Direct Transformation of Fructose and Glucose to 5-Hydroxymethylfurfural in Ionic Liquids under Mild Conditions

Xiaoqian Guo,[a,b] Changhui Zhu,[a,b] and Feng Guo [a,c,*]

Direct dehydration of fructose and glucose to 5-hydroxymethylfurfural (5-HMF) was studied using ionic liquids (ILs) without adding any catalysts. Various ILs were screened, and the highest 5-HMF yield of 95.6% was obtained using 1-butyl-3-methylimidazolium tosylate ([BMIM][TSO]) at 353 K for 30 min. Proton nuclear magnetic resonance (^{1}H NMR) spectra confirmed that the sulfonate hydrolysates of anions of [BMIM][TSO] acted as active sites for the dehydration of fructose to 5-HMF. The [BMIM][TSO] catalyzed dehydration reaction showed relatively low activation energy (Ea). A mixture of dimethyl sulfoxide and 1-sulfobutyl-3-methylimidazolium trifluoromethane sulfate (DMSO-[BSO_3HMIM][OTF]) was used at 413 K for 50 min for the dehydration of glucose, which yielded 59.8% 5-HMF. The addition of *t*-butanol, as an isomerization promoter, to DMSO-[BSO_3HMIM][OTF] led to a higher 5-HMF selectivity without sacrificing 5-HMF yield.

Keywords: Fructose; Glucose; Dehydration; 5-Hydroxymethylfurfural; Ionic liquids

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INTRODUCTION

With limited fossil fuel resources, the production of chemicals and biofuels from renewable biomass is becoming more important and interesting. Global annual biomass growth on the continent amounts to 118×10^9 tons of dry matter (Bobleter 1994); almost all of this lignocellulosic biomass (*e.g.*, wood and grass) contains 75% polysaccharides, which could provide a rich resource of monosaccharides (*e.g.*, glucose and fructose). These sugars are ideal raw materials for the production of 5-hydroxymethylfurfural (5-HMF) (Yang *et al*. 2015). 5-HMF and its derivatives have great potential in the production of fuels, fine chemicals, pharmaceuticals, plastics, 2,5-dimethylfuran (DMF), aldehydes, alcohols, amines, and useful acids (Shi *et al*. 2016).

Many catalysts have been used to convert fructose or glucose into 5-HMF. They include homogenous acids (*e.g.*, H_2SO_4, HCl, and tetraethyl ammonium chloride (TEAC)) (Chen *et al*. 1991; Hansen *et al*. 2009; Cao *et al*. 2011a), transition metal ions (*e.g.*, Cr^{3+} and Cr^{2+}) (Yong *et al*. 2008; Zhao *et al*. 2010; Qi *et al*. 2010), and solid acids (*e.g.*, H-form zeolites, hydrated niobium pentoxide, sulfonic ion-exchange resin, tungsten salts, and Cr-heteropolyacid) (Yong *et al*. 2009; Yang *et al*. 2011; Otomo *et al*. 2014; Pérez-Maqueda *et al*. 2014; Liu *et al*. 2015b). Five reaction systems, including biomass with water, organic solvents (OS), OS-water mixtures, biphasic water/OS, and ionic liquids (ILs), are usually employed for 5-HMF production. However, most of them are not ideal for converting hexose because of their low selectivities and the difficulty of catalyst recycling (Li *et al*. 2010).

Ionic liquids have been widely used as novel reaction media for various catalytic reactions (Liu *et al*. 2012; Cevasco and Chiappe 2014; Liu *et al*. 2015a). Furthermore, ILs can serve as good solvents for various carbohydrates and are considered more environmentally friendly than traditional organic solvents (Wang *et al*. 2011). They can be used as green solvents for the conversion of glucose or fructose to 5-HMF (Yong *et al*. 2008). High 5-HMF yields of 80% to 96% have been obtained in ILs at moderate reaction temperatures of 353 to 423 K (Yong *et al*. 2008; Qi *et al*. 2010; Zhao *et al*. 2010). Recently, glucose and cellulose have been converted to 5-HMF with 60% to 80% yield in an IL with a $CrCl_3$ catalyst that was irradiated with microwave radiation (Cao *et al*. 2011b). Acidic ILs are a new type of solvent with high active site density and feature an extremely low volatility (Moreau *et al*. 2006; Ding *et al*. 2010; Chen *et al*. 2015; Ullah *et al*. 2015). Cations and anions of ILs can be designed to bind a series of moieties with specific properties to achieve high acidity.

