Catalysis Communications 24 (2012) 11–15

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Dual catalytic function of 1,3-dialkylimidzolium halide ionic liquid on the dehydration of fructose to 5-hydroxymethylfurfural

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ARTICLE INFO

Article history:
Received 9 November 2011
Received in revised form 8 February 2012
Accepted 1 March 2012
Available online 9 March 2012

Keywords:
Fructose
Dehydration
HMF
Alkylimidazolium-based ionic liquid
Halide

ABSTRACT

In the fructose dehydration to 5-hydroxymethylfurfural (HMF) in dimethyl sulfoxide, the catalytic function of 1,3-dialkylimidazolium-based ionic liquids with different counter-anions was investigated. It was found that the effects of alkyl chain length and additional alkyl group in Cl-containing ionic liquids were negligible whereas the activity of 1-butyl-3-methylimidazolium-based ionic liquids was considerably changed by varying the anion (particularly, halide ions). The latter finding was confirmed by the control experiment result that the addition of KBr or $Ca(CH_3COO)_2$ dramatically tuned the catalytic activity of 1-butyl-3-methylimidazolium chloride. From these results and the proposed reaction pathway, it was consequently believed that 1,3-dialkylimidazolium halide contained the dual catalytic function to act as both Brönsted acid and nucleophile for the fructose dehydration to HMF.

1. Introduction

In order to reduce the dependence of fossil fuels as well as to limit global warming caused by emission of greenhouse gasses, it is worthwhile developing highly energy-efficient conversion of cellulosic biomass into renewable liquid fuels and chemicals [1–3]. Among a variety of biomass-derived chemicals, 5-hydroxymethylfurfural (HMF) is a key intermediate to produce high energy-content fuels (e.g., 2,5-dimethylfuran) [4] and chemicals (e.g., 2,5-furandicarboxylic acid as a replacemnt of terephthalic, isophthalic and adipic acids) [5]. Thus, a great deal of attention has been paid to the dehydration of fructose using efficient catalytic systems coupled with a downstream separation process [6–9].

Since the dehydration reaction proceeds under an acidic condition, common mineral acids (H_2SO_4, H_3PO_4 and HCl) and solid acids (ion-exchage resins, sulfated zirconia, etc.) are used in many previous studies [6]. In recent years, various ionic liquids (ILs) have been applied for the dehydration of sugars, where ILs are utilized as a small amount of catalyst and/or a reaction medium [10–16]. Furthermore, the report of Zhang and coworkers [17] stimulated numerous studies to address ILs' potential for the production of HMF, and also opened the attempt to search for new solvents that can replace ILs due to their high cost. As an example, Binder and Raines [16] reported that *N*,*N*-dimethylacetamide (DMA) containing LiCl (DMA–LiCl) was as effective as 1-ethyl-3-methylimidazolium chloride for HMF synthesis.

Taking a glance at recent results regarding the conversion of fructose to HMF, we wondered the detailed reaction pathway on the fructose-to-HMF conversion using imidazolim-based ILs as a catalyst. As an acidic contribution to the reaction, the proton in imidazolium cations has a well-known Brönsted acidity. Nevertheless, several ILs with more and/or higher acidic characters have been developed in order to increase the reaction rate; for example, Moreau et al. [18] reported that 1-H-3-methylimidazolium chloride produced HMF in a yield of 92% within 15–45 min. On the other hand, previous studies were also conducted to vary ILs' anionic counterpart, where its nuclephilicity was adjusted or additional acidity was introduced. In the report by Binder and Raines [16], the effect of halide ions on the synthesis of HMF from fructose was intensively investigated with H_2SO_4 and imidazolum-based ILs being the catalyst and the additive, respectively. Despite these abundant results, alkylimidzolium-based ionic liquids may have intrinsic dehydration activities. In other words, ILs' constituents, cation and anion, may have each specific contribution to the fructose dehydration reaction.

