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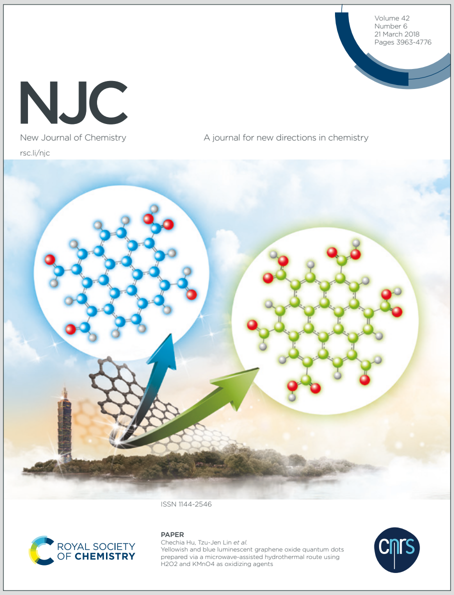

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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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Sugar dehydration to 5-hydroxymethylfurfural in mixtures of water/[Bmim]Cl catalyzed by iron sulfate

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Abstract: Ionic liquids (ILs) as an additive was employed in the selective conversion of bio-based carbohydrates to 5-hydroxymethylfurfural (HMF) in this work. The effect of adding various imidazole-based ionic liquids with different anion structures on the production of HMF from fructose was firstly investigated in aqueous media. The presence of 15 wt% of 1-butyl-3-methylimidazole chloride ([Bmim]Cl) ionic liquids in water with $Fe_2(SO_4)_3$ as the

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homogeneous catalyst provided a more effective HMF synthesis than that without [Bmim]Cl addition. The enhanced HMF yield was mainly attributed to the fact that [Bmim]Cl might play a vital role in stabilizing the HMF molecule, which could thereby suppress side reactions involving HMF (e.g., its rehydration to levulinic acid or/and polymerization to humins). NMR and FTIR analyses suggested that such stabilization effect stemmed from the interaction of [Bmim]Cl with the hydroxyl and aldehyde groups of HMF through hydrogen bond. By operation in a biphasic system (i.e., with biomass-derived THF solvent as the organic phase and the addition of NaCl salt into water for improving HMF partition), the HMF yield over $Fe_2(SO_4)_3$ catalyst in the presence of [Bmim]Cl additive could be further improved. The catalyst and ionic liquids were quite stable, which could be reused more than five cycles with a consistent activity. Similar enhancement effect of [Bmim]Cl was also demonstrated in HMF synthesis with better yields from other biomass feedstocks or derivatives (including glucose, sucrose, cellobiose, inulin and starch) in aqueous media.

Keywords: fructose; ionic liquids; 5-hydroxymethylfurfural; stabilization effect; aqueous media.

1. Introduction

Due to the rapid consumption of non-renewable fossil resources and the associated environmental pollutions, search for alternative renewable feedstocks has aroused great research attention.[1, 2] Biomass, the only abundant non-fossil carbon resource, is a good candidate for the sustainable production of liquid fuels, commodity/fine chemicals and functional materials with minimal environment effects.[3, 4] Bio-based platform compounds

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represent one key bridge for biomass valorization in such bio-refinery process,[5] where 5-hydroxymethylfurfural (HMF) is considered as one of the most important and versatile platform building blocks by the US Department of Energy.[6-8] For example, through a series of aldol-condensation reactions involving HMF some liquid alkane fuels are produced.[9] Hydrogenation and etherification of HMF lead to fuel additives like 2,5-dimethylfuran and 5-ethoxymethylfurfural.[10] Besides, HMF can be used to synthesize 2,5-furandicarboxylic acid, a promising monomer for the manufacture of bio-based polyethylene furanoate (with better mechanical strength and oxygen/CO_2 barrier properties) to replace the petroleum-based polyethylene terephthalate.[11]

In the past decades, numerous research efforts have been devoted to converting bio-based carbohydrates into HMF in various catalytic reaction systems, such as the use of catalysts (including among others mineral acid,[12, 13] metal salts[14] and solid acid catalysts like $HfO(PO_4)_2$,[15] activated carbon,[16] zeolite,[17] TiO_2,[18] Ta-W oxide[19] and novel mesoporous carbon[20]), and the use of water or other organic solvents,[21, 22] aqueous-organic biphasic solvent system[18, 23, 24] as well as sub- or supercritical systems.[25, 26] Fructose, derived from the hydrolysis of biomass (rich in the cellulosic component),[27, 28] is considered as a preferred starting feedstock for HMF synthesis since the furanic structures thereof make it easier to be converted with a higher selectivity towards HMF as compared to raw biomass. HMF synthesis from fructose has been studied by employing mineral acids or metal salts as the homogeneous acid catalyst, especially in a biphasic aqueous-organic solvent system that facilitated in-situ HMF extraction to the organic phase and thus suppressed its further degradation in aqueous reaction media.[29] Although biphasic system is efficient, the use of

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organic solvents with toxicity or high boiling points (e.g., MIBK and DMSO) is not favorable as this increases the environmental pollution risk, and leads to additional costs in the subsequent separation and purification. In this respect, bio-based organic solvent with low toxicity and boiling points (e.g., THF) represent a good alternative. In the ideal case, green and non-toxic water should be directly used as the only solvent, however, monophasic synthesis in water usually suffers from low HMF yield due to more side reaction occurrence involving HMF rehydration or polymerization or condensation.[30, 31] Therefore, more efforts are still needed in order to develop a greener and more effective solvent system for the high-yield HMF synthesis from fructose.

In recent years, ionic liquids with unique properties (e.g., greener and less toxic than common organic solvents, good chemical and thermal stability, negligible vapor pressure and nonflammability) as an attractive reaction medium for biomass transformation have attracted increased research attentions.[32-36] In particular, the dialkymidazole chloride ionic liquids have a superior dissolution ability for bio-based carbohydrates due to the formed hydrogen-bonding network between them, making it an attractive solvent for HMF synthesis.[8, 37-45] For example, Zhao and co-workers[41] firstly utilized $CrCl_2$ as catalyst and 1-ethyl-3-methylimidazolium chloride ([Emim]Cl) as solvent for fructose conversion. An HMF yield of 83% was obtained at 80 ^oC in 3 h. Later, Yong et al.[42] reported 96% yield of HMF from fructose in [Bmim]Cl ionic liquid media under catalysis of NHC-Cr (NHC=N-heterocyclic carbene) at 100 ^oC in 6 h. Qi et al.[43] also used [Bmim]Cl ionic liquid as solvent and ion-exchanged Amberlyst-15 resin as the solid catalyst for fructose dehydration to produce HMF with a yield of 78.1% in 6 h at room temperature. Furthermore,

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Moreau et al.[44] employed 1-H-methylimidazolium chloride ([Hmim]Cl) as both solvent and catalyst, and obtained 90% yield of HMF from fructose at 90 °C in 45 min. Li et al.[46] conducted the conversion of concentrated fructose (33%) to HMF under microwave irradiation, and 97% yield of HMF could be achieved in [Bmim]Cl medium without catalyst addition within 3min. Although good to excellent yields of HMF synthesized from fructose have been achieved in ionic liquid media, the essential role of ionic liquids in the reaction network and process involving fructose conversion is still not clear. Moreover, the separation of HMF from the ionic liquid solvent (e.g., via extraction in the product work-up or biphasic system operations) represents a barrier to be overcome for the practical application because of its (strong) intra-molecular interaction with HMF[47, 48] and high viscosity (that slows down significantly the mass transfer rate of HMF).[49] With regard to the HMF separation in ionic liquid, Hallett and co-workers recently proposed some different strategies, such as i) using a non-coordinating ionic liquid (e.g., [Bmim]OTf) as solvent,[50] ii) using hydrophobic methyltrioctylammonium ionic liquids with less water as media[51] and iii) in situ conversion of the formed HMF into useful furan chemicals like 2,5-diformylfuran (DFF).[52] Additionally, Wei et al.[53] studied the vacuum reactive distillation to separate HMF in ionic liquids, and obtained high isolated yield in short time but high requirements for vacuum conditions. Shi et al.[25] used supercritical CO_2 to induce a phase separation of miscible ionic liquid with acetone and thus increasing the partition coefficient, while the harsh conditions were needed. In this context, another attractive strategy is to use water with the ionic liquid additive as solvent, which could avoid the negative effect with high viscosity (as the ionic liquid-water mixture viscosity decreases exponentially with increasing water content[47]) and largely maintain the

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advantages of ionic liquids for synthesis. The dominant presence of water (as solvent) along with the ionic liquid (as additive) in the reaction solution is expected to also facilitate the HMF separation (e.g., to the extracting organic solvent). This strategy would thus benefit the development of a more economical and effective catalytic system for HMF production from biomass-derived feedstock.