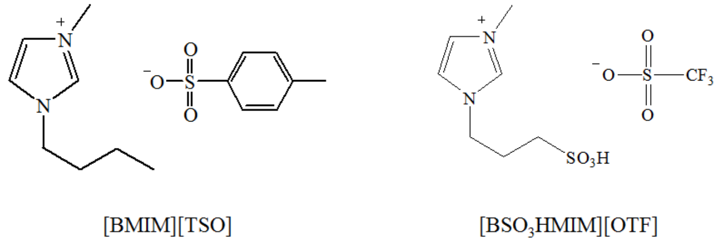
It has been demonstrated that the use of ILs can dramatically affect chemical reactions (Ullah *et al*. 2015). Because the sulfonic group ($-SO_3H$) is widely used to modify the acidity of polymers, 1-butyl sulfonic acid-3-methylimidazolium chloride ($[C_4SO_3HMIM][Cl]$) and 1-butyl sulfonic acid-3-methylimidazolium hydrogensulfate ($[C_4SO_3HMIM][HSO_4]$) were used as strong acidic ILs for cellulose hydrolysis to 95% glucose without further dehydration to 5-HMF (Jiang *et al*. 2011). An acidic IL, 1-*H*-3-methyl imidazolium chloride ([HMIM]Cl), was reported to achieve 92% HMF yield at 363 K within 15 to 45 min (Moreau *et al*. 2006). However, glucose is difficult to convert in HMIMCl, and only a 3% conversion was obtained after 30 min. The reasons given for why acidic ILs show low activity for the dehydration of glucose are as follows: (1) these acidic ILs are not strong enough to convert glucose into 5-HMF; and (2) selected reaction media do not facilitate the isomerization of glucose to fructose.

In this work, ILs were used as solvents and catalysts for the conversion of fructose and glucose into 5-HMF. Various ILs were screened, and high 5-HMF yields of above 90% were obtained by the dehydration of fructose at a low reaction temperature (353 K). The sulfonate anion acted as the active site for the dehydration of fructose and glucose to 5-HMF. Kinetic analysis of fructose dehydration was also studied. This work suggests that high 5-HMF yields can be achieved using sulfonate ILs without using any catalysts, which has not been reported in the scientific literature. Moreover, dimethyl sulfoxide (DMSO) and *t*-butanol additions were used to increase the yield and selectivity of 5-HMF in the dehydration of glucose.

EXPERIMENTAL

Materials and Experimental Procedures

Anhydrous fructose and glucose (purity > 99%) were purchased from BoMei Chemical Co., Ltd. (Hefei, China) and used without further purification. 5-HMF and levulinic acid were purchased from Aldrich (99% purity; USA). DMSO and *t*-butanol were obtained from GenView (99% purity, Tianjin, China) and Xilong Chem. Co., Ltd. (99% purity; Shantou, China). All ILs, 1-butyl-3-methylimidazolium tosylate ([BMIM][TSO]), 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]), 3-allyl-1-methylimidazolium chloride ([AMIM][Cl]), 1-ethyl-3-methylimidazolium bromide ([EMIM][Br]), 1-butylpyridinium tosylate ([BPy][TSO]), 1-butylpyridinium perchlorate ([BPy][ClO_4]), 1-butylpyridinium tetrafluoroborate ([BPy][PF_4]), and 1-sulfobutyl-3-methylimidazolium trifluoromethane sulfate ([BSO_3HMIM][OTF]) (purity 99%), were procured from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences (Lanzhou, Gansu). These ILs were dried in a rotary evaporator under a vacuum at 363 K for 12 h to remove moisture before use in experiments. Scheme 1 shows the molecular structures of [BMIM][TSO] and [BSO_3HMIM][OTF]. ^{1}H-NMR spectra of [BMIM][TSO] were obtained using a Bruker AVANCE-II 600 NMR (Bruker BioSpin GmbH, Rheinstetten, Germany). The NMR solvent used for ILs was $CDCl_3$; NMR spectra were collected at a sample temperature of 295 K.



