different temperatures. Conditions: $[C_{16}mim]FeCl_4~0.03$ g, fructose 0.1 g, [Bmim]Cl~1.0050 g

observed at different temperatures, which shows a sharp increase in the initial phase and then a gradual decrease. This behavior is due to that the polycondensation of HMF is boosted with prolonging reaction time to generate insoluble humins and other by-products (De et al. 2011). Meanwhile, the high temperature is beneficial to the formation of HMF at initial stage. Increasing the temperature can reduce the time of reaching the highest yield. It only tooks 20 min to reach the maximum yield of HMF at 100 °C, but at 90, 80, 70 and 60 °C, the time consumed are 30, 40, 50 and 60 min, respectively. This is due to the face that the dehydration of fructose is an endothermic reaction (Choudhary et al. 2012). It is worth noting that the higher temperature is, the faster HMF yield descends with the prolonging reaction time. It may be because the undesirable side reactions are also promoted while the dehydration reaction is accelerated under too high reaction temperature.

Therefore, the optimum condition of dehydration reaction is 80 $^{\circ}$ C for 40 min.

Effect of the initial addition amount of fructose on its dehydration

To achieve the industrialized production of HMF, it is indispensable to explore the influence of initial addition amount of substrate on the dehydration reaction. As can be shown in Table 3, the HMF yield constantly rises with the increasing addition amount of fructose when adding less initial amount of substrate. The highest yield reaches 92.8% with 0.10 g fructose as substrate. However, when the initial amount of fructose is over 0.10 g, HMF yield gradually decreases with the increasing of the initial addition amount of fructose. Especially when initial amount of fructose increases to 0.4 g, HMF yield declines sharply. This may be ascribed that the catalytic sites of the reaction system are relatively high with the low initial amount of fructose, leading to better promote dehydration of fructose. However, when the initially added dosage of fructose is too large, the probability of collision between molecules is improved. The coking reaction and the crosslinking polymerizations between generated HMF or between fructose and HMF are conducted to generate soluble polymers and insoluble humins, leading to decrease the HMF yield (Chheda and Dumesic 2007). From

Table 3 The effect of the dosages of fructose on the the HMF yield

Entry	M ^a /g	M ^b /g	C°/%	HMF yield/%
1	0.05	0.03	4.7	89.7
2	0.10	0.03	9.0	92.8
3	0.20	0.03	16.6	90.5
4	0.30	0.03	23.0	87.6
5	0.40	0.03	28.5	75.2

Conditions: [Bmim]Cl 1.0050 g, 80 °C, 40 min

^a The initial addition amount of fructose

^b The addition amount of [C₁₆mim]FeCl₄

^c The initial concentration of fructose

Table 4 The effect of different solid acid catalysts on the HMF yield

comprehensive consideration of the yield and economy, the mass of 0.1 g is chosen as the optimum dosage of fructose.

Effect of different solid acid catalysts on the dehydration of fructose

For further exploring the advantage of C_{16} mimFeCl₄, a series of solid acid catalysts (resins, salts, organic–inorganic hybrid, SO₃H-functionalized acidic mesoporous materials) in other researchers' work was compared and the result is shown in Table 4. The HMF yield reaches 75.3–90.8% in other catalytic system, which is lower than that in C_{16} mimFeCl₄–[Bmim]Cl system (our work). Moreover, obvious advantage of reaction time and temperature is observed in our work. Hence, the C_{16} mimFeCl₄ used in synthesis of HMF from fructose has remarkable application prospects in the future.

Recycling of C₁₆mimFeCl₄/[Bmim]Cl system

To investigate the recycling performance of the catalyst, the reusability of the catalyst system [C16mim]FeCl4/ [Bmim]Cl is explored in the experiment. Experiment was carried out at 80 °C for 40 min. The dosage of [C16mim]FeCl₄, [Bmim]Cl and fructose was 0.03, 1.0050 and 0.1 g, respectively. After the first reaction stopped run, 1 g of distilled water was added to reduce the viscosity of ionic liquid, thus facilitating the subsequent extraction of HMF. The separation of HMF from the mixture was carried out by extracting with ethyl acetate (Qi et al. 2009). It can be found through UV-Vis that 90-95% of HMF could be extracted by using ethyl acetate as extraction agent. Subsequently, the rest of ethyl acetate and water was removed by vacuum drying at 60 °C for 24 h. Fresh fructose was directly added into the dried mixture for the next reaction. As shown in Fig. 8, the yield of HMF decreases gradually in the former three experiments, and declines obviously with the increasing recycle times. The results indicate that the catalyst system has better recycle performance in limiting recycling runs. However, with the increasing times of the catalytic system, the water generated during the