Thus, the present work has been focused on revealing the catalytic capability of imidazolium-based ionic liquids on the dehydration of fructose to HMF. For comparison, Nafion NR50, acetic acid and $CaCl_2$ were used as a catalyst. Then, the effect of chloride-containing cations with different hydrocarbon substituents attached to the imidazolium ring was investigated for the reaction. In addition, the effect of the anion of imidazolium-based ILs was determined with Cl^-, Br^-, BF_4^-, PF_6^-, $CH_3SO_4^-$ and acetate (OAc^-). To confirm the anion's effect, the

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doi:10.1016/j.catcom.2012.03.005

control experiment was conducted by adding several promoters or inhibitors to the reaction mixture containing an imidazolium-based chloride ionic liquid. From these results, the reaction network was described on the fructose dehydration and a discussion was formulated for the roles of the cation and anion of 1,3-dialkylimidzolium halide.

2. Experimental

2.1. Materials

Fructose (Sigma, ≥99%), dimethyl sulfoxide (DMSO, Junsei, ≥99.89%, water max. 0.2%), Nafion NR50 (Wako), acetic acid (Yakuri, 99.7%), $CaCl_2$ (Junsei, ≥95.0%), and $Ca(CH_3COO)_2 \cdot xH_2O$ (Aldrich, 99%) were used without purification.

1-butyl-3-methylimidazolium chloride (C_4mimCl, >98%), 1-butyl-3-methylimidazolium bromide (C_4mimBr, >98%), 1-butyl-3-methylimidazolium methylsulfate ($C_4mimCH_3SO_4$, >99%), 1-butyl-3-methylimidazolium acetate (C_4mimOAc, >99%), 1-hexyl-3-methylimidazolium chloride (C_6mimCl, >99%), 1-hexyl-2,3-dimethylimidazolium chloride (C_6mmimCl, >99%), and 1-butyl-2,3-dimethylimidazolium chloride (C_4mmimCl, >98%), 1-octyl-3-methylimidazolium chloride (C_8mimCl, >98%), and 1-octyl-2,3-dimethylimidazolium chloride (C_8mmimCl, >98%) were supplied by C-TRI (South Korea). KBr (≥99%), 1-butyl-3-methylimidazolium tetrafluoroborate (C_4mimBF_4, ≥98.5%), and 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6, ≥98.5%) were purchased from Sigma-Aldrich.

2.2. Activity test

Prior to the reaction, all ionic liquids were pretreated under vacuum at 105 °C for 24 h. In a typical experiment, a pre-dried ionic liquid was added to the fructose solution in DMSO (2 mL), where the fructose concentration was 2.5 wt.%. The reaction was initiated by immersing the glass reactor of 10 mL in oil bath pre-heated at 80 °C (t = 0). It took less than 10 min to reach the reaction temperature. In order for the temperature of whole system to remain constant, the thermo oil and the reactant solution were stirred using magnetic bars in the oil bath and glass reactors, respectively. Furthermore, since the experiments were repeated more than three times for reproducibility, the average of these data was presented in this work. The reaction temperature of 80 °C was selected, because DMSO acts as the catalyst for the dehydration of fructose to 5-hydroxymethylfurfural at 150 °C through formation of a key intermediate, (4R, 5R)-4-hydroxy-5-hydroxymethyl-4,5-dihydrofuran-2-carbaldehyde [19]. In the preliminary blank test with fructose and DMSO, only 13% of HMF yield was observed at 80 °C for 3 h.

In several control experiments for confirming the effect of ILs' anions, $Ca(CH_3COO)_2$, KBr, CH_3COOH or Nafion NR50, whose amount was calculated and weighed beforehand, was added into the reaction mixture at the reaction time of 1 h.