Metal chlorides (e.g., $FeCl_3$) as catalyst have already been widely used in ionic liquids for the fructose or glucose conversion.[41, 54, 55] Zhou et al.[55] directly used $FeCl_3$ as catalyst to convert fructose to HMF in [Bmim]Cl medium, and achieved a high HMF yield of 90.8% under 100 ^{o}C for 4 h. Liu et al.[54] synthesized some Fe-containing ionic liquids catalysts (e.g., $[C_{16}mim]FeCl_4$) used for fructose conversion to HMF, and 92.8% yield of HMF was achieved in [Bmim]Cl medium under optimized conditions but its stability was not very well. Additionally, Zhao et al.[41] tested the performance of $FeCl_3$ in glucose conversion but worked less effective. However, there are relatively few works reported with metal sulfate catalysts. Meanwhile, as reported, the Cl^- ion of chloride salts could act as a nucleophile to facilitate the transformation of fructose,[56] which was thus likely to influence the results. In order to further investigate the performance of sulfate catalysts in ionic liquid-based medium, expand the use of metal salts in ionic liquid media and avoid the interference of chloride ion of metal chloride catalysts, conversion of fructose to HMF catalyzed by metal sulfates combined with several types of imidazole ionic liquids as additive has been studied in monophasic water and biphasic systems. Commercially available metal sulfate catalysts like $Fe_2(SO_4)_3$, that are low-cost, environmental benign, stable with good catalytic performance, have been rarely tested in bio-based carbohydrate dehydration reactions (in ionic liquid media). The effect of

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reaction temperature and time, metal sulfate catalyst type, the presence of dialkylimidazol-based ionic liquid and its dosage on the HMF yield was investigated. After adding a small ratio of [Bmim]Cl into water or NaCl-H_2O/THF biphasic system, a significant enhancement in the HMF yield over the selected $Fe_2(SO_4)_3$ catalyst was observed owing to the stabilization effect of [Bmim]Cl. The stabilization effect and mechanism were further investigated through control experiments (using HMF as the substrate), aided by NMR and FTIR analyses. The enhancement effect of [Bmim]Cl was also tested in HMF synthesis from other bio-based feedstocks (including glucose, sucrose, cellobiose, inulin and starch) in aqueous media. The recyclability of ionic liquids and catalyst was further demonstrated.

2. Experimental section

2.1. Materials and experimental methods

Fructose (99%), glucose (99%), cellobiose (98%) and inulin (97%) were obtained from Aladdin Industrial Corporation. Sucrose and starch were purchased from Tianjin Da Mao chemical reagent factory. Hydroxylmethylfurfural (HMF; 95%), levulinic acid (LA; 99%) and tetrahydrofuran (THF; 99%) were purchased from Aladdin Industrial Corporation. Ionic liquids including 1-butyl-3-methylimidazole chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium bromide ([Bmim]Br), 1-ethyl-3-methylimidazolium chloride ([Emim]Cl), 1-butyl-3-methylimidazole hydrogensulfate ([Bmim]HSO_4), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6) were purchased from Shanghai Macklin Biochemical Co., Ltd. Metal salts including $Zr(SO_4)_2$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $MgSO_4$, $NiSO_4$, $ZnSO_4$, $FeSO_4$ and NaCl were received from Aladdin Industrial

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Corporation. All the chemicals mentioned above were used directly without treatment. The stainless steel autoclave reactor (100 mL) equipped with mechanical stirrer and automatic temperature control unit was ordered from Anhui Kemi Machinery Technology Co., LTD.

A typical experimental procedure was that a mixture of 1.0 g substrate (e.g., fructose, glucose, sucrose, cellobiose, inulin or starch), 3.0 g ionic liquids (e.g., [Emim]Cl, [Bmim]Cl, [Bmim]Br, [Bmim]BF_4, [Bmim]HSO_4 or [Bmim]PF_6), 0.5 g catalyst (e.g., $Zr(SO_4)_2$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $MgSO_4$, $NiSO_4$, $ZnSO_4$ or $FeSO_4$) and 20 mL solvent (e.g., deionized water in the case of monophasic operation or 30wt% NaCl-water/THF in the case of biphasic operation) were loaded in the 100 mL stainless steel autoclave reactor with a Teflon lining. After being sealed, air inside the reactor was replaced with high purity nitrogen for at least three times to avoid the occurrence of possible oxidation reactions. Then, the reaction mixture was heated to the target temperature (120 ^{o}C - 170 ^{o}C) and maintained for a certain reaction time (the moment when the reactor was heated to the target reaction temperature was considered the starting time), after which the reactor was immersed into water (ca. 28 ^{o}C) quickly in order to quench the reaction. The reaction mixture was subsequently filtrated with the sand core funnel (G4) to collect the black solid materials (named as insoluble humins) which were washed with deionized water and then dried overnight before being weighed. The remaining liquid mixture for monophasic operation was then stored for later HPLC analysis. For biphasic operation in water-THF system, the two-phase liquid mixture was directly diluted to 50 mL with deionized water in order to make it a monophasic mixture (given miscibility of THF and water at room temperature) before further analyses (*vide infra*).

2.2. Liquid product analysis

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The quantitative analyses of liquid products were conducted using the high-performance liquid chromatograph (HPLC Waters e2695) with the Shodex SH1011 sugar column. Prior to HPLC detection, all collected liquid samples were diluted 10 times with deionized water and then filtrated with 0.22 μm filter membrane (PES). The products (glucose, fructose, HMF, LA and FA) were detected by the Waters 410 refractive index detector and Waters 2489 UV detector. The mobile phase was 5 mM sulfuric acid aqueous solution with a flow rate of 0.5 mL/min and the column temperature was maintained at 50 °C. The substrate conversion, the yields and selectivities of products, and the yield of insoluble solid humins are calculated based on the following equations:

$$\text{Substrate conversion (mol \%)} = \left(1 - \frac{\text{moles of final substrate}}{\text{moles of initial substrate}}\right) \times 100\% \qquad (1)$$

$$\text{Product yield (mol \%)} = \frac{\text{moles of carbon of product obtained}}{\text{moles of carbon of initial substrate}} \times 100\% \qquad (2)$$

$$\text{Product selectivity (\%)} = \frac{\text{yield of product obtained}}{\text{substrate conversion}} \times 100\% \qquad (3)$$

$$\text{Insoluble humin yield (wt\%)} = \frac{\text{mass of solid humins obtained}}{\text{mass of initial substrate}} \times 100\% \qquad (4)$$

2.3. Characterization with ^{1}H NMR and FTIR

The ^{1}H NMR spectra of the standard HMF and [Bmim]Cl ionic liquid samples as well as their mixtures in D_2O were recorded by liquid NMR spectrometer (400 MHz AVANCE III, Bruker, Switzerland) at 298 K with 12 μs pulse width, and a total of 32 scans were collected. The mixture samples were prepared through mixing HMF (20wt%) with [Bmim]Cl and stirring for 1.5 h at room temperature and 140 ^{o}C, respectively. The above samples were dissolved in D_2O prior to NMR testing. The wavenumber shifts of O-H stretching vibration

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and C=O stretching vibration in the HMF molecule were recorded by Fourier transformed infrared (FTIR) spectrum (Brucker TENSOR-27) with an average of 32 scans from 400 to 4000 cm^{-1} at 4 cm^{-1} resolution. The samples were prepared by the KBr pellet method. Typically, the HMF sample was firstly ground into fine particles under the infrared baking lamp, and then evenly mixed with dry KBr powder at a mass ratio of 1-2:100. Finally, the mixture above was placed into the mould that was placed on the infrared tablet press (FW-5) for 1 min to obtain a wafer disc for use in FTIR for testing. With regard to FT-IR testing of the sample treated at 140 ^{o}C, the mixture of HMF and [Bmim]Cl was first heated at 140 ^{o}C in oil bath with magnetic stirring for 1.5 h. After that, the obtained mixture was waited for FT-IR measurement. For HMF-[Bmim]Cl mixture testing, a drop of sample (liquid form about 5 mg) was dripped onto the prepared KBr wafer disc for FTIR analysis.

