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An efficient catalytic dehydration of fructose and sucrose to 5-hydroxymethylfurfural with protic ionic liquids

Xinli Tong, Yang Ma, Yongdan Li *

Tianjin Key Laboratory of Applied Catalysis Science and Technology and State Key Laboratory of Chemical Engineering, School of Chemical Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

The renewable furan-based platform chemical, 5-hydroxymethylfurfural (HMF), has been efficiently synthesized from D-fructose and sucrose in the presence of a catalytic amount of protic ionic liquids. The 1-methylimidazolium-based and *N*-methylmorpholinium-based ionic liquids are employed. As a result, 74.8% and 47.5% yields of HMF are obtained from D-fructose and sucrose, respectively, at 90 °C for 2 h under nitrogen atmosphere when *N*-methylmorpholinium methyl sulfonate ($[NMM]^+[CH_3SO_3]^-$) is used as the catalyst in an *N*,*N*-dimethylformamide–lithium bromide (DMF–LiBr) system. The acidities of ionic liquids are determined by the Hammett method, and the correlation between acidity and catalytic activity is discussed. Moreover, the effects of reaction temperature and time are investigated, and a plausible reaction mechanism for the dehydration of D-fructose is proposed.

1. Introduction

At the present time, the limit of fossil fuel reserves is quite clear, and the concerns over global warming are growing; thus, the catalytic transformation of biomass to value-added chemicals has come under intense focus in recent years.[1,2] The efficient conversion of sugars to fine chemicals has especially attracted a great deal of attention.[3–6] Fructose and sucrose have been considered as superior carbohydrate compounds from which various furan chemicals can be obtained.[7,8] For example, the very useful 5-hydroxymethylfurfural (HMF) has been produced from the catalytic dehydration of fructose and sucrose.[9,10] Nowadays, it has been proposed that HMF has a great potential to serve as a substrate for the preparation of non-petroleum-derived building blocks in fine chemicals.[11,12] Thus, HMF has been referred to as a renewable furan-based platform chemical.[8,13]

Several catalytic systems including liquid mineral acids,[14,15] solid acids[16,17] and a metallic compound[18] have been developed to achieve efficient transformation of fructose to HMF. Although these catalysts could improve the dehydration of fructose, these systems suffer from the need for relatively high reaction temperatures, poor yields or low product selectivities. For example, a poor yield arose from the decomposition and polymerization of HMF after its being produced, and the main by-products included levulinic acid, formic acid and humin, among other components.[5,9,19] The production of HMF in a high yield and by a cost-effective technique is still a challenge.

In recent years, room temperature ionic liquids (ILs) have been used in the dehydration of fructose to HMF.[20–23] Neutral ionic liquids can promote the dehydration reaction due to the enhanced dissolution of catalysts and substrates; for example, Moreau's group[20] reported that the ILs $[bmim]PF_6$ and $[bmim]BF_4$ are suitable reaction media for the dehydration of D-fructose with Amberlyst-15 as a catalyst. Moreover, in the IL [emim]Cl, chromium(II) chloride could efficiently catalyze the dehydration of D-fructose, leading to a yield of HMF near 70%.[21] On the other hand, several special ILs such as 1*H*-3-methylimidazolium chloride and choline chloride/citric acid are also employed as both solvent and catalyst for D-fructose dehydration, in which the molar ratio of IL to D-fructose is 12:1 or 5:1.[22,23] From the above-mentioned strategies, it is seen that ILs have exhibited prominent solvent effects in the dehydration of sugar; however, they are often used and consumed in considerably large amounts. Recently, based on the efficient O-*tert*-butoxycarbonylation of 2-naphthol with a catalytic amount [bmim][OAc], the catalytic concept of ILs has been brought forward, and the catalytic synthesis of HMF with ILs is considered as a promising direction in chemical research.[24] Considering the existence of proton and hydrogen-bonding effects,[25] protic ILs can be helpful in the catalytic dehydration of fructose and sucrose. In the previous work, we studied the dehydration of fructose catalyzed by *N*-methyl-2-pyrrolidonium-based ionic liquids in dimethyl sulfoxide (DMSO) solvent.[26] In this communication, we report the efficient dehydration of D-fructose and sucrose with a 'catalytic amount' of *N*-methylmorpholiniun methylsulfonate

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* Corresponding author. Tel.: +86 22 27405613; fax: +86 22 27405243.
E-mail address: ydli@tju.edu.cn (Y. Li).