After termination of the reaction, the product solution was quenched in ice water, filtered and finally analyzed by a Perkin Elmer HPLC equipped with RI detector and Bio-Rad HPX-87 C column with 0.6 mL/min of distilled water at 80 °C. Due to the formation of a few byproducts, the quantitative amounts of fructose and HMF (mol) were measured for quantification. Because 1 mole fructose is converted into 1 mole HMF, the maximum amount of HMF generated is equal to the amount of initial fructose. Thus, the conversion of fructose and HMF yield were calculated as follows:

$$Fructose\ \ conversion(\%) = \frac{Fructose\,consumed(mol)}{Initial\ fructose(mol)} \times 100$$

$$HMF\ \ yield(\%) = \frac{HMF\,produced(mol)}{Initial\ fructose(mol)} \times 100$$

3. Results and discussion

3.1. Catalytic activity of imidazolium-based ionic liquids

First of all, the catalytic activity of C_4mimCl was compared with those of Nafion NR50, CH_3COOH and $CaCl_2$ on the dehydration of fructose into HMF (Table 1). Among the catalysts, Nafion NR50 showed the highest catalytic performance, where the HMF yield approached ca. 80% at the reaction time of 5 h. The catalyst, C_4mimCl, also converted fructose into HMF at the considerable yield of 56%. However, acetic acid was believed to have a negligible activity, because the HMF yield was very similar to that obtained in the blank test. On the other hand, it should be noted that the activity of $CaCl_2$ was slightly lower than that of C_4mimCl, but higher about two-fold than that of acetic acid. This suggests that the chloride ion acts as the catalyst for the conversion of fructose into HMF, which is in agreement with the results of Binder and Raines [16]. From the above results, it was assumed that both C_4mim^+ and Cl^- may be responsible for the fructose-to-HMF conversion.

As a first assessment to address the intrinsic activity of imidazolium-based ILs, the effects of alkyl chain length and additional alkyl group attached to the imidazolium ring were investigated. Since imidazolium cations with more hydrophobic characters exhibit a weaker association with the chloride ion [20], they would be expected to have a positive effective charge of H atom on the C_2 position (i.e., C(2)–H) of imidazolim ring and, in turn, become more active. Thus, 1-*R*-3-methylimidazolium chloride and 1-*R*-2,3-dimethylimidazolium chloride, where *R* represents butyl (C_4), hexyl (C_6) and octyl (C_8), were applied for the dehydration of fructose. As clearly shown in Fig. 1, the activities of all the Cl-containing ionic liquids were very similar in terms of the fructose conversion as well as HMF yield whose trends were sigmoid due to an erroneous zero time caused by a temperature difference between the reaction mixture and oil bath. Therefore, the length of the alkyl chain and the additional alkyl group in imidazolium-based ionic liquids did not afford any noticeable improvement in the fructose dehydration. This is related with the pKa values of alkylimidazolium chloride ionic liquids in DMSO, which will be explained later.

Next, the anion could be supposed to alter the ability of imidazolium cations acting as an acid catalyst and take parts in the dehydration reaction as a neucleophile. The activities of ionic liquids with various counter-anions associated with the C_4mim cation were thus investigated in order to rationalize the above supposition. Fig. 2 depicts the fructose conversion, HMF yield in a unit of % and mol/mol whose latter is equal to the amount of HMF produced per that of ionic liquid (C_4mimCl, C_4mimBr, C_4mimBF_4, C_4mimPF_6, $C_4mimCH_3SO_4$ or C_4mimOAc) added to the reaction mixture as a function of the reaction time. As a result, the anion significantly affected the catalytic activity of C_4mim-based ionic liquids. In comparison with C_4mimCl (HMF productivity = 3.1 mol/mol·h at 2 h), C_4mimBr in

Table 1
Catalytic activities of C_4mimCl, Nafion NR50, CH_3COOH and $CaCl_2$ for the dehydration of fructose.[a]

	Reaction time (h)	Fructose conversion (%)	HMF yield (%)	HMF/catalyst (mol/mol)
C_4mimCl	2	70	31	6.3
	5	97	56	11
Nafion NR50	2	76	57	10
	5	95	79	14
CH_3COOH	2	53	6.6	1.3
	5	74	29	5.7
$CaCl_2$	2	57	13	2.7
	5	95	55	11

[a] Reaction condition: fructose (50 mg), catalyst/fructose (0.05 mol/mol;), DMSO (2 mL), 353 K. In the case of Nafion NR50 having the ion exchange capacity of 0.8 meq/g, the weight of catalyst added was 20 mg.