3. Results and discussion

3.1. Fructose conversion in water in the presence of ionic liquids

The effect of various dialkylimidazol-based ionic liquids on the fructose conversion to HMF in water over $Fe_2(SO_4)_3$ catalyst was investigated at 140 ^{o}C, as presented in Table 1. In the absence of ionic liquids, an HMF yield of 39.3% was obtained at 93.1% fructose conversion along with 8.2% LA yield in 1.5 h (entry 1). Interestingly, when adding 15wt% imidazole ionic liquids with different structures including [Emim]Cl, [Bmim]Br and [Bmim]Cl, HMF yields were obviously improved to 48.2%, 50.4% and 54.9% respectively, with the fructose conversion being almost unchanged (entries 2-4). Simultaneously, the by-product LA yields were significantly decreased to 2.9%, 3.9% and 2.1%, respectively. These results suggest that adding a small amount of imidazole ionic liquids with halogen anions was favorable for more

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selective HMF formation from fructose, by suppressing e.g., its rehydration to LA (and FA). Moreover, the addition of ionic liquids like [Bmim]BF_4 and [Bmim]PF_6 had a negative effect on improving the HMF yield in this system (entries 5 and 6). The lower or little HMF yield in [Bmim]BF_4 and [Bmim]PF_6 media was also observed in the works by Cao et al.[57] and Zhang et al.[58] while the reason for this is still unclear. Unfortunately, when using [Bmim]HSO_4 as the additive, the HMF yield sharply decreased to 15.1%, accompanied by a significant increase of the LA yield to 29.0% (entry 7). The main reason is that the strong acidic HSO_4^- in [Bmim]HSO_4 can further facilitate the rehydration of HMF to produce LA.[59, 60] All the above results indicate that dialkylimidazole-based ionic liquids with halogen anions could effectively improve the selectivity and yield towards HMF in water media while the others (e.g., [Bmim]BF_4, [Bmim]PF_6 and [Bmim]HSO_4) exhibited the negative effect.

Table 1 Effect of adding various ionic liquids on the HMF synthesis from fructose in water

Entry	Ionic liquids	Fructose conversion (%)	HMF selectivity (%)	Mole yield (%)	
				HMF	LA
1	Blank	93.1	41.9	39.3	8.2
2	[Emim]Cl	93.4	51.6	48.2	2.9
3	[Bmim]Br	92.8	54.3	50.4	3.9
4	[Bmim]Cl	93.9	59.0	54.9	2.1
5	[Bmim]BF_4	92.2	39.6	36.5	2.3
6	[Bmim]PF_6	99.1	23.4	23.2	13.7
7	[Bmim]HSO_4	99.6	15.2	15.1	29.0

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Reaction conditions: 5wt% of fructose, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 20 mL deionized water, 15wt% ionic liquid (if present), 140 ^oC, 1.5 h, nitrogen atmosphere. The fructose concentration and dosage of ionic liquids are relative to the mass of water (the same for other figures and tables hereafter).

3.2. Influence of metal sulfates with and without [Bmim]Cl

The [Bmim]Cl ILs as an additive exhibited the most enhancement of the HMF yield over $Fe_2(SO_4)_3$ catalyst (Table 1). In order to examine whether a similar yield enhancement exists over other metal sulfate catalysts, the fructose conversion in water was further studied over a series of metal sulfates in the presence and absence of [Bmim]Cl additive at 140 ^oC for 1.5 h (Fig. 1). The main products detected are HMF, LA and FA. In addition, humins were formed in most cases according to the color change of reaction solutions, possibly from the condensation or polymerization of HMF, fructose and its intermediates.[61] When comparing Figs. 1a and 1b, it is intriguing that the addition of [Bmim]Cl (15 wt%) in all cases could obviously enhance the HMF yield, though to different extent, and the fructose conversion was roughly unaffected. Among the tested metal sulfates, $Fe_2(SO_4)_3$ exhibited a relative superior HMF yield even in the absence of [Bmim]Cl, which might be closely related to the inherent catalytic activity of metal ions. As shown in previous reports, the homogeneous or heterogeneous iron-based catalysts are effective for the fructose dehydration.[62, 63] For instance, Li et al.[63] reported the synthesis of HMF over homogeneous iron-based catalyst ($FeCl_3$), and indicated that Fe^{3+} as the catalytic active specie was in favor of the fructose conversion to HMF. Similarly, Kim et al.[62] investigated the effect of heterogeneous N-heterocyclic carbine catalysts doped with different metal ions (e.g., Fe^{3+}, Fe^{2+}, Al^{3+}, Cr^{3+}

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and Sn^{4+}) on the fructose dehydration to HMF, and found that N-heterocyclic carbin-Fe(III) catalyst exhibited the optimal performance. After adding [Bmim]Cl additive, the HMF yield over $Fe_2(SO_4)_3$ was increased by far the highest by 15.6%. Therefore, $Fe_2(SO_4)_3$ is chosen as catalyst to further investigate the special role of [Bmim]Cl as additive in this reaction.

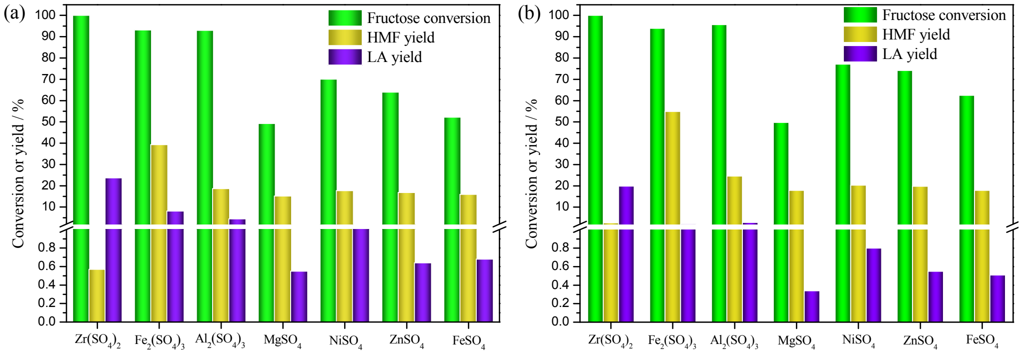

Fig. 1 Conversion of fructose to HMF over metal sulfate catalysts in aqueous media with (a) the absence of [Bmim]Cl and (b) the presence of [Bmim]Cl. Reaction conditions: 5 wt% of fructose, 0.5 g of metal sulfate catalyst, 20 mL deionized water, 15wt% [Bmim]Cl (if present), 140 °C, 1.5 h, nitrogen atmosphere.

3.3. Optimization of processing conditions for fructose conversion

3.3.1. Effect of reaction temperature. To gain insights into the influence of reaction temperature on the fructose conversion to HMF in the presence and absence of [Bmim]Cl, experiments were conducted in a temperature range from 120 to 160 °C (Table 2). The fructose conversion and HMF yield are significantly influenced by the reaction temperature. In both cases, the HMF yield increased dramatically upon increasing the temperature from 120 to ca. 140 °C, followed by its gradual decrease as the reaction temperature further increased to 160 °C. Simultaneously, the LA yield gradually increased for both cases. The decreased HMF yield at sufficiently higher temperatures was related to its accelerated

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degradation to by-products (among others LA) under acidic aqueous media.[64, 65] Therefore, high reaction temperatures not only accelerate the formation of HMF from fructose, but also lead to more side reactions involving HMF. As expected, the HMF yield in the presence of [Bmim]Cl was obviously higher than the case without [Bmim]Cl addition, while the LA yield was obviously lower. These results corroborate that [Bmim]Cl ILs added in the aqueous system did play a positive role in improving the HMF yield from fructose meanwhile posing a negative effect on the LA formation.

Table 2 Effect of reaction temperature on the fructose conversion in water with and without [Bmim]Cl addition

Entry	Temperature (^{o}C)	Fructose conversion (%)		HMF selectivity (%)		Mole yield (%)			
						HMF		LA	
		a	b	a	b	a	b	a	b
1	120	56.8	55.3	38.2	32.9	21.7	18.2	0	1.1
2	130	77.3	76.9	66.8	41.3	38.6	31.8	0.4	3.1
3	140	96.9	99.4	49.9	38.1	48.3	37.8	2.1	8.9
4	150	99.5	99.6	49.0	20.5	48.8	20.4	4.6	16.1
5	160	99.6	99.5	27.7	8.9	27.6	8.9	9.2	17.8

Reaction conditions: 5wt% of fructose, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 20 mL deionized water, 15wt% [Bmim]Cl (if present), 2.0 h, nitrogen atmosphere. [a]with [Bmim]Cl addition; [b]without [Bmim]Cl addition.

3.3.2. Effect of reaction time. Reaction time is another important factor that influences the reaction rate and conversion pathway for carbohydrates dehydration.[66] The fructose

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conversion and the yield of dehydration products and insoluble humins as a function of the reaction time were investigated under the optimized temperature of 140 ^{o}C as identified above. The fructose conversion in the aqueous system with and without adding [Bmim]Cl was found essentially the same and both achieved a full conversion when the reaction time was prolonged to 3 h (Fig. 2a). The corresponding HMF yield increased sharply within the first 1.5 h, especially for the case of adding 15wt% of [Bmim]Cl. Then, it decreased gradually, which was mainly attributed to the instability of HMF in acidic aqueous media towards further rehydration to form among others LA[67, 68] as well as polymerization to form humins.[69, 70] Notably, the decrease rate of the HMF yield in the presence of [Bmim]Cl was slower than in the absence of [Bmim]Cl (Fig. 2a). This phenomenon may be explained by the stabilizing effect of [Bmim]Cl on HMF (*vide infra*). Meanwhile, the yield of LA produced from the HMF rehydration increased with the reaction time, and was remarkably smaller in the presence of [Bmim]Cl than that without [Bmim]Cl addition (Fig. 2b). A similar trend in the insoluble humin formation was found (Fig. 2c). The relatively lower yield of insoluble humins was obtained with the addition of [Bmim]Cl, compared with the case without adding [Bmim]Cl even at prolonged reaction time. The results here demonstrate that HMF synthesized from fructose in aqueous media was somewhat stabilized by the added [Bmim]Cl, which thus decreased to some extent the formation of LA and insoluble humins from side reactions involving HMF, and significantly enhanced the HMF selectivity. A similar work with $FeCl_3$ as catalyst was conducted in ethanol-[Bmim]Cl solvent system by Zhou and co-workers,[55] they investigated the effect of ratio of ethanol to [Bmim]Cl on the conversion of fructose to furan derivates like HMF and 5-ethoxymethylfurfural (EMF), and

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revealed that a high yield of EMF could be obtained in single solvent of ethanol while the addition of [Bmim]Cl could largely suppress the etherification of HMF into EMF possibly due to its stabilization effect.