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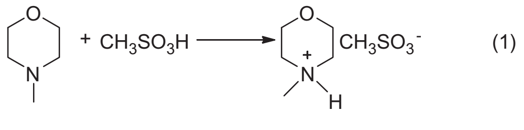
($[NMM]^+[CH_3SO_3]^-$) in an *N*,*N*-dimethylformamide–lithium bromide (DMF–LiBr) system. It is found that 74.8% and 47.5% yields of HMF are obtained with $[NMM]^+[CH_3SO_3]^-$ as a single catalyst in the dehydration of D-fructose and sucrose, respectively, in which the molar ratio of $[NMM]^+[CH_3SO_3]^-$ to substrate is only 0.1.

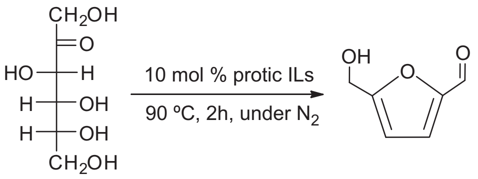
2. Results and discussion

The preparative procedures for the protic ILs, including 1-methylimidazolium hydrogen sulfate ($[MIM]^+[HSO_4]^-$), 1-methylimidazolium methyl sulfonate ($[MIM]^+[CH_3SO_3]^-$), *N*-methylmorpholinium hydrogen sulfate ($[NMM]^+[HSO_4]^-$) and $[NMM]^+[CH_3SO_3]^-$, are similar to those reported in the literature.[25,27,28] The synthesis sequence for $[NMM]^+[CH_3SO_3]^-$ is described in Scheme 1, in which *N*-methylmorpholine and CH_3SO_3H are used as raw materials. Detailed synthetic procedures for these ILs are given in Section 3.

The catalytic performance of protic ILs was first investigated in the dehydration of D-fructose (Scheme 2), where a molar ratio of the IL to substrate was kept less than 0.2, and the dehydration results are summarized in Table 1. It can be seen that the dehydration occurs only slightly with pure water as the solvent, in which only 0.1%, 1.4% or 0.7% yield of HMF is obtained, respectively, in the presence of 10.0 mol % $[MIM]^+[HSO_4]^-$, $[MIM]^+[CH_3SO_3]^-$ or $[NMM]^+[HSO_4]^-$ (entries 1–3), while, the IL $[NMM]^+[CH_3SO_3]^-$ exhibits the higher activity, and a 4.3% yield of HMF is obtained with 10.0 mol % $[NMM]^+[CH_3SO_3]^-$ as catalyst (entry 4). In order to further reveal the catalytic performance of these protic ILs, a composite DMF–LiBr solvent system was chosen as a reaction medium for the D-fructose dehydration. It was found that all protic ILs exhibit better catalytic performance in the DMF–LiBr system (entries 5–8). Of especial note is the fact that the yield of HMF reached a value as high as 74.8% when $[NMM]^+[CH_3SO_3]^-$ is used as a catalyst (entry 8). Moreover, it can also be seen that for the same cation the ILs containing the $[CH_3SO_3]^-$ ion exhibit better catalytic activity than those ILs containing $[HSO_4]^-$ in this system. When $[MIM]^+[HSO_4]^-$ or $[NMM]^+[HSO_4]^-$ was employed as catalyst, only 5.3% or 23.4% yield of HMF was obtained (entries 5 and 7), whereas, the yield of HMF was increased to 12.5% and 74.8% in the presence of $[MIM]^+[CH_3SO_3]^-$ and $[NMM]^+[CH_3SO_3]^-$ (entries 6 and 8), respectively. Moreover, when the DMF, DMF–LiCl, DMF–NaBr or DMF–KBr system was used as the solvent, the yield of HMF was, respectively, 25.4%, 70.5%, 69.2% or 67.5% in the dehydration of D-fructose with $[NMM]^+[CH_3SO_3]^-$ as a catalyst (entries 9–12). These results indicate that the combination of DMF and halogen ion is preferable in the D-fructose dehydration. Meanwhile, a blank test was also performed in the absence of any catalyst under similar conditions, and only 0.2% yield of HMF was obtained (entry 13). Furthermore, the dehydration of sucrose was also investigated with $[NMM]^+[CH_3SO_3]^-$ as the catalyst. It was found that yields of 47.5% and 35.2% were obtained in DMF–LiBr and DMF–LiCl systems, respectively (entries 14 and 15). Thus, it can be concluded that efficient sugar dehydration was achieved in the presence of $[NMM]^+[CH_3SO_3]^-$ when a combination of DMF and halogen ion was used as the reaction medium.