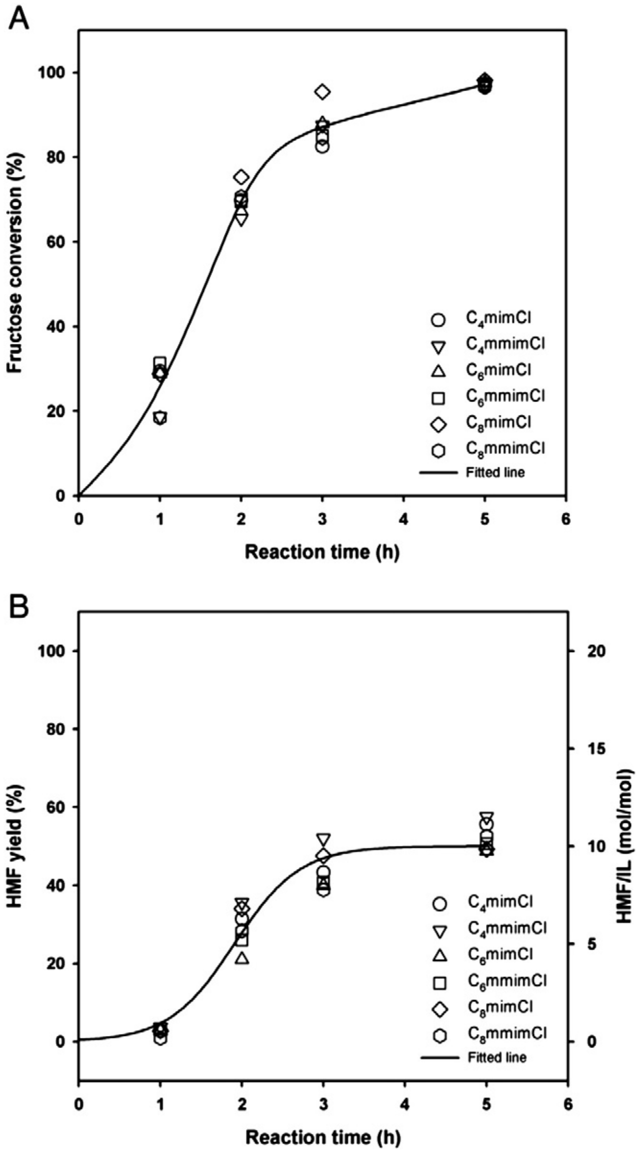

Fig. 1. Effect of alkyl chains attached to an imidazolium ring of Cl-containing ionic liquids for the fructose dehydration under the same condition as presented in Table 1: A) fructose conversion and B) HMF yield.