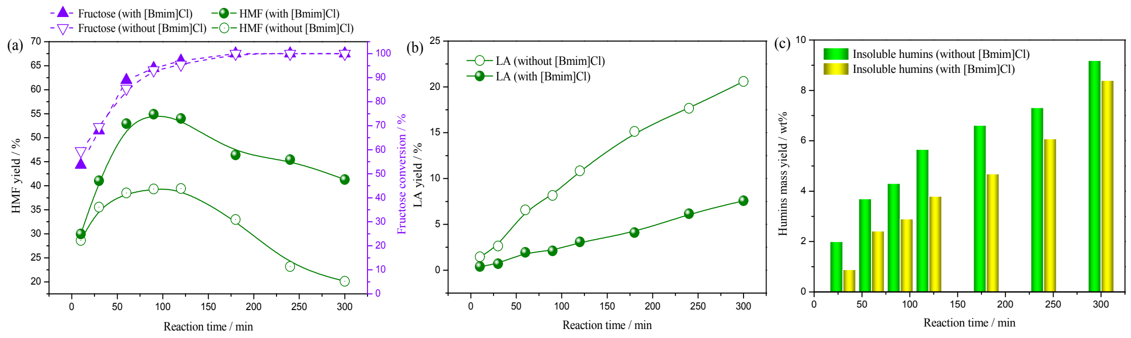

Fig. 2 Effect of reaction time on the HMF synthesis from fructose in the presence and absence of [Bmim]Cl: (a) the fructose conversion and HMF yield, (b) LA yield and (c) insoluble solid humin yield. Reaction conditions: 5wt% of fructose, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 20 mL deionized water, 15wt% [Bmim]Cl (if present), 140 ^oC, nitrogen atmosphere.

3.3.3. Effect of [Bmim]Cl dosage. To further examine the effect of adding [Bmim]Cl on enhancing and optimizing the HMF yield, the [Bmim]Cl dosage was varied in the experiments conducted at 140 ^oC and 1.5 h reaction time (Fig. 3). The fructose conversion was increased first and then slightly decreased when raising the [Bmim]Cl dosage from 5wt% to 25wt% (Fig. 3). A similar trend was observed in the HMF yield. It increased significantly from 33.1% to 51.7% as the [Bmim]Cl dosages increased from 5wt% to 15wt%. After that, further improving the dosage gave a slight decrease in the HMF yield, possibly due to the slightly mass transfer limitations with the increasing content of [Bmim]Cl causing the polymerization of HMF itself or with fructose at the high temperature conditions (e.g., 140 ^oC).[47, 71] As expected, the LA yield gradually decreased with increasing [Bmim]Cl dosage

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(Fig. 3), given less HMF being consumed in the rehydration reaction.[72] The results above further suggest that adding [Bmim]Cl (up to ca. 15wt%) in this system could stabilize HMF so that its further rehydration to LA was suppressed.

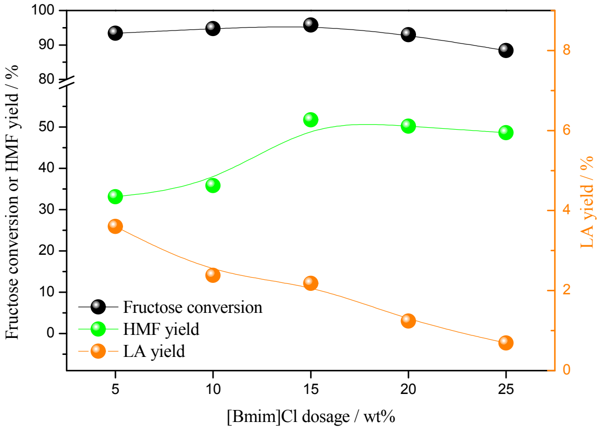

Fig. 3 Fructose conversion and yields of HMF and LA as a function of [Bmim]Cl dosages. Reaction conditions: 5wt% of fructose, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 20 mL deionized water, [Bmim]Cl (5 - 25wt%), 140 °C, 1.5 h, nitrogen atmosphere.

As reported, water had a strong effect on the yield and selectivity of HMF in ionic liquids media.[50, 73] In this work, we mainly focused on the effect of ionic liquid as an additive on the fructose conversion in the dominant solvent of water. The role of water in this system was not further considered since some related research works have been extensively discussed in ionic liquids as the dominant solvent. For example, Li et al.[73] reported a similar system composed of ionic liquid (e.g., [Bmim]Cl) as the dominant solvent and water as co-solvent for fructose dehydration with HCl catalyst, in which they detailedly discussed the effect of water content on the HMF yield, demonstrating that a low water content (below 15.4wt%) in [Bmim]Cl system exhibited a less effect on the HMF yield while a higher one (above 47.5wt%) was extremely detrimental to both reaction rate and HMF yield. Besides, Ghatta et

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al.[50] further investigated the role of water addition in non-halogenated and non-coordinating ionic liquids [Bmim]OTf media on improving HMF yield. It demonstrated that the dehydration of fructose to HMF in these non-coordinating ionic liquids solvents (e.g., [Bmim]OTf, [Bmim]BF_4 and [Bmim]PF_6) without water addition could afford a poor performance due to the lack of hydrogen bonding between fructose and solvent. Whereas, this could be successfully achieved in halogen-based ionic liquids.[74] Meanwhile, they suggested that the addition of a spot of water (e.g., 3.5%) into ionic liquids with non-coordinating anion could dramatically improve the HMF yield by regulating the acidity of catalyst and partially suppressing the side reaction involving HMF via stabilization, while an excessive amount of water could result in an obviously lower efficiency due to the deactivation of protons as catalyst in the system, such as no reaction being observed at all when using pure water as solvent.[50]

To further examine whether [Bmim]Cl has a catalytic effect in aqueous media, the fructose conversion without catalyst was performed in the presence of various dosages of [Bmim]Cl under otherwise the same reaction conditions as shown above. Fig. 4 reveals that the fructose conversion and HMF yield were much lower (being 11.9% and 6.2%, respectively) in the case without adding any amount of [Bmim]Cl additive. After adding [Bmim]Cl, both increased to some extent with the ionic liquid dosage up to ca. 10wt%. This increase is mainly ascribed to the fact that the added [Bmim]Cl is capable of slightly catalyzing the dehydration of fructose to produce HMF owing to its weak acidity stemmed from the acidic H posited on C-2 of imidazole cation[75]. However, further increasing the dosage to 25wt% led to a slight decrease in the HMF yield and fructose conversion, which

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could be also due to the negative effect with high mixture viscosity and slow mass transport therein.[47, 71] Additionally, the HMF yield obtained here in the absence of $Fe_2(SO_4)_3$ was much lower compared with the case with $Fe_2(SO_4)_3$ addition (e.g., Fig. 3), indicating that the catalytic active species in this system was mainly from the $Fe_2(SO_4)_3$ catalyst.

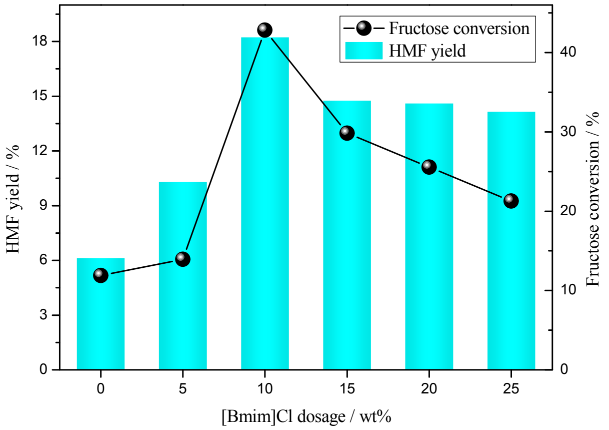

Fig. 4 Effect of [Bmim]Cl addition on the dehydration of fructose without catalyst. Reaction conditions: 5wt% of fructose, 20 mL deionized water, [Bmim]Cl (0 - 25wt%), 140 °C, 1.5 h, nitrogen atmosphere.