Scheme 1. Molecular structure of [BMIM][TSO] and [BSO_3HMIM][OTF]

Fructose and glucose were dehydrated in selected ILs (*i.e.*, [BMIM][TSO], [BMIM][Cl], [AMIM][Cl], [EMIM][Br], [BPy][TSO], [BPy][ClO_4], [BPy][PF_4], and [BSO_3HMIM][OTF]). A typical fructose dehydration reaction was performed with 2 g of IL added to a flask that was heated in a water bath at 353 K. Subsequently, 0.2 g of anhydrous fructose was added to the IL solution with stirring to start the reaction, which lasted for 30 min. The dehydration of glucose was investigated in [BSO_3HMIM][OTF] with dimethyl sulfoxide (DMSO) as an IL diluent. In a typical run, 0.225 g of glucose, 1.5 g of [BSO_3HMIM][OTF], and 3 g of DMSO were placed in a 50-mL three-necked round-bottomed flask immersed in oil bath and reacted at 413 K with stirring at 200 rpm for 50 min. To improve the reaction efficiency and selectivity, *t*-butanol was studied as a promoter of the isomerization of glucose to fructose. All experiments were repeated three times, and the reported values are the averages of the three replicates.

Analytical Methods

After the reaction was completed, products were collected for analyses. High-performance liquid chromatography (HPLC) was performed with a Shimadzu LC-20A (Japan). Fructose was analyzed with a HPLC Aminex HPX-87H column (Bio-Rad; Richmond, CA, USA) and was measured by a refractive index (RI) detector. 5-HMF was analyzed with the same HPLC column, but was measured with an ultraviolet (UV) detector at a wavelength of 280 nm. The column oven temperature was set at 323 K, and the mobile phase was 5 mmol sulfuric acid at a flow rate of 0.6 mL/min. The hexose conversion, 5-HMF yield, and 5-HMF selectivity were calculated as follows:

$$\text{Hexose conversion (mol \%)} = \frac{(1 - \textit{hexose molar concentration})\times 100}{\textit{initial hexose molar concentration}} \quad (1)$$

$$\text{5-HMF yield (mol \%)} = \frac{(5 - \textit{HMF molar concentration})\times 100}{\textit{initial hexose molar concentration}} \quad (2)$$

$$\text{5-MHF selectivity (\%)} = \frac{5 - \textit{HMF yield}}{\textit{Hexose conversion rate}} \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Seven ILs were tested for fructose dehydration at 353 K (Fig. 1). After a reaction time of 60 min, a fructose conversion greater than 68% and a 5-HMF yield greater than 57% were achieved in [BMIM][TSO] and [BPy][TSO] (Fig. 1; a and e, respectively). These ILs are usually classified as neutral ILs and show negligible activity for reactions. However, during the preparation of these ILs, no free sulfuric acid was used in their preparation; the only acid used was *p*-toluenesulfonic acid. It has been reported that small amounts of impurities (*i.e.*, tosylate and sulfonate) in ILs can be hydrolyzed to form free acid (*e.g.*, H_2SO_4) (Yasaka *et al*. 2009). Importantly, the ^{1}H-NMR spectra of [BMIM][TSO] exhibited a peak at 2.03 ppm, which denoted the water impurity with free acid (Fig. 2). Tosylate-based ILs contain the tosylate anion ([TSO]$^-$), the IL's cation, [HSO_4]$^-$, solvated H_2SO_4 ([$H_3(SO_4)_2$]$^-$), and hydrogen-bonded H_2SO_4 clusters (Gräsvik *et al*. 2014).

