Catalytic Production of Hydroxymethylfurfural from Fructose Using Brönsted-Lewis Acidic Ionic Liquid

Shi-Wei Liu, Shan-Shan Kong, Lu Li*, Shi-Tao Yu, Fu-Sheng Liu, Cong-Xia Xie
College of Chemical Engineering, Qingdao University of Science and Technology,
Qingdao 266042, P. R. China
zhanglilu@126.com*

Summary: The dehydration of fructose to 5-hydroxymethylfurfural (HMF) was investigated in the presence of the Brönsted-Lewis acidic ionic liquids (ILs). It was found that IL (3-sulfonic acid)-propyl-triethylammonium chlorochromate $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ (molar fraction of $CrCl_2$ $x = 0.55$) had a good catalytic performance with 93.4% yield of HMF. IL acid site played a more significant role than its Brönsted counterpart in the reaction, and a synergetic effect of Brönsted and Lewis acid sites enhanced IL catalytic performance. The reusability of IL was good which could be reused up to 5 times without apparent decrease in the yield of HMF.

Key words：Acidic ionic liquid; Fructose; 5-Hydroxymethylfurfural; Catalysis

Introduction

5-Hydroxymethylfurfural (HMF) is one key furan derivative readily accessible from renewable resources like carbohydrates, in particular through acid-catalyzed dehydration of fructose or fructose-precursors. It is a suitable starting material for the preparation of further furan monomers required for the preparation of non-petroleum-derived polymeric materials, such as polyesters, polyamides and polyurethanes [1, 2]. Usually the traditional inorganic acids, such as H_2SO_4 and HCl, were used as catalysts in the dehydration [3]. The drawbacks of these processes included serious corrosion of equipments, complicated separation procedures, environmental problems, and no recyclable of catalysts. In order to avoid these problems, reusable or recyclable catalysts were preferred for use in the reaction as they provided for increased efficiency, economic and industrial feasibility. Examples of these kinds of catalysts included acidic ion-exchange resin [4], transition metal phosphate [5] and H-mordenite [6] but are not limited to them. However, they also had shortcomings, such as restricted accessibility to the matrix bound catalytic sites, high molecular weight/active site ratios, and rapid deactivation from coking. Therefore, it is necessary to explore a new approach for the synthesis of HMF from fructose. HMF is actually formed by dehydration of fructose in its furanose form through a series of furan intermediates [7]. The process is composed of several elementary reactions, such as protonation, deprotonation, and dehydration. Generally, Brönsted acid is on favorable to protonation and dehydration, and Lewis acid facilitates to deprotonation [3, 8].

As a kind of environmental-friendly catalysts, Brönsted or Lewis acidic ionic liquids (ILs) attracts great attentions of the scientists and engineers in the world, and many organic reactions, such as esterification [9], dehydration [10], alkylation [11], acylation [12] and carbonylation [13], were even reported with excellent conversion, selectivity, and reusability. Studies involving the utilization of ILs as reaction media or catalysts for the dehydration of hexose into HMF have been reported. For example, Moreau *et al*., demonstrated that neutral ILs, such as $[BMIm]PF_6$ and $[BMIm]BF_4$, acted as a suitable reaction medium for the dehydration of fructose to HMF in presence of the acidic catalyst Amberlyst-15 [14]. The Brönsted acidic IL 1-H-3-methyl imidazolium chloride could be used as the solvent and catalyst for the dehydration of fructose and sucrose to produce HMF [15]. Recently, metal chlorides in the neutral IL [EMIm]Cl effectively catalyzed hexose to form HMF. These results suggested that ILs as solvents or catalysts played a positive role in the dehydration of hexose to produce HMF [8]. In our laboratory, some Brönsted-Lewis acidic ILs were synthesized, characterized and used in the polymerization [16, 17]. The results indicated that Brönsted-Lewis acidic ILs were both Brönsted and Lewis acidic and had better catalytic performance for the polymerization than the traditional catalysts. Due to the presence of Brönsted and Lewis acid sites, these ILs can selectively catalyze different reaction mechanisms and enhance

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*To whom all correspondence should be addressed.

the reaction conversion and selectivity. As an extension of our ongoing study of these ILs, we reported herein their application as catalysts for the dehydration of fructose to produce HMF, together with an effort to characterize this kind of ILs using UV-visible spectroscopy. The results showed that acid type of IL played a significant role in the efficiency of the reaction.