ıtalyst ,	Temperature and time	HMF yield/%	References
nberlyst-15 resin	80 °C, 10 min	83.0	Qi et al. (2009)
owex-50wx8-100 resin	80 °C, 10 min	81.0	
O_4^{2-}/ZrO_2	100 °C, 30 min	88.4	Qi et al. (2011)
BA-15-SO ₃ H	120 °C, 1 h	80.3	Guo et al. (2012)
Cl ₃ ·6H ₂ O	100 °C, 120 min	75.3	Cao et al. (2011)
Cl ₃	200 °C, 4 h	90.8	Zhou et al. (2014)
6mimFeCl4	80 °C, 40 min	92.8	Our work
r)))) () ()	alyst aberlyst-15 resin wex-50wx8-100 resin $_4^{2-}/ZrO_2$ A-15-SO ₃ H Cl ₃ ·6H ₂ O Cl ₃ mimFeCl ₄	ralyst Temperature and time aberlyst-15 resin 80 °C, 10 min wex-50wx8-100 resin 80 °C, 10 min $_4^{2-}$ /ZrO ₂ 100 °C, 30 min A-15-SO ₃ H 120 °C, 1 h Cl ₃ ·6H ₂ O 100 °C, 120 min Cl ₃ 200 °C, 4 h mimFeCl ₄ 80 °C, 40 min	ralystTemperature and timeHMF yield/%aberlyst-15 resin80 °C, 10 min83.0wex-50wx8-100 resin80 °C, 10 min81.0 $_4^{2-}/ZrO_2$ 100 °C, 30 min88.4A-15-SO_3H120 °C, 1 h80.3Cl_3·6H_2O100 °C, 120 min75.3Cl_3200 °C, 4 h90.8mimFeCl_480 °C, 40 min92.8



Fig. 8 Recycling of C_{16} mimFeCl₄–[Bmim]Cl system. Conditions: fructose 0.1 g, [C_{16} mim]FeCl₄ 0.03 g, [Bmim]Cl 1.0050 g, 80 °C, 40 min

reaction contacts with the active centers of the catalyst, meanwhile the by-product generated during the reaction covers the surface of the catalyst and reduces the active site, ultimately leads to a decline of catalytic activity. Meanwhile, a slight effect on the results of the recycling experiment may be caused by the incompletely extracted HMF and the unreacted fructose in the previous reaction.

Conclusion

Four Fe-containing ILs were prepared and determined by different characterization methods. All of Fe-containing ILs still maintained the imidazole cation structure in the original ionic liquids and owned FeCl_4^- anion. The effects of cation on the dehydration of fructose were discussed and $[C_{16}\text{mim}]\text{FeCl}_4$ had the excellent catalytic performance. The yield of HMF reached to 92.8% with 0.03 g $[C_{16}\text{mim}]\text{FeCl}_4$ and 0.1 g fructose in 1.0050 g [Bmim]Cl at 80 °C for 40 min.

Acknowledgments The authors thank the financial support for this study by the National Natural Science Foundation of China (21106057, 21406092, 21506080, 31170672), and Advanced Talents of Jiangsu University (10JDG143), China Postdoctoral Science Foundation (2014T70489, 2013M541621, 1302152C).

References

- Alexander MV, Khandekar AC, Samant SD (2004) Sulfonylation reactions of aromatics using FeCl₃-based ionic liquids. J Mol Catal A 223:75–83. doi:10.1016/j.molcata.2003.10.066
- Bahr JL, Yang JP, Kosynkin DV, Bronikowski MJ, Smalley RE, Tour JM (2001) Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: a bucky paper