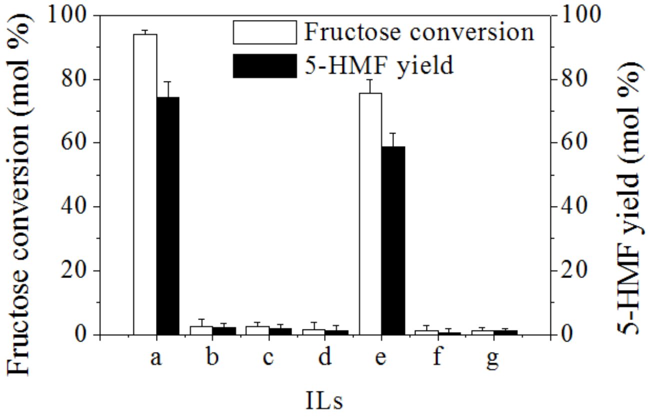


Fig. 1. Fructose conversion and 5-HMF yield using various ILs with 2 g of IL and 0.2 g of fructose reaction temperature of 353 K and reaction time of 60 min: (a) [BMIm][TSO]; (b) [BMIm][Cl]; (c) [AMIm][Cl]; (d) [EMIm][Br]; (e) [BPy][TSO]; (f) [BPy][ClO_4]; and (g) [BPy][PF_4]

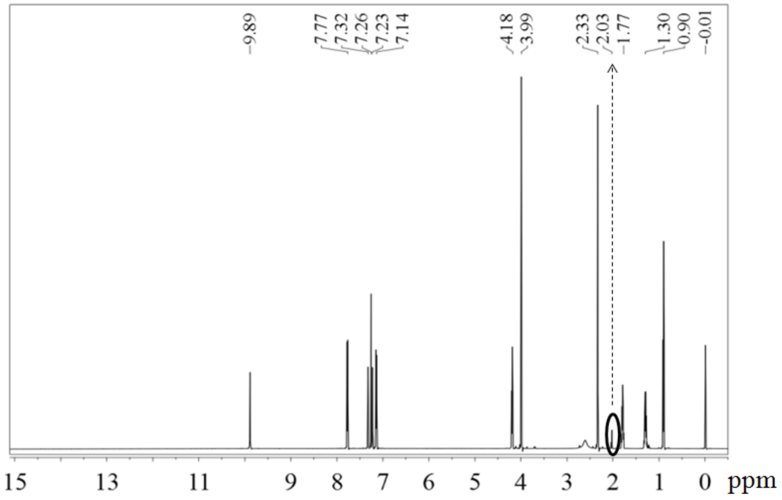


Fig. 2. ^{1}H NMR peaks of sulfuric acid in the ionic liquid [BMIm][TSO]

The acidity of sulfuric acid in these ILs is strongly influenced by the amount of water contained in the ILs. The water formed during the fructose dehydration reaction promoted the hydrolysis of the hydrogen sulfate anion, which in turn accelerated the rate of fructose dehydration. Therefore, [BMIM][TSO] served as both reservoir of acid species and solvent of fructose. ILs with the corresponding anions of Cl^-, Br^-, ClO_4^- and PF_4^- had low activity (Fig. 1; b, c, d, f, and g), which indicated that the acidity of the IL was critical for the dehydration reaction. This also further confirmed that the dehydration reaction is selective for acidic anion types. Moreover, both the intra-molecular hydrogen bonds in ILs (between $-HSO_3$ and -CH- in imidazole ring) and the inter-molecular hydrogen bonds between anion and substrate have important effects on the acidity enhancement (Shi *et al*. 2012; Zhang *et al*. 2015). Experiments showed that imidazole-based ILs (*i.e*., [BMIM][TSO]) had higher activity than pyridinium-based ILs (*i.e*., [BPy][TSO]) (Fig. 1; a *vs*. e). Therefore, [BMIM][TSO] was chosen for additional examination of the dehydration reaction.