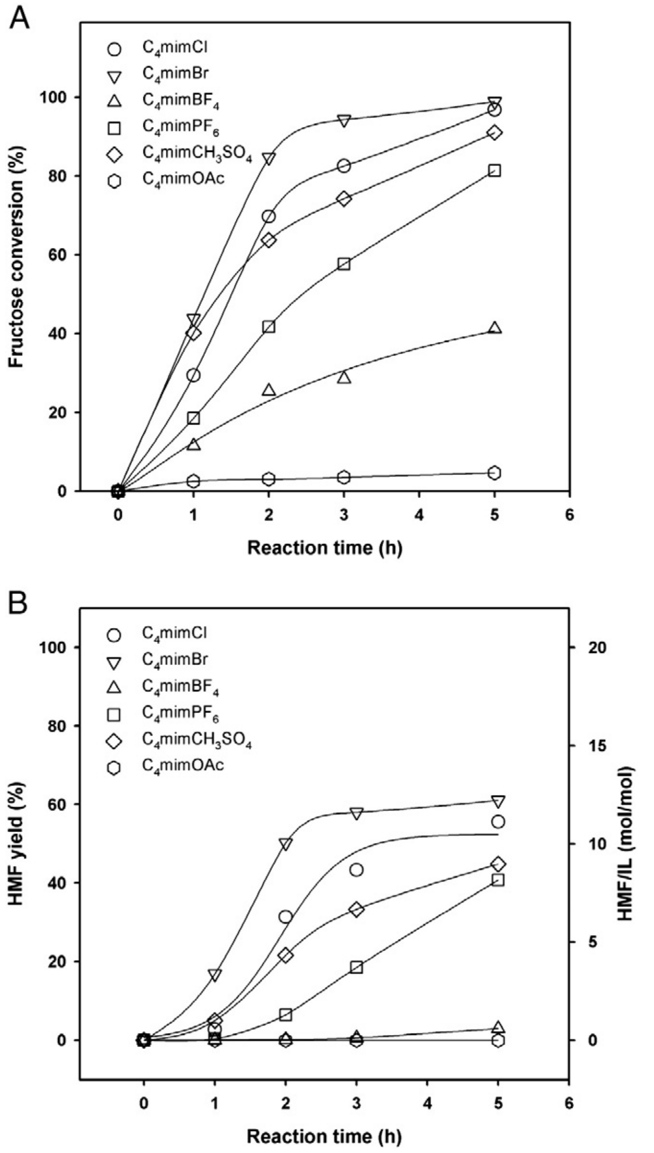

Fig. 2. Effect of anions coordinated to the C_4mim-based ionic liquids for the fructose dehydration under the same condition as presented in Table 1: A) fructose conversion and B) HMF yield.

DMSO produced more HMF from fructose (productivity = 5.0 mol/mol·h at 2 h), because bromide is a better nucleophile. $C_4mimCH_3SO_4$ and C_4mimPF_6 showed the HMF productivities of 2.2 and 0.65 mol/mol·h at 2 h, respectively, whereas C_4mimOAc and C_4mimBF_4 yielded only a negligible amount of HMF. For interpretation of these results, we tried to correlate the above results obtained at 2 h with the dissociation constant of the ionic liquids, since more associated ion pairs are less effective for acid-catalyzed reactions. As a result, it did not appear to be meaningful because the pKa values of C_4mimCl, C_4mimBr, C_4mimBF_4, and C_4mimPF_6 in DMSO were almost similar (22.0–22.1) [21]. This implies that only the dissociated C_4mim cation, which is well known to be relatively acidic, may not be responsible for the conversion of fructose into HMF.

In order to verify the effect of anions of C_4mim-based ionic liquids on the fructose dehydration, the control experiment was conducted to add a certain substance ($Ca(CH_3COO)_2$, KBr, CH_3COOH or Nafion NR50) into the reaction mixture containing C_4mimCl, fructose and DMSO at the reaction time of 1 h (Fig. 3). The addition of protons (i.e., Nafion NR 50) indeed led to a substantial improvement in the HMF production. In contrast, $Ca(CH_3COO)_2$ perfectly inhibited the activity of C_4mimCl, showing no HMF formation. This is considered that the acetate anion can be strongly associated to C(2)–H of the C_4mim cation, due to its Brönsted basic character. On the other hand, from the results obtained by the addition of KBr or CH_3COOH, an induction period appeared to be necessary for the fructose-to-HMF conversion; at 2 h, the HMF productivities (3.5 and 0.9 by the addition of KBr and CH_3COOH, respectively) were lower than that of C_4mimCl. However, as the reaction progressed, the two additives showed the similar fructose conversion and HMF yield/productivity to those of C_4mimCl. This could be explained in terms of the reaction mechanism, as described below.

3.2. Reaction network on the fructose dehydration by 1,3-dialkylimidazolium chloride

In general, there are two different options explaining the reaction network on the fructose dehydration into HMF: the open-chain [22] and cyclic pathways [23]. On the basis of the fact that a fructofuranose is preferred than an open-chain form in the solvent of DMSO [19] and the previous report in which a sequence of reaction proceeding via a fructofuranosyl-ion intermediate is dominant [24], the cyclic pathway is taken into account for establishing the reaction mechanism in this work.