Scheme 1. The synthesis of the IL $[NMM]^+[CH_3SO_3]^-$.



Scheme 2. The dehydration of D-fructose with protic ILs.

Table 1
Dehydration of D-fructose and sucrose with different protic ILs[a]

Entry	Substrate	Ionic liquid	Solvent[b]	Yield[c] (%)
1	D-Fructose	$[MIM]^+[HSO_4]^-$	H_2O	0.1
2	D-Fructose	$[MIM]^+[CH_3SO_3]^-$	H_2O	1.4
3	D-Fructose	$[NMM]^+[HSO_4]^-$	H_2O	0.7
4	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	H_2O	4.3
5	D-Fructose	$[MIM]^+ [HSO_4]^-$	DMF–LiBr	5.3
6	D-Fructose	$[MIM]^+[CH_3SO_3]^-$	DMF–LiBr	12.5
7	D-Fructose	$[NMM]^+[HSO_4]^-$	DMF–LiBr	23.4
8	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	DMF–LiBr	74.8
9	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	DMF	25.4
10	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	DMF–LiCl	70.5
11	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	DMF–NaBr	69.2
12	D-Fructose	$[NMM]^+[CH_3SO_3]^-$	DMF–KBr	67.5
13	D-Fructose	No	DMF–LiBr	0.2
14[d]	Sucrose	$[NMM]^+[CH_3SO_3]^-$	DMF–LiBr	47.5
15[d]	Sucrose	$[NMM]^+[CH_3SO_3]^-$	DMF–LiCl	35.2

[a] Reaction conditions: 1.0 g D-fructose or sucrose, 10.0 mol % protic ILs, in 10 mL of solvent, reaction time 2 h, temperature 90 °C.

[b] The mass ratio of DMF and MX (LiBr, LiCl, NaBr or KBr) is 70:1 for the experiments using a DMF–MX system as solvent.

[c] The results are obtained by HPLC analysis.

[d] The result is obtained in 1.5 h.

It is generally recognized that the activity of a catalyst is closely related to its acidity in the dehydration reaction.[5–10] Thus, the Hammett acidity function (H_0) of ILs was measured using 4-nitroaniline or 2,4-dichloroaniline as the indicator, which is similar to the method used in the previous work.[29,30] The absorbances of the solutions of ILs and indicator were measured using a Perkin Elmer Lambda 900 UV–vis spectrophotometer and the data obtained are listed in Table 2. The H_0 value was calculated by the equation $H_0 = pK_a(In) + \log([In]/[InH^+])$. It was found that the change of absorbance with 4-nitroaniline as the indicator was much smaller than that with 2,4-dichloroaniline as the indicator upon the addition of the protic ILs. So, 2,4-dichloroaniline should be a more suitable indicator for comparing the Hammett acidity of these protic ILs. Furthermore, the calculated results showed that the H_0 value of $[MIM]^+[HSO_4]^-$ is the highest and the H_0 value of $[NMM]^+[CH_3SO_3]^-$ is the smallest in DMF–LiBr system. Consequently, protonic acidity of $[NMM]^+[CH_3SO_3]^-$ is the strongest in all these four protic ILs. Related to the catalytic results in Table 1, it can be concluded that the catalytic activity of the IL has a close correlation with its acidity. In addition, the H_0 values and protonic acidities of $[NMM]^+[HSO_4]^-$ and $[MIM]^+[CH_3SO_3]^-$ are very similar in the DMF–LiBr system; however, the catalytic activity of $[NMM]^+[HSO_4]^-$ is much higher than that of $[MIM]^+[CH_3SO_3]^-$ (entries 6 and 7 in Table 1), which is probably due to steric effects and the nucleophilic effect of the $[NMM]^+$ cation in the dehydration reaction.