electrode. J Am Chem Soc 123:6536–6542. doi:10.1021/ Ja010462s

- Bica K, Gaertner P (2006) An iron-containing ionic liquid as recyclable catalyst for aryl grignard cross-coupling of alkyl halides. Org Lett 8:733–735. doi:10.1021/ol052965z
- Cao Q, Guo XC, Yao SX, Guan J, Wang XY, Mu XD, Zhang DK (2011) Conversion of hexose into 5-hydroxymethylfurfural in imidazolium ionic liquids with and without a catalyst. Carbohydr Res 346:956–959. doi:10.1016/j.carres.2011.03.015
- Chheda JN, Dumesic JA (2007) An overview of dehydration, aldolcondensation and hydrogenation processes for production of liquid alkanes from biomass-derived carbohydrates. Catal Today 123:59–70. doi:10.1016/j.cattod.2006.12.006
- Choudhary V, Burnett RI, Vlachos DG, Sandler SI (2012) Dehydration of glucose to 5-(hydroxymethyl)furfural and anhydroglucose: thermodynamic insights. J Phys Chem C 116:5116–5120. doi:10.1021/jp2113895
- Csihony S, Mehdi H, Horvath IT (2001) In situ infrared spectroscopic studies of the Friedel-Crafts acetylation of benzene in ionic liquids using AlCl₃ and FeCl₃. Green Chem 3:307–309. doi:10. 1039/B107515m
- De S, Dutta S, Saha B (2011) Microwave assisted conversion of carbohydrates and biopolymers to 5-hydroxymethylfurfural with aluminium chloride catalyst in water. Green Chem 13:2859–2868. doi:10.1039/C1GC15550D
- Del Sesto RE, McCleskey T, Burrell AK, Baker GA, Thompson JD, Scott BL, Wilkes JS, Williams P (2008) Structure and magnetic behavior of transition metal based ionic liquids. Chem Commun 4:447–449. doi:10.1039/b711189d
- Dornath P, Fan W (2014) Dehydration of fructose into furans over zeolite catalyst using carbon black as adsorbent. Microporous Mesoporous Mater 191:10–17. doi:10.1016/j.micromeso.2014. 02.031
- Dutta S, De S, Saha B (2012) A brief summary of the synthesis of polyester building-block chemicals and biofuels from 5-hydroxymethylfurfural. ChemPlusChem 77:259–272. doi:10.1002/cplu. 201100035
- Gallezot P (2012) Conversion of biomass to selected chemical products. Chem Soc Rev 41:1538–1558. doi:10.1039/ c1cs15147a
- Guo XC, Cao Q, Jiang YJ, Guan J, Wang XY, Mu XD (2012) Selective dehydration of fructose to 5-hydroxymethylfurfural catalyzed by mesoporous SBA-15-SO₃H in ionic liquid BmimCl. Carbohydr Res 351:35–41. doi:10.1016/j.carres.2012.01.003
- Harmer MA, Junk CP, Rostovtsev VV, Marshall WJ, Grieco LM, Vickery J, Miller R, Work S (2009) Catalytic reactions using superacids in new types of ionic liquids. Green Chem 11:517–525. doi:10.1039/b818788f
- HoangTran P, Do NB, NgocLe T (2014) Improvement of the Friedel-Crafts benzoylation by using bismuth trifluoromethanesulfonate in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid under microwave irradiation. Tetrahedron Lett 55:205–208. doi:10.1016/j.tetlet.2013.10.155
- Kim JY, Kim JT, Song EA, Min YK, Hamaguchi H (2008) Polypyrrole nanostructures self-assembled in magnetic ionic liquid as a template. Macromolecules 41:2886–2889. doi:10. 1021/ma01333k
- Lee SH, Ha SH, You CY, Koo YM (2007) Recovery of magnetic ionic liquid [bmim]FeCl4 using electromagnet. Korean J Chem Eng 24:436–437. doi:10.1007/s11814-007-0075-x
- Li Y, Liu H, Song CH, Gu XM, Li HM, Zhu WS, Yin S, Han CR (2013) The dehydration of fructose to 5-hydroxymethylfurfural efficiently catalyzed by acidic ion-exchange resin in ionic liquid. Bioresour Technol 133:347–353. doi:10.1016/j.biortech.2013. 01.038