Dehydration process variables (*i.e*., fructose concentration, reaction temperature, and reaction time) were optimized for 5-HMF production in [BMIM][TSO]. In addition to the major product of 5-HMF, by-products such as levulinic acid (< 20%), formic acid (< 7%), glucose (< 1%), and furfural (< 2%), were also produced. Reaction temperature had a considerable influence on both fructose conversion and 5-HMF yield (Fig. 3). At 333 K for 60 min, 96% of the fructose was converted, which afforded a 74% yield of 5-HMF. As the reaction temperature was further increased, the reaction time required to obtain the peak 5-HMF yield decreased (Fig. 3; right graph). At 353 K and 30 min reaction time, the conversion of fructose reached 100% and the 5-HMF yield reached 95.6%. Longer reaction times (> 30 min) at 353 K caused the 5-HMF yield to steadily decrease. The byproducts yield reached 30% after 60 min. As reaction time increased, the color of product mixtures changed from colorless to yellow to deep brown. This was caused by the polymerization of 5-HMF and fructose (Qi *et al*. 2009). Water is an inhibitor of the dehydration of fructose and aids the further decomposition of 5-HMF (Hsu *et al.* 2011). Therefore, 5-HMF selectivity could be improved by removing water formed from fructose dehydration. It is relatively simple to remove water in ILs by reduced pressure distillation. The optimum reaction time at 353 K was set to 30 min in the subsequent experiments.

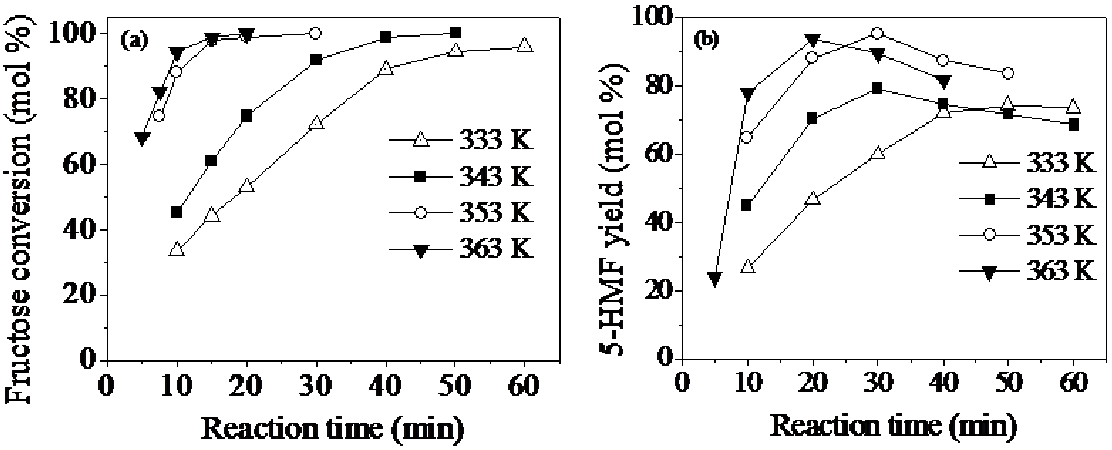


Fig. 3. (a) Conversion of fructose and (b) 5-HMF yield *vs*. reaction temperature with [BMIm][TSO] (2 g) and fructose (0.2 g)

High concentrations of fructose in the IL is necessary for the economical production of 5-HMF. Various initial concentrations of fructose (5% to 40% (w/w)) had little effect on its conversion in [BMIM][TSO] (Fig. 4). However, the 5-HMF yield gradually decreased from 95.6% to 62.7% as the initial fructose concentration increased from 10% to 40% (w/w). It is presumed that the IL solution viscosity became high because of the high fructose concentration, which negatively impacted the dehydration reaction. Román-Leshkov *et al.* (2007) developed a process to convert highly concentrated fructose (30% (w/w) to 5-HMF in H_2O-salt/butanol and achieved 74% fructose conversion and 65.9% 5-HMF yield at a temperature of 453 K. Compared with other catalytic reaction systems (Table 1), the 95.6% 5-HMF yield obtained in the present study without adding any catalyst was similar to the 96% yield reported by Yong *et al.* (2008). This was accomplished at a lower reaction temperature and a shorter reaction time than that reported by Yong *et al.* (2008) (353 K at 30 min *vs*. 373 K for 360 min, respectively).