3.4. Stabilization effect of [Bmim]Cl on HMF

To investigate the interaction between [Bmim]Cl and HMF, several control experiments with HMF as the substrate were performed in water at 140 °C. Results in aqueous systems are obtained in four cases (Fig. 5): 1) with adding $Fe_2(SO_4)_3$ catalyst; 2) with adding both $Fe_2(SO_4)_3$ catalyst and [Bmim]Cl ILs; 3) without adding $Fe_2(SO_4)_3$ catalyst and [Bmim]Cl; and 4) with adding [Bmim]Cl. It can be seen that HMF in hydrothermal environment was unstable. The HMF conversion reached 19.1% in 1.5 h in the absence of $Fe_2(SO_4)_3$ and [Bmim]Cl while no LA was found (Fig. 5a; case 3), suggesting that the formation of byproduct (humins) is dominant. According to the investigation of humin formation by Patil

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et al.,[76, 77] the humin growth was primary through the aldol addition/condensation involving HMF (not LA or FA) and the formed humins still maintained the furan ring group of HMF. Similar humin formation mechanism was also proposed by Tsilomelekis et al.[31] Interestingly, after adding 15wt% of [Bmim]Cl additive, the HMF conversion was remarkably lowered to 2.4% under otherwise the same reaction conditions (Fig. 5a; case 4), indicating the possible interaction of [Bmim]Cl with HMF enhancing its stability. The stability of HMF in water without the presence of [Bmim]Cl was, however, easily weakened by adding $Fe_2(SO_4)_3$ catalyst, where the HMF conversion in 1.5 h was increased to 46.4% and the corresponding yield of LA (derived from the HMF rehydration) was up to 14.9% due to catalytic effect (Fig. 5a; case 1). Fortunately, when adding [Bmim]Cl additive into the reaction system, the HMF conversion dropped to 28.0% over the catalyst with the corresponding yield of LA of only 2.2% (Fig. 5a; case 2). Fig. 5b further shows that in the presence of [Bmim]Cl, the HMF conversion slightly increased from 16.6% to 33.8% over $Fe_2(SO_4)_3$ catalyst when the reaction time was extended from 10 min to 180 min (case 2). Meanwhile, the LA yield only increased from 0% to 5.0%. In contrast, the HMF conversion in the absence of [Bmim]Cl was sharply improved from 28.5% to 63.4% over the catalyst (case 1). The corresponding LA yield dramatically increased from 5.2% to 24.2%. These results strongly indicate that [Bmim]Cl present in the aqueous media could stabilize HMF, preventing it from being consumed in side reactions like the rehydration to LA to a certain degree.

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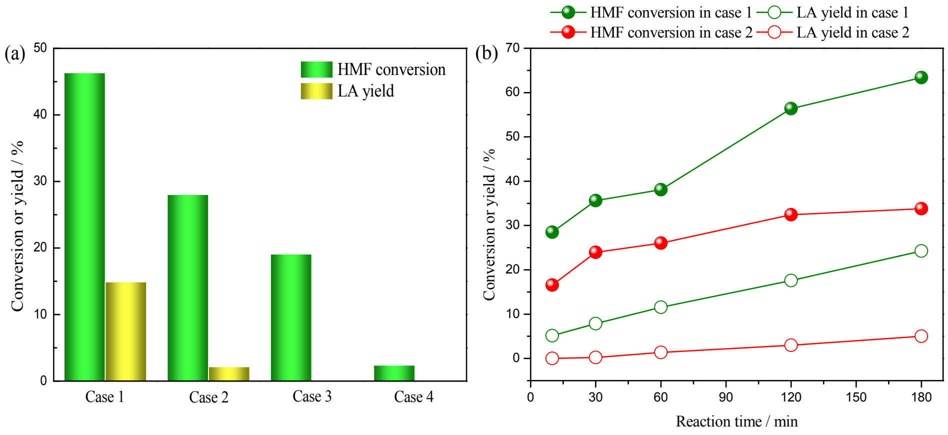

Fig. 5 Effect of [Bmim]Cl presence on the HMF conversion and LA yield in water (a) under cases 1-4 (with or without the presence of [Bmim]Cl or $Fe_2(SO_4)_3$ catalyst) and 1.5 h reaction time; (b) as a function of the reaction time in the absence (case 1) and presence (case 2) of [Bmim]Cl. Reaction conditions: 0.2 g of HMF, 0.5 g of $Fe_2(SO_4)_3$ catalyst (if present), 15wt% of [Bmim]Cl (if present), 20 mL deionized water, 140 ^oC, nitrogen atmosphere. Case 3 without adding $Fe_2(SO_4)_3$ catalyst and [Bmim]Cl; Case 4 with only adding [Bmim]Cl.

3.5. Stabilizing mechanism of [Bmim]Cl on HMF

Enlightened by the experimental results above, a hypothesis is made that HMF stabilized by [Bmim]Cl ionic liquids is primarily ascribed to the special intermolecular interactions between them.[48] To provide some evidences, FT-IR spectra of samples, including HMF as well as mixtures of HMF with [Bmim]Cl stirred for 1.5 h at room temperature or 140 ^oC, were collected (Fig. 6). The results show that all samples have the same structures and functional groups while the peak intensity is different. The two spectra of the mixtures stirred at room temperature and 140 ^oC were quite similar. The typical peaks for furan ring were also observed in all cases. It is noteworthy that the peak in the range of 3450-3410 cm^{-1}, assigned to O-H stretching vibration in the hydroxyl group of HMF, was weakened and decreased in

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wavenumber after mixing [Bmim]Cl with HMF (Fig. 6a). Additionally, the peaks at 1630 cm^{-1} representing C=O stretching vibration in the aldehyde group of HMF were observed. After mixing with [Bmim]Cl, the peak of aldehyde group of HMF shifted from 1630 cm^{-1} to 1670 cm^{-1} (Fig. 6b). These phenomena are possibly caused by the interactions between [Bmim]Cl and HMF (under both room and reaction temperatures). Wang et al.[78] investigated the FT-IR spectra of pure HMF and mixture of HMF with different amount of [Bmim][N(CN)$_2$], and also found that the O-H peak of HMF in the mixture shifted to low wavenumber with increasing the amount of ILs due to the hydrogen bond interaction while the C=O peak of HMF with the increase of [Bmim]BF$_4$ amount only slightly shifted to high wavenumber due to the weakest hydrogen bond formation ability of BF$_4^-$ anion. Moreover, Ghatta and his co-workers performed the infrared spectra of HMF in various ionic liquids to analyze the shifts of hydroxyl and carbonyl group, and revealed that the hydroxyl of HMF in [N(Me)Oct$_3$]Cl and [N(Me)Oct$_3$]Br exhibited the red shifts due to the higher hydrogen bond ability of Cl$^-$ and Br$^-$ anions, in well line with our results, while it in [N(Me)Oct$_3$][NTf$_2$] showed a slight blue shift due to a lower hydrogen bond ability of [NTf$_2$]$^-$.[51] The carbonyl of HMF in the three ionic liquids showed a slight red shift, a little different from our observation. As reported, water molecules could interact with the aldehyde to form germinal diols especially at a high water content.[79] In the present work, the formation of germinal diols might be enhanced by the addition of ionic liquids, causing an obvious peak shift of aldehyde due to a combined interaction with both water and Cl$^-$ anion[51].

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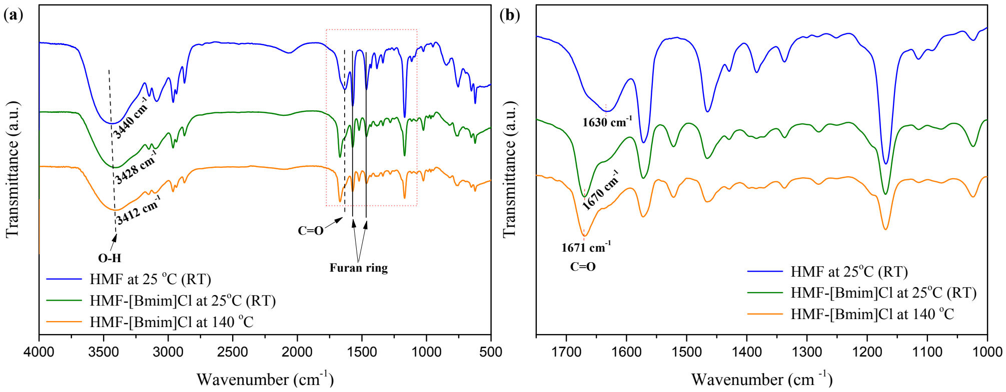

Fig. 6 FT-IR spectra of samples including HMF, mixture of HMF with [Bmim]Cl stirred at room temperature (RT) for 1.5 h and mixture of HMF with [Bmim]Cl stirred at 140 °C for 1.5 h. Fig. 6b is a partial enlargement of Fig. 6a.