In the following, the effects of temperature on the dehydration of D-fructose with $[NMM]^+[CH_3SO_3]^-$ as a catalyst are presented in Figure 1. It is seen that the yield of HMF increases from 40 °C to 90 °C, and the yield decreases after 90 °C, which is attributed to the occurrence of side reactions.

The effect of reaction time on the dehydration of D-fructose and sucrose with $[NMM]^+[CH_3SO_3]^-$ is outlined in Figure 2. In the dehydration of D-fructose, the yield of HMF increases gradually before 60 min, and the yield remains almost unchanged during the period of 60–120 min, however, which shows that the conversion of HMF

Table 2
Hammett function values of different protic ILs[a]

Ionic liquid	Using 4-nitroaniline as the indicator in EtOH[b]				Using 2, 4-dichloroaniline as the indicator in DMF–LiBr[c]		
	Absorbance	[In]/%	$[InH^+]$/%	H_0	[In]/%	$[InH^+]$/%	H_0
No	1.13	100	0	—	100	0	—
$[MIM]^+[HSO_4]^-$	1.13	100	0	—	65.1	34.9	2.27
$[MIM]^+[CH_3SO_3]^-$	1.12	99.1	0.9	3.03	50.7	49.3	2.01
$[NMM]^+[HSO_4]^-$	1.12	99.1	0.9	3.03	55.0	45.0	2.09
$[NMM]^+[CH_3SO_3]^-$	1.08	95.6	4.4	2.33	28.8	71.2	1.61

[a] In—the molar concentration of indicator in the solvent; InH^+—the molar concentration of the protonated indicator; $H_0 = pK_a(In) + \log([In]/[InH^+])$.

[b] pK_a (4-nitroaniline) = 0.99; $c(In) = 7.5 \times 10^{-5}$ mol/L; c(sample) = 30 mmol/L; temperature = 25 °C.

[c] pK_a (2,4-dichloroaniline) = 2.00; c(LiBr) = 1.5 mmol/L; $c(In) = 7.5 \times 10^{-5}$ mol/L; c(sample) = 15 mmol/L.

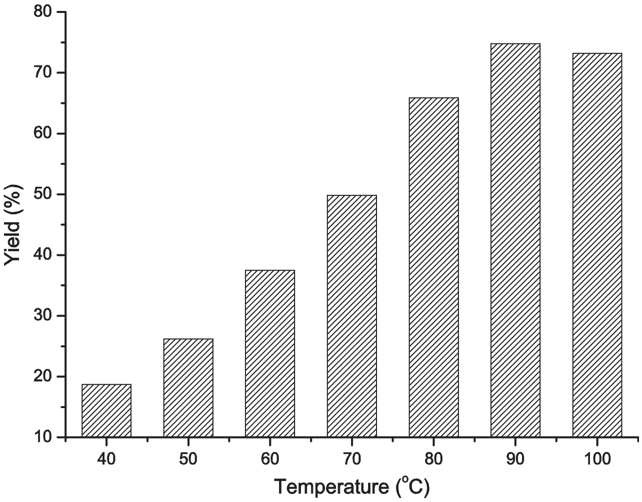


Figure 1. Effect of temperature on the dehydration of D-fructose.

to by-product is probably more rapid than the generation of HMF after 120 min. The dehydration of sucrose is slightly different from the dehydration of D-fructose, as the yield of HMF increases during 10–90 min, and the yield decreases when the reaction time is extended to 120 min and 150 min.

Based on the experimental data and the acidity testing, a possible reaction mechanism for the D-fructose dehydration is proposed as Scheme 3. Firstly, D-fructose loses one water molecule by elimination of H_2O between the C-4 OH group and the C-5 H atom, which is relatively easy and non-selective under acidic conditions.[31] Then, the second water molecule is lost at the secondary C-3 carbon, which should be the rate-determining step due to the existence of steric effects.[32] When the IL $[NMM]^+[CH_3SO_3]^-$ is employed as catalyst, due to the existence of both a proton and an oxygen atom, this process can be performed more rapidly based on O···H···O hydrogen bonding and the nucleophilic effect, which also explains the higher activity of $[NMM]^+[CH_3SO_3]^-$ in the dehydration. Finally, the third water molecule is lost and HMF is produced, which is also comparatively easy owing to the appearance of the conjugated double bond.