While referring to the reports of Antal et al. [24], and Binder and Raines [16], we could draw the reaction network shown in Fig. 4. In the reaction of fructofuranose with C_4mimCl, the OH group at C-1 would be attacked by the dissociated C_4mim cation of which C(2)–H is acidic, thus forming the complex **1**. Then, the removal of OH leads to the formation of the intermediate **2** and $C_4mim^+OH^-$ (**3**). The former compound is spontaneously converted to the fructofuranosyl oxocarbenium ions (**4** and **5**). At this point, two pathways, nucleophile and base, is possible to form the enol (**7**), as described in Binder and Raines [16]. According to the nucleophile pathway, the Cl anion dissociated from C_4mimCl can attack the oxocarbenium to form a 2-deoxy-2-chloro intermediate (**6**) that is less prone to both side reactions and reversion to fructose. Alternatively, the chloride ion could form the enol by acting as a base that deprotonates C-1 [16]. The following steps lead to the conversion of the aldehyde intermediate (**8**) finally to HMF through the dehydration reaction, which is faster compared with the formation of the aldehyde **8**.

From the above explanation, it could be suggested that, due to a weak association between C_4mim^+ and Cl^-, the former cation dissociated serves as a Brönsted acid and the latter anion takes part as a nucelophile in the fructose-to-HMF conversion. This plausible suggestion is supported by the following findings. 1) The variation of alkyl groups attached to the imidazolium cation assoiated with chloride did not give any improvement in the HMF production, due to their similar pKa values of around 22 in DMSO [21]. 2) The dissociation strength between C_4mim^+ and anion is very critical to affect the IL's activity on the fructose conversion into HMF, because the anion indeed participates in the reaction as shown in Fig. 4. 3) The nucleophile pathway is considered to be valid from the result that C_4mimBr showed the better catalytic performance than C_4mimCl since bromide is a better nucelophile and leaving group than chloride, which is in accordance with the result of Binder and Raines [16]. 4) The finding that the addition of $Ca(CH_3COO)_2$ inhibited the HMF production explains that the acetate anion becomes associated with C_4mim^+, thus being inactive and, further, not triggering the conversion of fructose. This was confirmed by ^{1}H NMR spectroscopy (600 MHz) that the chemical shift of C(2)–H appeared downfield (from 9.142 to 9.168 ppm) as a result of $Ca(CH_3COO)_2$ addition (Fig. 5). 5) From the result obtained by the addition of KBr, a nucleophile is necessary to facilitate the HMF production and, specifically, the formation of 2-deoxy-2-chloro intermediate (**6**). 6) Finally, the