To further confirm the interactions between [Bmim]Cl and HMF, ^{1}H NMR spectra of HMF and [Bmim]Cl samples as well as their mixtures were measured. As shown in Fig. 7a, the chemical shift peaks of hydrogen atom in the aldehyde and hydroxyl groups of HMF appeared at δ 9.28 ppm and δ 4.55 ppm, respectively. In the mixture of HMF and [Bmim]Cl (after being stirred at room temperature or 140 °C for 1.5 h), the corresponding chemical shift peak changed, respectively, to δ 9.44 ppm or δ 9.46 ppm for hydrogen atom in the aldehyde groups of HMF, and to δ 4.63 ppm or δ 4.64 ppm for hydroxyl groups of HMF (Figs. 7b and c). These results indicate that [Bmim]Cl interacted with the aldehyde and hydroxyl groups of HMF, which caused the increase in chemical shift of H-1 and H-5 on HMF. This interaction might lead to the formation of an HMF-[Bmim]Cl intermediate through hydrogen bond that protected the HMF molecule. Lungwitz et al.[80] demonstrated that the hydrogen bond accepting ability of 1-alkyl-3-methylimidazolium-based ionic liquids is mainly determined by anions. Moreover, Singh and Kumar[81] suggested that the Cl^- anion in [Bmim]Cl, with strong electronegativity, is a strong hydrogen bond acceptor. The Cl^- anion could thus bind with the

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hydrogen atom of aldehyde and hydroxyl groups of HMF through -Cl···H- hydrogen bond. The larger the chemical shifts changed for hydrogen atom, the stronger the hydrogen bond formed.[82] The results obtained by ^{1}H NMR analysis are in well accordance with FTIR analysis.

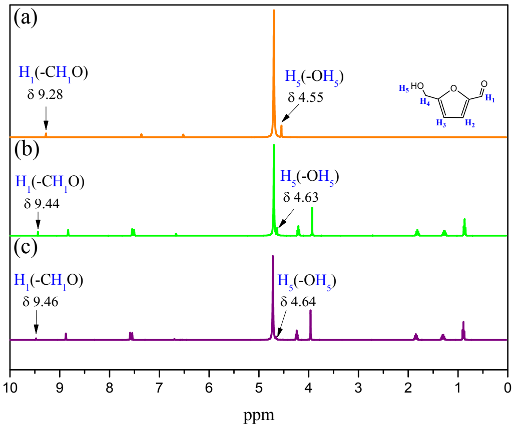

Fig. 7 Typical ^{1}H NMR spectra for samples in D_2O: (a) HMF, (b) mixture of HMF and [Bmim]Cl stirred at room temperature for 1.5 h and (c) mixture of HMF and [Bmim]Cl stirred at 140 °C for 1.5 h.

In addition, the chemical shift of H-2 atom posited on C-2 atom of imidazole cations in [Bmim]Cl was found at δ 8.88 ppm (Fig. 8a). However, when [Bmim]Cl was mixed with HMF, and stirred at room temperature and 140 °C for 1.5 h, its chemical shifts changed to δ 8.91 ppm and δ 8.93 ppm, respectively (Figs. 8b and c), suggesting the existence of weak hydrogen-bonding force that has affected the H-2 atom of imidazole cations. The H-2 atom is more active than H-4 or H-5 one owing to its location between two electronegative nitrogen atoms.[82] The hydrogen-bonding donating ability of imidazole cations is primarily determined by H-2 atom at C-2 position.[75] As known, the carbonyl group in HMF has a great polarity so that the oxygen atom with a partial negative charge displays electronegative. Similarly, the oxygen atom in the hydroxyl group of HMF also possesses a pair of free electrons.

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Consequently, the H-2 atom, as a hydrogen-bonding donor, may interact with oxygen atoms in the aldehyde and hydroxyl groups of HMF via hydrogen bond.

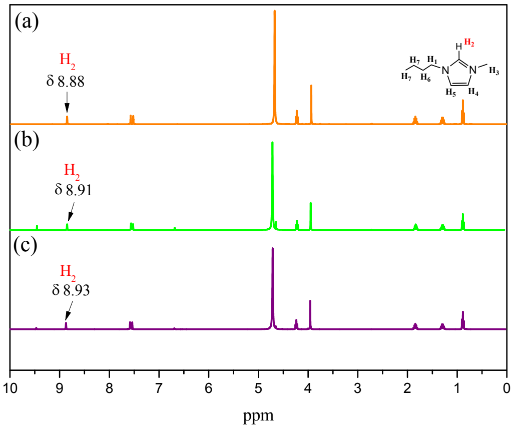

Fig. 8 Typical ^{1}H NMR spectra for samples in D_2O: (a) [Bmim]Cl ILs, (b) mixture of HMF and [Bmim]Cl stirred at room temperature for 1.5 h and (c) mixture of HMF and [Bmim]Cl stirred at 140 °C for 1.5 h.

Some extra ^{1}H NMR characterizations were also conducted for samples of furfuryl alcohol and furfural that possess similar groups to HMF. According to ^{1}H NMR analysis, the same results as that of HMF could be obtained from the case of furfuryl alcohol and furfural as presented in Figs. 9 and 10. After mixing with [Bmim]Cl, the chemical shifts of hydrogen in the aldehyde group of furfural and hydroxyl group of furfuryl alcohol both became larger, and that of H-2 in imidazole cations increased as well. These results provide some additional support for the existence of interactions of [Bmim]Cl with the aldehyde and hydroxyl group of HMF.

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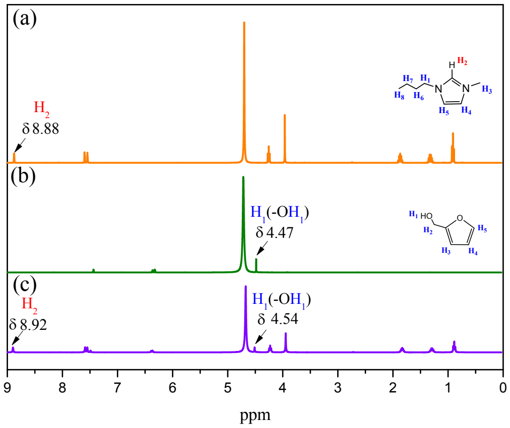

Fig. 9 Typical ^{1}H NMR spectra for samples in D_2O: (a) [Bmim]Cl, (b) furfuryl alcohol and (c) the mixture of furfuryl alcohol and [Bmim]Cl stirred at room temperature for 1.5h.

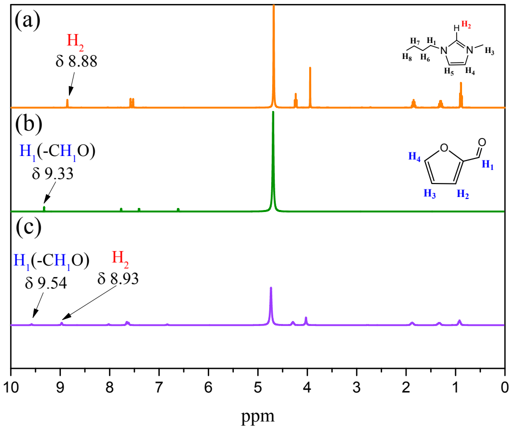

Fig. 10 Typical ^{1}H NMR spectra for samples in D_2O: (a) [Bmim]Cl ILs, (b) furfural and (c) the mixture of furfural and [Bmim]Cl stirred at room temperature for 1.5 h.

Based on the experimental data and characterization results from ^{1}H NMR and FTIR, a plausible mechanism for the stabilization effect of [Bmim]Cl on HMF is proposed (Scheme 1). Generally, the consumption of HMF in acid-catalyzed conversion of carbohydrates mainly undergoes two patterns in conventional reaction media.[83] One is the rehydration of HMF with two water molecules to form LA and FA, the other is the self- and cross-polymerization of HMF with sugars and/or its intermediates to produce the soluble or insoluble humins. Yang et

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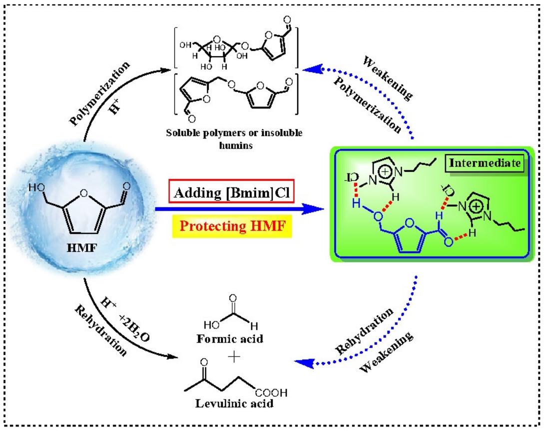
al.[84] demonstrated that the reaction process for fructose conversion to LA involved the formation of HMF, of which the hydroxyl and aldehyde groups were facilely protonated through the attack of acidic protons H^+ in the aqueous solution, and then converted to the activated intermediates. These activated intermediates might be further transformed into LA as well as polymerized with HMF or/and fructose to produce polymers such as humins because of the parallel relationship between the rehydration and polymerization reactions.[84] Besides, Galkin et al.[85] studied the process of HMF aging in detail, revealed that HMF molecules in solution in the presence of acidic impurities could be further degraded to form the dimers and oligomers through the intermolecular etherification involving the active hydroxyl groups of HMF.