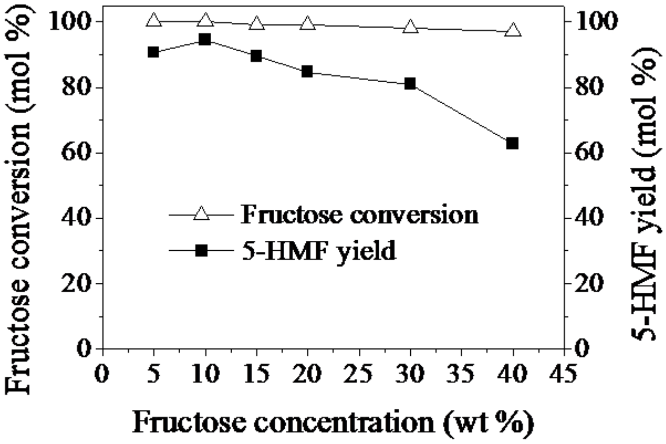


Fig. 4. Conversion of fructose and 5-HMF yield *vs.* initial fructose concentration (% (w/w)) in [BMIm][TSO] (2 g) at reaction temperature of 353 K and reaction time of 30 min

Table 1. Summary of Dehydration of Fructose to 5-HMF in Different Reaction Systems

Reaction media	Catalyst	Catalyst usage	Fructose concentration	Temperature and time	5-HMF yield (%)	References
Hot water	TiO_2	1 wt %	2 wt %	473 K for 5 min	47	Qi *et al.* 2008
H_2O-2-butanol	$Nb_2O_5 \cdot nH_2O$	8.3 wt %	0.024 g/mL	433 K for 120 min	89	Yang *et al.*2011
Aqueous system	Ion-exchange resin	2 wt %	20 wt %	423 K for 10 min	91.7	Qi *et al.* 2008
[BMIm]Cl	$CrCl_2$	9 mol %	10 wt %	373 K for 360 min	96	Yong *et al.* 2008
[BMIm]Cl-acetone	Amberlyst 15	5 wt %	5 wt %	298 K for 360 min	90.3	Qi *et al.* 2009
[BMIm]TSO	-	-	10 wt %	353 K for 30 min	95.6	This work

It is widely accepted that the dehydration of fructose follows a first-order reaction rate (Bicker *et al*. 2003). A kinetic study of fructose dehydration in [BMIM][TSO] was performed by plotting ln(1-X) *vs*. reaction time (where X is expressed as a ratio instead of a percentage) to obtain rate constants (k) at corresponding reaction temperatures (K). An Arrhenius plot was generated from this data (Fig. 5). From this plot, the activation energy, E_a, was calculated to be 51.5 kJ/mol, which is relatively low compared with the previous works (Qi *et al*. 2008).

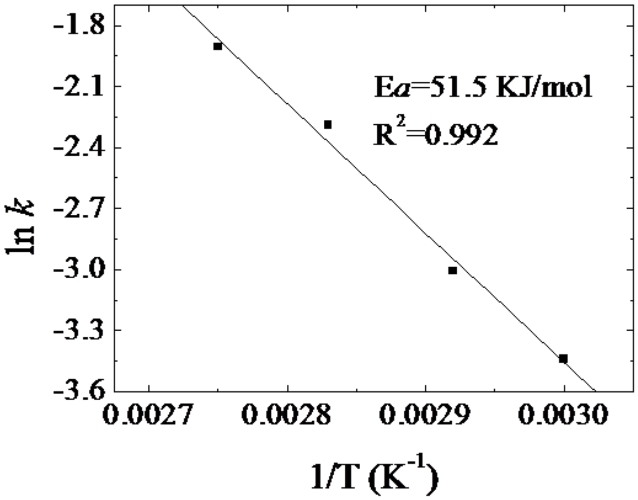


Fig. 5. Conversion of fructose and 5-HMF yield *vs*. reaction temperature in [BMIm][TSO] (2 g) with fructose (0.2 g) for reaction time of 30 min (k is rate constant)