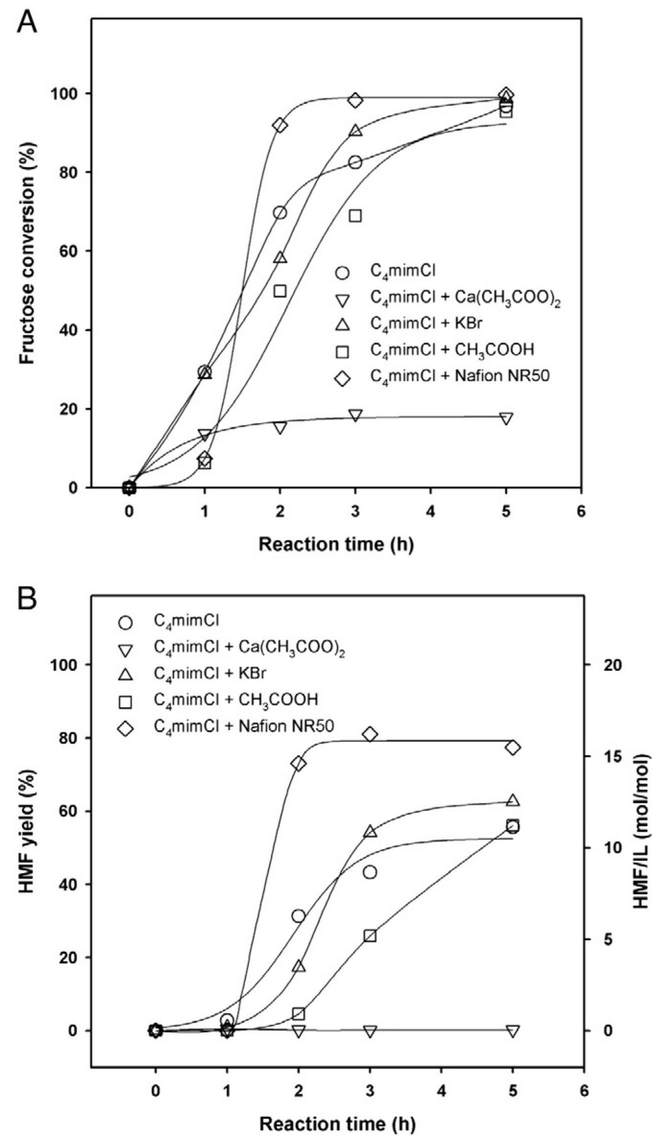

Fig. 3. Catalytic activities of C_4mimCl without and with the addition of $Ca(CH_3COO)_2$, KBr, CH_3COOH or Nafion NR50 at the reaction time of 1 h for the fructose dehydration at 80 °C in DMSO: A) fructose conversion and B) HMF yield.

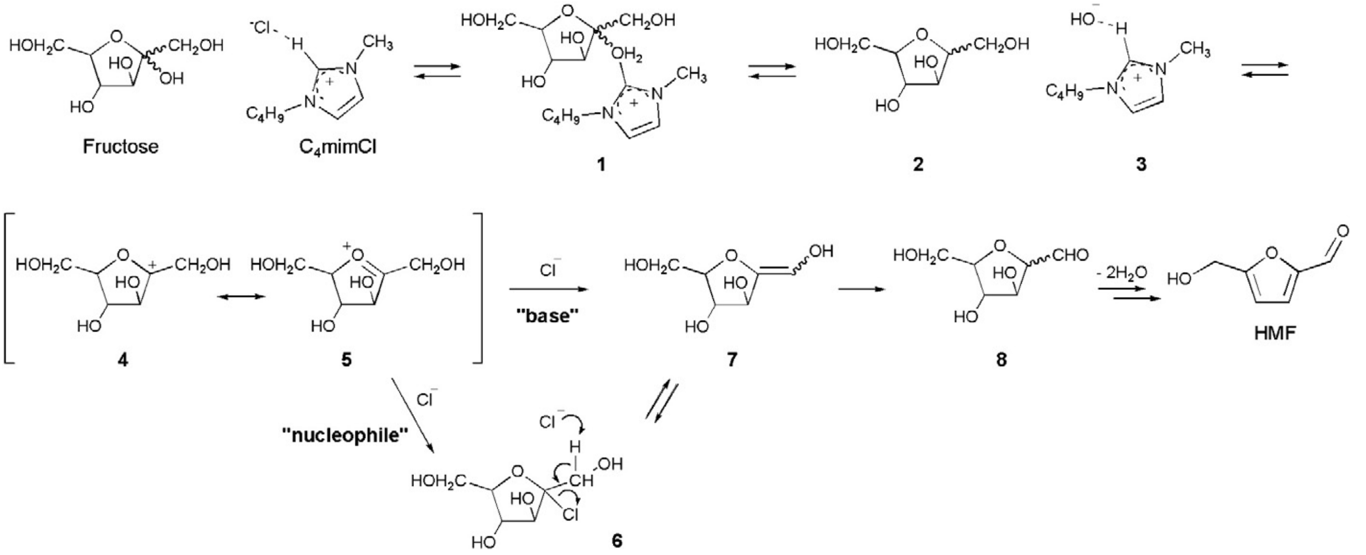

Fig. 4. Reaction network on the fructose dehydration catalyzed by C_4mimCl acting as both Brönsted acid and nucleophile.