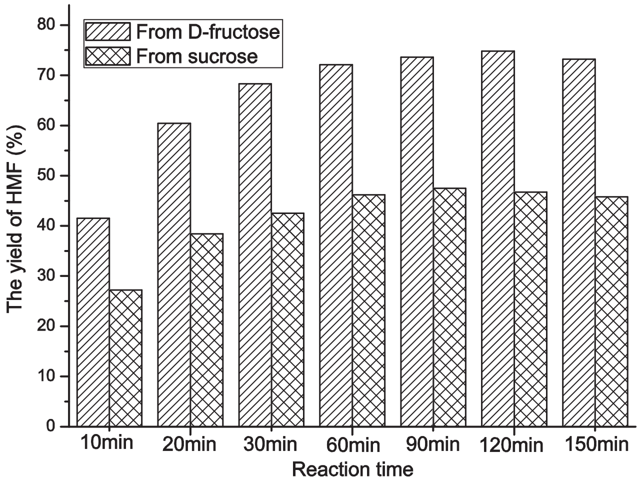


Figure 2. Effect of reaction time on the dehydration of D-fructose and sucrose.

3. Experimental

3.1. Reagents and instruments

N-Methylmorpholine, 1-methylimidazole, methanesulfonic acid (CH_3SO_3H), H_2SO_4, D-fructose, sucrose, LiBr, LiCl, NaBr, KBr, anhydrous EtOH, EtOAc and $NaHCO_3$ were analytical grade and used without further purification. Pure H_2O was furnished by the Ultrapure Water System (electrical resistivity 10–16 mΩ cm). DMF was rectified before being used. NMR spectra were recorded on a Varian Inova 500-MHZ spectrometer. ESIMS analyses were performed by using a TSQ Quantum Access (Thermo Fisher, USA) spectrometer (methanol solvent). The qualitative analyses of the products were carried out using an Aglient 6890/5973 GC–MS, and the quantitative analyses were performed on a Waters 1525 HPLC equipped with both UV and refractive index detectors.

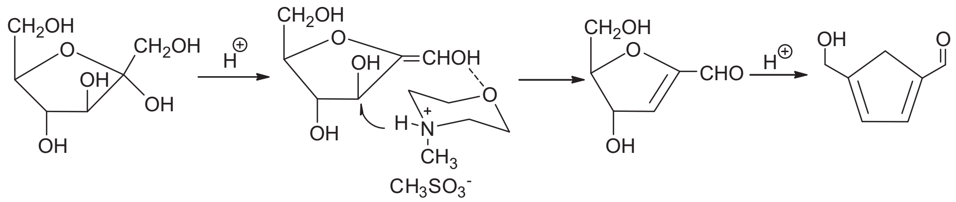
3.2. Synthetic procedure and characterization data for ionic liquids (ILs)

3.2.1. Synthesis and characterization of $[NMM]^+[CH_3SO_3]^-$

$[NMM]^+[CH_3SO_3]^-$ was synthesized by the following procedure: *N*-methylmorpholine (10.1 g, 0.1 mol) was added to a 100-mL flask with a magnetic stirrer. Then, methanesulfonic acid (9.6 g, 0.1 mol) was dropped slowly into the flask over a period of 0.5 h in an ice bath. The reaction was allowed to run for another 5 h at room temperature. The mixture was washed three times using EtOAc and further dried at 90 °C under vacuum for 4 h. ^1H NMR (DMSO-d_6): δ 2.388 (s, 3H), 2.793 (s, 3H), 3.019–3.074 (t, 2H, *J* 12.5 Hz), 3.329–3.355 (d, 2H, *J* 12.2 Hz), 3.581–3.635 (t, 2H, *J* 12.5 Hz), 3.931–3.963 (d, 2H, *J* 12.9 Hz), 9.758 (s, 1H); ^{13}C NMR (D_2O): δ 38.56, 43.25, 53.27,63.91. ESIMS: *m/z* (+) 102.21, *m/z* (−) 95.03.