When [BMIM][TSO] was used to dehydrate glucose for 2 h at 393 K, the IL yielded only 0.2% 5-HMF. Thus, [BSO_3HMIM][OTF] was studied as both a solvent for glucose and a catalyst for the dehydration of glucose. When [BSO_3HMIM][OTF] was used to dehydrate glucose, the yield of 5-HMF was increased to 18.8% under the same reaction conditions. Unfortunately, glucose was rapidly converted to solid humins when using [BSO_3HMIM][OTF] as the sole reaction medium. To obtain a high 5-HMF yields with low levels of side-products, the dehydration of glucose was carried out using a DMSO-[BSO_3HMIM][OTF] mixture (2/1 w/w ratio); the reaction temperature in this medium was the first optimized. The glucose loading in [BSO_3HMIM][OTF] was 15% (w/w). The results indicated that the reaction temperature appreciably affected the dehydration of glucose into 5-HMF (Fig. 6).

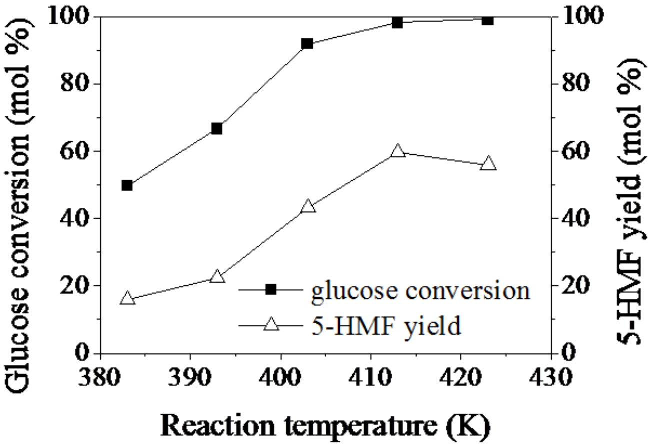


Fig. 6. Conversion of glucose and 5-HMF yield *vs.* reaction temperature (K) in DMSO - [BSO_3HMIM][OTF] mixture with weight ratio of 2/1 (4.5 g) at: 383 K, 60 min; 393 K, 60 min; 403 K, 60 min; 413 K, 50 min; and 423 K, 40 min

The glucose conversion at 383 K was only 49.7%. When the reaction temperature was higher than 413 K, the conversion approached nearly 100%. Meanwhile, the 5-HMF yield increased from 22.4% to 59.8%. However, the amount of side-products formed was 38.4%, wherein levulinic acid accounted for only < 1%. The polymerization of 5-HMF and glucose was considered a key undesirable reaction.

In previous work (Guo *et al*. 2012), fructose conversion in DMSO-[BMIM][Cl] mixtures catalyzed by lignin-derived carbonaceous substances was studied. It was found that high 5-HMF yield and selectivity were obtained as the DMSO content in [BMIM][Cl] was increased. It was suggested that the hydroxyl group of these protic solvents on the ILs may easily react with the intermediate fructofuranosyl cations to form 5-HMF and that the formation of soluble polymers and of solid humins was inhibited (Locas and Yaylayan 2008). A similar conclusion was drawn in this study (Fig. 7). An increase in the weight ratio of DMSO to [BSO_3HMIM][OTF] from 2/1 to 9/1 led to a considerable decrease in 5-HMF yield, as well as 5-HMF selectivity. This is because the amount of acid sites supplied by [BSO_3HMIM][OTF] was diluted by the addition of DMSO. Using DMSO as control, the 5-HMF yield was only 0.41%. Therefore, a 2/1 ratio of DMSO to-[BSO_3HMIM][OTF] was determined to be the optimum mixture. Addition of DMSO avoid to form solid humans and would substantially reduce the production cost of 5-HMF by decreasing the amount of [BSO_3HMIM][OTF].