Scheme 1 Possible mechanism for the stabilizing effect of [Bmim]Cl on HMF.

When a certain amount of [Bmim]Cl was added to the acidic aqueous reaction system, the hydrogen and oxygen atoms in the hydroxyl and aldehyde groups of HMF could form the hydrogen bond via the respective interaction with Cl^- anions of [Bmim]Cl and H-2 atoms on imidazole cations. Such interactions between [Bmim]Cl and HMF might lead to the formation of the [Bmim]Cl-HMF intermediate (Scheme 1). Then, the hydroxyl and aldehyde groups of HMF were protected by [Bmim]Cl so as to hinder the attack from acidic protons

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H^+, subsequently stabilizing the HMF molecule. As a result, the rehydration reaction of HMF could be effectively suppressed even though lots of water existed in the reaction system (as seen in Figs. 2b and 5). Similarly, the humin production from side reactions involving HMF was also suppressed to some extent (Fig. 2c). The results here are in line with the work of Guo et al.[86] who suggested that $[C_4mim]HSO_4$ ionic liquids could stabilize HMF through hydrogen bonding.

3.6. Effect of [Bmim]Cl on other carbohydrate conversion

Other carbohydrates (including glucose, disaccharide and polysaccharide) have been also studied as feedstock for the HMF synthesis over $Fe_2(SO_4)_3$ catalyst in water with the presence of [Bmim]Cl to investigate whether a similar yield promotion effect exists.

3.6.1. Effect on glucose conversion. Fig. 11 depicts the product distribution for glucose conversion with increasing reaction time in the presence and absence of [Bmim]Cl in aqueous media. A higher reaction temperature of 170 ^oC is used to account for the lower reactivity of glucose than fructose towards HMF. With increasing reaction time, the HMF yield reached a clear maximum while that of the by-product LA continued to rise in both cases. The HMF yield in the case with [Bmim]Cl addition appeared always higher than that without [Bmim]Cl while the LA yield was lower in the former case due to the stabilization effect of [Bmim]Cl on HMF. The best yield of HMF in the presence of [Bmim]Cl was 27.8% within 30 min. These yield trends were similar to the cases with fructose as the substrate (Fig. 2). In addition, it seems that the glucose conversion with [Bmim]Cl addition was slightly higher than that without [Bmim]Cl. The yield of fructose isomerized from glucose in the presence of [Bmim]Cl was found negligibly small while it was present (though in a small

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amount) without [Bmim]Cl addition during the initial 140 min. These phenomena possibly suggest that [Bmim]Cl could promote the conversion of glucose and (subsequently the formed) fructose to some extent. Lai et al.[87] conducted a DFT calculation on the fructose dehydration in [Bmim]Cl to explore the energy profile of reaction. They found that the [Bmim]Cl media could turn the fructose dehydration from a thermodynamically unfavorable into a thermodynamically favorable reaction, thus implying that [Bmim]Cl is likely to play a role in activating fructose to facilitate its conversion.

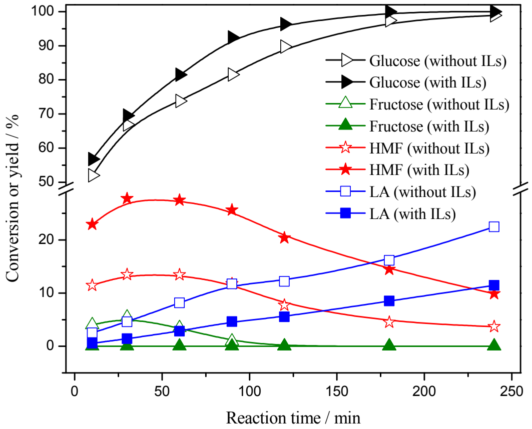

Fig. 11 Glucose conversion as a function of the reaction time in the presence or absence of [Bmim]Cl in water. Reaction conditions: 5wt% of glucose, 0.5 g of $Fe_2(SO_4)_3$, 15wt% [Bmim]Cl (if present), 20 mL deionized water, 170 ^oC, nitrogen atmosphere.

3.6.2. Effect on disaccharide and polysaccharide conversion. Due to the positive effect of [Bmim]Cl as an additive on the fructose and glucose conversion towards HMF, the HMF synthesis from more abundant carbohydrates (including sucrose, cellobiose, inulin and starch) were studied in aqueous media under similar reaction conditions in the presence and absence of [Bmim]Cl. It is seen from Fig. 12 that a similar promotion of the HMF yield by [Bmim]Cl did exist for all biomass-derived C6 carbohydrates investigated as a result of the stabilization effect of [Bmim]Cl on HMF. Although the HMF yield obtained from glucose,

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disaccharides and polysaccharides was not outstanding given that $Fe_2(SO_4)_3$ might not be the best catalyst for different carbohydrates, the proof-of-principle results here highlight the promising strategy of using [Bmim]Cl as an additive for enhanced HMF selectivity and yield.

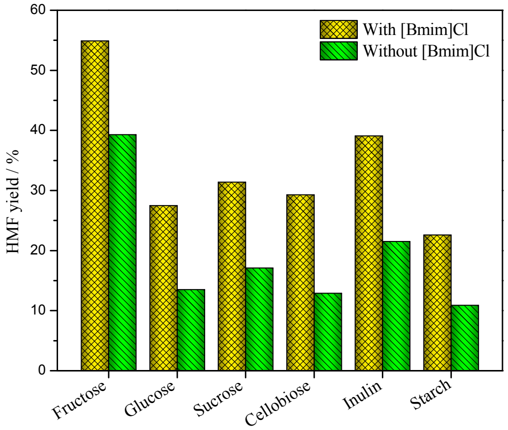

Fig. 12 Conversion of various biomass carbohydrates in the presence and absence of [Bmim]Cl in water. Reaction conditions: 5wt% of substrates, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 20 mL deionized water, 15wt% of [Bmim]Cl (if present), nitrogen atmosphere. Fructose was reacted at 140 ^{o}C for 1.5 h. Glucose, cellobiose and starch were reacted at 170 ^{o}C for 1.0 h. Sucrose was reacted at 150 ^{o}C for 1.5 h. Inulin was reacted at 150 ^{o}C for 2.0 h.

Based on all the above discussion and analysis, the catalytic reaction network for bio-based carbohydrate conversion to HMF in water in the presence and absence of [Bmim]Cl additive is illustrated in Scheme 2. HMF (synthesized from biomass-based feedstocks or derivatives) in conventional water system can be facilely consumed through side reactions involving HMF (e.g., HMF rehydration to LA and polymerization to form humins) under catalysis of acid catalysts. However, when adding a small ratio of [Bmim]Cl additive into the water system, the rehydration and polymerization reactions can be effectively suppressed to some extent due to the stabilization effect of [Bmim]Cl, leading to enhanced HMF yield and selectivity.

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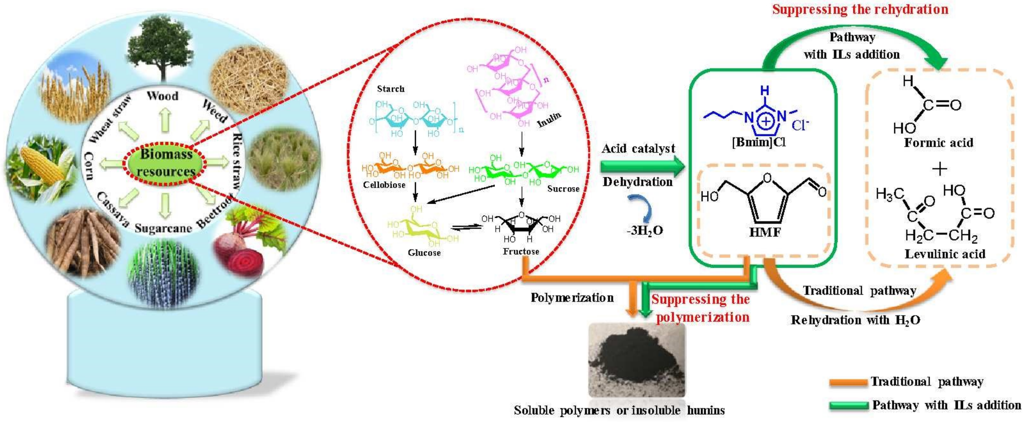

Scheme 2 Catalytic reaction route for the conversion of carbohydrates into HMF with and without [Bmim]Cl addition in aqueous media.