- Liu H, Hua C, Song CH, Dai SF, Wang HW, Zhu WS, Li HM (2015) Commercially available ammonium salt-catalyzed efficient dehydration of fructose to 5-hydroxymethylfurfural in ionic liquid. Inorg Chim Acta 428:32–36. doi:10.1016/j.ica.2015.01. 016
- Martinez-Magadan JM, Oviedo-Roa R, Garcia P, Martinez-Palou R (2012) DFT study of the interaction between ethanethiol and Fecontaining ionic liquids for desulfuration of natural gasoline. Fuel Process Technol 97:24–29. doi:10.1016/j.fuproc.2012.01. 007
- Melero JA, Iglesias J, Garcia A (2012) Biomass as renewable feedstock in standard refinery units. Feasibility, opportunities and challenges. Energy Environ Sci 5:7393–7420. doi:10.1039/ c2ee21231e
- Nguyen MD, Nguyen LV, Jeon EH, Kim JH, Cheong M, Kim HS, Lee JS (2008) Fe-containing ionic liquids as catalysts for the dimerization of bicyclo[2.2.1]hepta-2,5-diene. J Catal 258:5–13. doi:10.1016/j.jcat.2008.05.008
- Pei XW, Yan YH, Yan LY, Yang P, Wang JL, Xu R, Chan-Park MB (2010) A magnetically responsive material of single-walled carbon nanotubes functionalized with magnetic ionic liquid. Carbon 48:2501–2505. doi:10.1016/j.carbon.2010.03.023
- Qi XH, Watanabe M, Aida TM, Smith RL (2009) Efficient process for conversion of fructose to 5-hydroxymethylfurfural with ionic liquids. Green Chem 11:1327–1331. doi:10.1039/b905975j
- Qi XH, Guo HX, Li LY (2011) Efficient conversion of fructose to 5-hydroxymethylfurfural catalyzed by sulfated zirconia in ionic liquids. Ind Eng Chem Res 50:7985–7989. doi:10.1021/ ie200488k
- Rosatella AA, Simeonov SP, Frade RFM, Afonso CAM (2011) 5-Hydroxymethylfurfural (HMF) as a building block platform: biological properties, synthesis and synthetic applications. Green Chem 13:754–793. doi:10.1039/c0gc00401d
- Shang SM, Li L, Yang XM, Zheng L (2009) Synthesis and characterization of poly(3-methyl thiophene) nanospheres in magnetic ionic liquid. J Colloid Interface Sci 333:415–418. doi:10.1016/j.jcjs.2009.01.021
- Sun Y, Liu P, Liu Z (2016) Catalytic conversion of carbohydrates to 5-hydroxymethylfurfural from the waste liquid of acid hydrolysis NCC. Carbohydr Polym 142:177–182. doi:10.1016/j.carb pol.2016.01.053
- Takagaki A, Nishimura S, Ebitani K (2012) Catalytic transformations of biomass-derived materials into value-added chemicals. Catal Surv Asia 6:164–182. doi:10.1007/s10563-012-9142-3

- Van Putten RJ, van der Waal JC, de Jong E, Rasrendra CB, Heeres HJ, de Vries JG (2013) Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chem Rev 113:1499–1597. doi:10.1021/cr300182k
- Wang H, Yan RY, Li ZX, Zhang XP, Zhang SJ (2010) Fe-containing magnetic ionic liquid as an effective catalyst for the glycolysis of poly(ethylene terephthalate). Catal Commun 11:763–767. doi:10.1016/j.catcom.2010.02.011
- Wang JL, Yao HW, Nie Y, Bai L, Zhang XP, Li JW (2012) Application of iron-containing magnetic ionic liquids in extraction process of coal direct liquefaction residues. Ind Eng Chem Res 51:3776–3782. doi:10.1021/ie202940k
- Warnke Z, Styczen E, Wyrzykowski D, Sikorski A, Klak J, Mrozinski J (2010) Structural and physico-chemical characteristics of tetraethylammonium tetrachloridoferrate(III). Struct Chem 21:285–289. doi:10.1007/s11224-009-9537-6
- Wei YY, Zhao Y, Li LA, Yang XM, Yu XH, Yan GP (2010) Magnetic ionic liquid-assisted synthesis of polypyrrole/AgCl nanocomposites. Polym Adv Technol 21:742–745. doi:10.1002/ pat.1682
- Xia Y, Yan CH, Li Z, Gao HH, Sun HM, Shen Q, Zhang Y (2012) Synthesis, structure of iron(III)-containing imidazolium salts and their catalytic activity in the alkylation of aryl Grignard reagents. Chin Sci Bull 58:493–499. doi:10.1007/s11434-012-5513-4
- Yang FL, Liu QS, Yue M, Bai XF, Du YG (2011) Tantalum compounds as heterogeneous catalysts for saccharide dehydration to 5-hydroxymethylfurfural. Chem Commun 47:4469–4471. doi:10.1039/c0cc05138a
- Yao AN, Chu TW (2013) Fe-containing ionic liquids as effective and recoverable oxidants for dissolution of UO2 in the presence of imidazolium chlorides. Dalton Trans 42:8413–8419. doi:10. 1039/c3dt32832e
- Zhao HB, Holladay JE, Brown H, Zhang ZC (2007) Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. Science 316:1597–1600. doi:10.1126/science.1141199
- Zhao J, Zhou CM, He C, Dai YH, Jia XL, Yang YH (2016) Efficient dehydration of fructose to 5-hydroxymethylfurfural over sulfonated carbon sphere solid acid catalysts. Catal Today 264:123–130. doi:10.1016/j.cattod.2015.07.005
- Zhou XM, Zhang ZH, Liu B, Zhou Q, Wang SG, Deng KJ (2014) Catalytic conversion of fructose into furans using FeCl₃ as catalyst. J Ind Eng Chem 20:644–649. doi:10.1016/j.jiec.2013. 05.028