3.2.2. Synthesis and characterization of $[MIM]^+[CH_3SO_3]^-$

The preparation of $[MIM]^+[CH_3SO_3]^-$ is similar to that of $[NMM]^+[CH_3SO_3]^-$. The corresponding NMR and ESIMS spectral data are as follows: ^1H NMR (DMSO-d_6): δ 2.328 (s, 3H), 3.400 (s, 1H), 3.851 (s, 3H), 7.646–7.675 (d, 2H, *J* 14.5 Hz), 9.038 (s, 1H); ^{13}C NMR (D_2O): δ 33.51, 38.52, 57.48, 119.53, 123.04. ESIMS: *m/z* (+) 83.26, *m/z* (−) 95.04.



Scheme 3. Possible mechanism for the dehydration of D-fructose.

3.2.3. Synthesis and characterization of $[NMM]^+[HSO_4]^-$

$[NMM]^+[HSO_4]^-$ is prepared by mixing *N*-methylmorpholine with concd H_2SO_4 (98%) at 0 °C and stirring for 2 h at room temperature. After that the liquid is washed with EtOAc three times and dried at 80 °C in vacuum. $[NMM]^+[HSO_4]^-$ was obtained in quantitative yield. ^1H NMR (DMSO-d_6): δ 2.79 (s, 3H), 3.186 (s, 4H), 3.735 (s, 4H); ^{13}C NMR (D_2O): δ 43.26, 53.23, 63.85. ESIMS: *m/z* (+) 102.23, *m/z* (−) 96.99.

3.2.4. Synthesis and characterization of $[MIM]^+[HSO_4]^-$

$[MIM]^+[HSO_4]^-$ was prepared under conditions similar to those used for $[NMM]^+[HSO_4]^-$. The corresponding NMR and ESIMS spectral data are as follows: ^1H NMR (DMSO-d_6): δ 3.850 (s, 3H), 7.645–7.674 (d, 2H, *J* 25.1 Hz), 9.037 (s, 1H); ^{13}C NMR (D_2O): δ 35.46, 57.40, 119.48, 122.97. ESIMS: *m/z* (+) 83.26, *m/z* (−) 97.02.

3.3. Reaction conditions for the dehydration of D-fructose and sucrose

A typical procedure for the dehydration of D-fructose and sucrose is as follows: D-fructose (1.0 g, 5.6 mmol) or sucrose (1.0 g, 2.9 mmol), $[NMM]^+[CH_3SO_3]^-$ (0.104 g, 10.0 mol %) and 10 mL of DMF–LiBr (70:1, mass ratio) solution are charged into a 100-mL flask equipped with a magnetic stirrer and a condenser. The apparatus was placed under an N_2 atmosphere, and the mixture was stirred and preheated to 90 °C with an oil bath and then maintained at 90 °C for 2 h. After the reaction, the mixture was decanted into a volumetric flask with pure H_2O or EtOH as the diluent, and the products were then analyzed by HPLC with both UV and refractive index detectors.

3.4. Separation procedure for HMF

After the reaction, the mixture was transferred into a 250-mL flask, and then satd aq $NaHCO_3$ was added. The liquid mixture obtained was stirred with a magnetic stirrer overnight and extracted three times with EtOAc, and then the organic phase was collected, dried with anhyd Na_2SO_4 and distilled under reduced pressure to obtain pure HMF as the main product. The purity was >98% for HPLC analysis.

4. Conclusions

In summary, efficient catalytic syntheses of HMF from D-fructose and sucrose have been successfully performed in the presence of catalytic amounts of protic ILs under mild conditions. The IL $[NMM]^+[CH_3SO_3]^-$ shows very high catalytic activity. A 74.8% or 47.5% yield of HMF is obtained from D-fructose or sucrose, respectively, when $[NMM]^+[CH_3SO_3]^-$ is used as the catalyst in the DMF–LiBr system at 90 °C for 2 h. Furthermore, the acidities of ILs were measured by the Hammett method, which have a close correlation to the observed catalytic activities. The effects of reaction temperature and reaction time on the dehydration reaction were examined, and a possible reaction mechanism for the D-fructose dehydration is proposed.

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Supplementary data

Supplementary data (HPLC measurements for products, original NMR spetra and ESIMS spectra) associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.05.019.

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