3.7. Stability of catalyst and [Bmim]Cl

The stability of catalyst and ionic liquids is of great importance for the technical and economic aspects of practical applications. Here, the recyclability of $Fe_2(SO_4)_3$ catalyst and [Bmim]Cl ionic liquid additive was tested in the fructose conversion to HMF with water as solvent. After each cycle, the reaction mixture was adequately extracted by ethyl acetate to remove the HMF product. Then, the remaining reaction mixture was dried in a vacuum oven at 60 °C overnight to remove the residual ethyl acetate and water. Finally, the recovered mixtures containing the used $Fe_2(SO_4)_3$ and [Bmim]Cl or/and the residual humins were directly employed in the next cycle after adding fresh fructose. Note that under the current reaction conditions (140 °C), the $Fe_2(SO_4)_3$ catalyst (0.5 g in 20 mL water) seemed to be well dissolved and thus functioned as a homogeneous catalyst. The reusability of catalyst and ionic liquids was tested for five consecutive cycles (Fig. 13). The fructose conversion and HMF yield exhibited a negligible decrease after five consecutive runs, possibly due to the slight loss of catalyst during the extraction process. Thus, the performance of $Fe_2(SO_4)_3$ and

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[Bmim]Cl is considered stable for converting fructose into HMF in water, which provides a new strategy for the utilization of ionic liquids in the transformation of biomass resources to value-added chemicals.

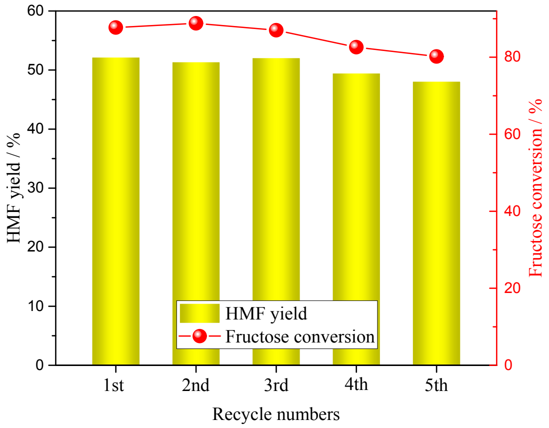

Fig. 13 Recyclability of $Fe_2(SO_4)_3$ catalyst and [Bmim]Cl ionic liquids for converting fructose to HMF in water. Reaction conditions: 5wt% of fructose, 0.5 g of $Fe_2(SO_4)_3$ catalyst, 15wt% of [Bmim]Cl, 20 mL deionized water, 140 °C, 1.5 h, nitrogen atmosphere.

3.8. Promotion effect of [Bmim]Cl in biphasic system

As known, the biphasic system is recognized as a common and effective solvent system for enhancing the HMF synthesis from bio-based carbohydrates.[88] To test the promotion effect of [Bmim]Cl additive on the HMF yield in biphasic system, the conversion of fructose to HMF over $Fe_2(SO_4)_3$ catalyst in the presence and absence of [Bmim]Cl was conducted in NaCl-H_2O/THF biphasic system, based on the further considerations that THF is a renewable bio-based solvent[89] with a low boiling point (60 °C) and the addition of salts (e.g., NaCl) in water further enhances the partition of HMF towards the organic phase. It can be seen from Table 3 that an HMF yield of 39.3% was obtained in monophasic aqueous media over $Fe_2(SO_4)_3$ catalyst at 140 °C in 90 min in the absence of [Bmim]Cl and NaCl (entry 1), while it could be improved to 54.9% in the presence of [Bmim]Cl (entry 2). Under otherwise the

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same reaction conditions, the biphasic system operation (at a water/THF volume ratio of 1:1) led to a better HMF yield, being 44.7% in the absence of [Bmim]Cl and NaCl (entry 3) and 58.2% with [Bmim]Cl addition (entry 4). This indicates that the additional extraction of HMF into THF improved the HMF yield to some extent. And more importantly, the [Bmim]Cl additive plays a positive role in somewhat significantly enhancing the HMF yield in biphasic system as well. A further increase of the HMF yield in biphasic system could be realized via the addition of NaCl in water (entry 5) combined with the increase of the organic to aqueous volume ratio (entries 6-8), in order to improve the HMF extraction. At a water/THF volume ratio of 1:3, an HMF yield of 65.8% was found when both [Bmim]Cl and NaCl were present in the system (entry 7). After that, a further increase of the water/THF volume ratio seems not very beneficial since the HMF yield was almost unchanged (entry 8), with the additional consideration that the excessive use of organic solvents would increase the cost in the downstream product work-up and solvent recovery.

The above results demonstrate that the addition of [Bmim]Cl into biphasic system is a useful strategy for further enhancing the HMF yield. Besides, it seems that the stabilization effect of [Bmim]Cl on HMF worked properly in biphasic system. In other words, the intramolecular interaction [Bmim]Cl on HMF seems not so strong that the extraction of HMF to the organic phase is hindered, which can thus facilitate the HMF separation and the recycling of ILs as well. It is envisaged that the current strategy using additives of ILs in monophasic water or biphasic solvent systems also holds for (homogeneous or heterogeneous) catalysts that are more effective for HMF synthesis from among other fructose, which would lead to even further promising results.

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Table 3 Dehydration of fructose to HMF in monophasic water or water/THF biphasic system

Entry	Volume of water (mL)	Volume of THF (mL)	Volume ratio of water to THF (-)	Fructose conversion (%)	Mole yield (%)	
					HMF	LA
1	20	0	-	93.1	39.3	8.2
2[a]	20	0	-	93.9	54.9	2.1
3	10	10	1:1	97.5	44.7	1.7
4[a]	10	10	1:1	98.1	58.2	0.4
5[b]	10	10	1:1	98.5	61.5	0.1
6[b]	10	20	1:2	98.3	64.6	0.1
7[b]	10	30	1:3	97.8	65.8	0
8[b]	10	40	1:4	98.0	65.6	0

Reaction conditions: 5wt% of fructose, $Fe_2(SO_4)_3$ catalyst (0.5 g for the case of 20 mL water (entries 1-2) and 0.25 g for the case of 10 mL water (entries 3-8)), 15wt% of [Bmim]Cl (if present), 30wt% NaCl (if present), 140 ^oC, 1.5 h, nitrogen atmosphere. The fructose concentration, dosage of ionic liquids and NaCl are relative to the mass of water.

[a] with adding [Bmim]Cl.

[b] with adding [Bmim]Cl and NaCl.

4. Conclusions

A sustainable and feasible catalytic system was developed for the transformation of carbohydrates into HMF with ionic liquids as an additive in aqueous media. Adding a small

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ratio of [Bmim]Cl into the reaction system was found effective for promoting the HMF yield. A best HMF yield of 54.9% in water was achieved at 140 ^oC in 90 min with [Bmim]Cl addition, compared with 39.3% HMF yield in the absence of [Bmim]Cl. The positive role of [Bmim]Cl additive was primarily ascribed to its stabilizing effect on HMF. As revealed by FTIR and ^1H NMR characterization, the possible mechanism is that [Bmim]Cl could interact with HMF through hydrogen bond to form the [Bmim]Cl-HMF intermediate. This intermediate was capable of protecting the hydroxyl and aldehyde groups in HMF from the attack of acidic protons so as to stabilize HMF molecules, effectively suppressing the rehydration and polymerization reactions involving HMF. Similar enhancement effect of [Bmim]Cl was also demonstrated in HMF synthesis with better yields from other biomass feedstocks or derivatives (e.g., glucose, sucrose, cellobiose, inulin and starch) in aqueous media. The catalyst and ionic liquids still retained a stable activity after five consecutive cycles. The HMF yield in the presence of [Bmim]Cl could be further improved to 65.8% at 140 ^oC within 90 min via operation in biphasic NaCl-H_2O/THF system. The current strategy using additives of ILs in monophasic water or biphasic solvent systems also holds for (homogeneous or heterogeneous) catalysts that are more effective for HMF synthesis from among others fructose, which would lead to even further promising results. This work provides a new strategy for the utilization of ionic liquids in the transformation of biomass resources to value-added chemicals.

Declaration of competing interest

There are no conflicts of interest to declare.

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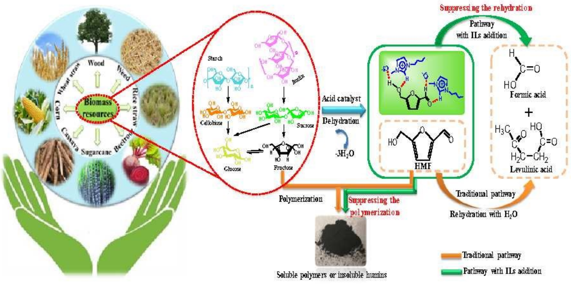
Graphical abstract



Stabilization effect of [Bmim]Cl on HMF is demonstrated, which can suppress the rehydration and polymerization side-reactions and enhance HMF yield.