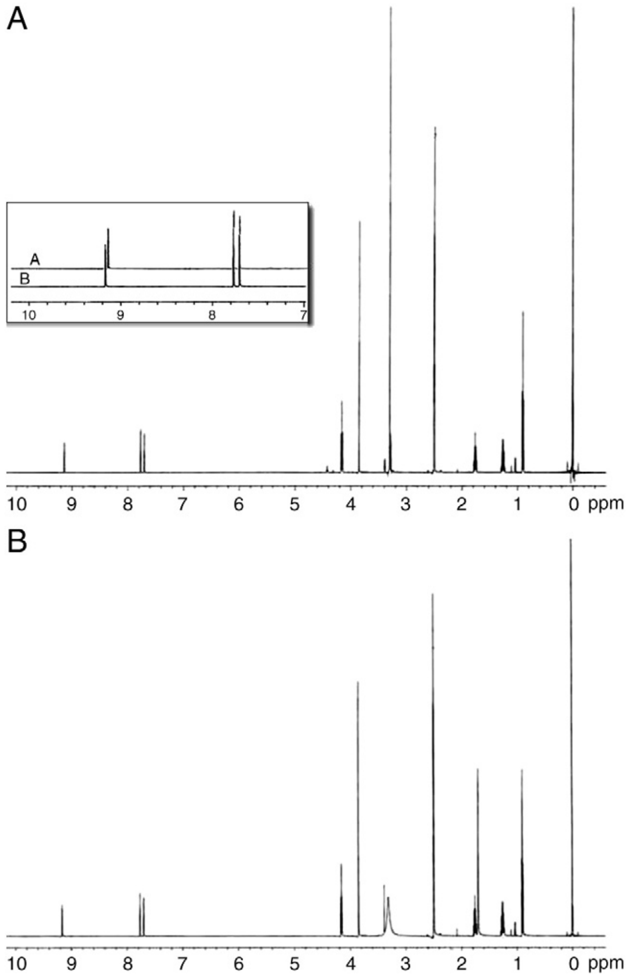

Fig. 5. NMR spectra of C_4mimCl (A), and a mixture of C_4mimCl and $Ca(CH_3COO)_2$ (B) in deuterated DMSO.

fact that the induction period exists upon the addition of KBr or CH_3COOH tells that the ion-exchange reaction, resulting in the ion association and/or dissociation, gradually occurs compared to the dehydration reaction.

4. Conclusions

While investigating the reaction pathway for the fructose dehydration to HMF, several insights can be drawn for further studies. On a first hand, the furanose form is of advantage rather than the pyranose in terms of the conformation of fructose for the dehydration reaction. This was accomplished by using the DMSO solvent in this work. Next, for the HMF production, the fructofuranosyl oxocarbenium ions (**4** and **5**) are a key intermediate, which was successfully formed by the Brönsted acid that is C(2)–H of 1,3-dialkylimidazolium-based ionic liquids. Finally, a better nucleophile (halide ions in this work) is required to follow the nucleophile pathway via the formation of 2-deoxy-2-chloro intermediate (**6**). This step would be very crucial in acquiring the higher yield of HMF from fructose. Therefore, it was considered that all the above requirements are fulfilled with the reaction system in which 1,3-dialkylimidazolium-based ionic liquids with halide anions in DMSO work for the fructose-to-HMF conversion. This is due to their dual catalytic function. Consequently, if the above reaction system is achieved at a similar level by using an industrially feasible approach, new possibilities would be offered for utilizing HMF as a platform chemical to produce a variety of biomass-based fuels and chemicals.

Acknowledgments

The financial support by the Korea Ministry of Knowledge Economy (Project No. KC000622) is greatly appreciated. This work is also the outcome of a Manpower Development Program for Energy & Resources supported by the Ministry of Knowledge and Economy (MKE).

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