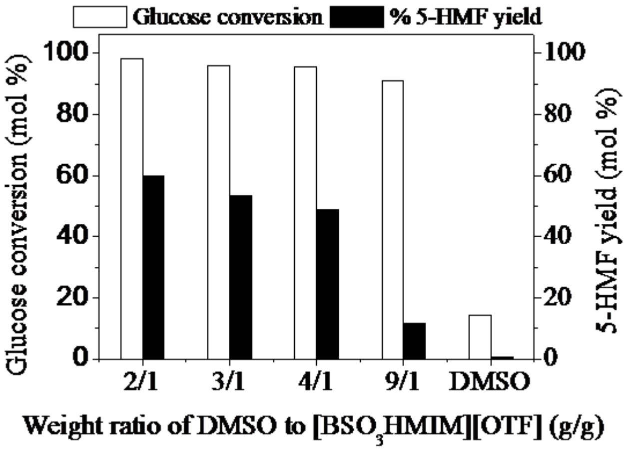


Fig. 7. Effect of DMSO/[BSO_3HMIM][OTF] weight ratio on glucose dehydration in DMSO - [BSO_3HMIM][OTF] system at 413 K for 50 min

Isomerization of glucose to fructose is a rate-limiting step in the dehydration of glucose (Pidko *et al*. 2012). Most of the proposed solutions have focused on screening or modifying catalysts to gain a better reaction selectivity. Alkoxides, such as potassium *tert*-butoxide in *t*-butanol, have been successfully used for the isomerization of fatty acids (White and Quackenbush 1959). However, the dehydration reaction was performed in acid catalytic system. Alkoxides are not appropriate for the dehydration of fructose as they would consume acid species. In the present study, *t*-butanol was added to DMSO-[BSO_3HMIM][OTF] and tested as an isomerization promoter (Fig. 8). However, the isomerization of glucose did not occur in mixtures of *t*-butanol with DMSO-[BSO_3HMIM][OTF] because the 5-HMF yield did not increased. The glucose conversion and 5-HMF yield decreased as the *t*-butanol addition increased to 2.4 mL. The 5-HMF yield showed small decreases as the *t*-butanol dosage increased from 0 mL to 1.2 mL, whereas the 5-HMF selectivity exhibited the opposite trend (from 61.1% to 68.5%). Further increasing the *t*-butanol dosage caused a sharp decrease in the 5-HMF yield. These investigations demonstrated that the addition of *t*-butanol inhibited the formation of soluble polymers and solid humins.

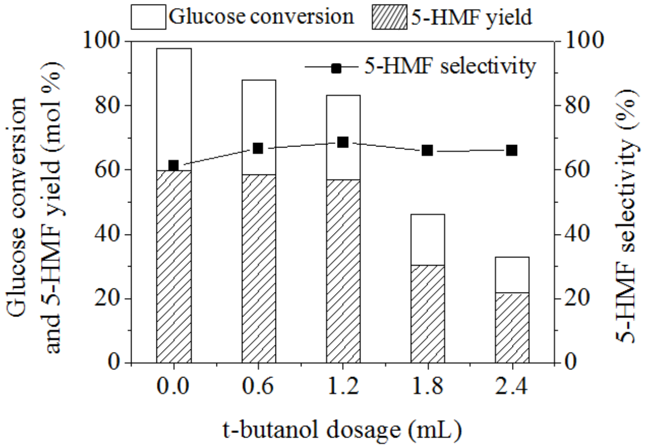


Fig. 8. Effect of *t*-butanol on 5-HMF selectivity of glucose dehydration in DMSO - [BSO_3HMIM][OTF] mixture (2/1w/w ratio; 4.5 g) at 413 K for 50 min

CONCLUSIONS

1. Compared with Cl^-, Br^-, ClO_4^-, and PF_4^- anions, sulfonates had higher catalytic activity in the dehydration of fructose. Sulfonate hydrolysates exhibited good activities in the dehydration of fructose to 5-HMF. Imidazole-based ionic liquids (ILs) had higher activity than pyridinium-based ILs.
2. [BMIM[TSO] was chosen for the detailed study of the dehydration reaction, and a 5-HMF yield of 95.6% was obtained at 353 K for 30 min. Kinetic studies showed that the reaction had a low activation energy (51.5 kJ/mol).
3. [BSO_3HMIM][OTF] dehydrated glucose with a 5-HMF yield of 59.8%. Addition of *t*-butanol into DMSO-[BSO_3HMIM][OTF] mixture improved the selectivity of 5-HMF by inhibiting polymerization reactions of glucose with 5-HMF.

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