Experimental

Preparation of ILs

Using the procedure in the literature [16], 1,3-propane sultone was reacted with triethylamine to give 3-(triethylamine-N-yl)-propane-1-sultonate (TEA-PS) as a white powder. Then TEA-PS was reacted with an equal mole of hydrochloric acid to give (3-sulfonic acid)-propyl-triethylammonium chloride [HO_3S-$(CH_2)_3$-NEt_3]Cl as a white viscous liquid at room temperature. Brönsted-Lewis acidic ILs were prepared by the reaction of [HO_3S-$(CH_2)_3$-NEt_3]Cl with metal chlorides, including $FeCl_2$, $ZnCl_2$ and $CrCl_2$. The Lewis acidity of IL depended on the metal chloride mass. When the molar fraction of metal chloride was less than 0.5, IL only had Brönsted acidity and no Lewis acidity, and above this value, the obtained IL was Brönsted-Lewis acidic. The reaction formula for the synthesis of IL [HO_3S-$(CH_2)_3$-NEt_3]Cl-$CrCl_2$ (x = 0.67) was showed in Scheme-1. The acidities of ILs were characterized and determined on the basis of the Hammett acidity function [18]. As shown in the following equation, the Hammett acidity function is expressed as: H_o= PK (I)$_{aq+}$ log ([I]/[IH]$^+$). Where pK(I)$_{aq}$ is the pKa value of the indicator *p*-nitroaniline referred to as the aqueous solution, [IH]$^+$ and [I] are the molar concentrations of the protonated and unprotonated forms of the indicator respectively, which is usually determined by UV-visible spectroscopy [19]. [HO_3S-$(CH_2)_3$-NEt_3]Cl-$CrCl_2$ (x = 0.67): IR (KBr disc, cm^{-1}): v 3348, 2992, 1625, 1487, 1452, 1399, 1252, 1232, 1155, 1041, 940, 811, 794, 731, 692, 517. ^{1}H-NMR (500MHz, D_2O, ppm): δ 2.18 (m, 2H), 2.80(t, 2H), 3.77(s, 3H), 4.24(t, 2H), 7.30(s, 1H), 7.38(s, 1H), 8.61(s, 1H). ^{13}C NMR (255MHz, D_2O, ppm): δ 24.86, 35.40, 47.05, 47.84, 122.23, 123.45, 134.86.

Catalytic Properties Test

In a typical experiment, 2 g fructose, 15 g solvent n-butanol and 1.2 g IL were added into a 50ml stainless steel autoclave and reacted for 15 min at 180 °C (Scheme-2). After the reaction, the reaction mixture was cooled, and the upper layer, containing the product, solvent n-butanol and unreacted reactant, was separated from IL layer at the bottom of the flask simply by decantation. IL layer was reused directly in the cycle experiments. All samples of the upper layer were analyzed by HP-LC which was a Shimadzu LC-6A pump and a refractive index RID-6A detector. The used column was a Biorad HPX-87H (300 mm × 7.8 mm). Deionized water was the eluent (0.6 ml/min), and sorbose was the internal standard. HMF yield was directly given by the system of LC chemstation according to the area of chromatograph peak.
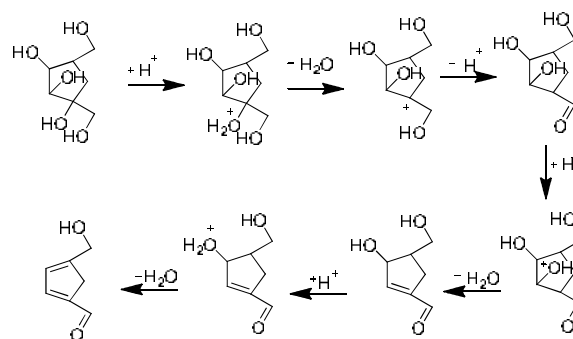
Scheme-1:   Dehydration of fructose to HMF.

Results and Discussion

Effects of Different Catalysts on the Dehydration

As can be seen from Table-1, compared with the traditional catalyst H_2SO_4 (30%) (Entry 4), all Brönsted-Lewis acidic ILs exhibited better catalytic performance. Especially, IL [HO_3S-$(CH_2)_3$-NEt_3]Cl-$CrCl_2$ (x = 0.55) exhibited good catalytic property with more than 93 % yield of the product HMF (Entry 13). When Lewis acidic IL [C_4mim]Cl-$CrCl_2$ (x = 0.55) and Brönsted acidic IL [HO_3S-$(CH_2)_3$-NEt_3]Cl were used as catalysts (Entries 2 and 3), HMF yields were only 63.9% and 80.1%, respectively. When the fractions of metal chloride (x) were less than 0.5 (Entries 6, 9 and 12), the obtained ILs were only Brönsted acidic, and their Hammett acidity functions (H$_0$) were near to those of Brönsted-Lewis acidic ILs which x value were more than 0.5, but the results of the dehydration used them as catalysts were not satisfy. The above results indicated that the acid type of catalyst played a significant role in the dehydration. The good catalytic performance of Brönsted-Lewis acidic IL is due to its

types of Brönsted and Lewis acidities and a synergetic effect between them. The Brönsted and Lewis acid sites can selectively catalyze different reaction steps, such as protonation, deprotonation and dehydration, in the dehydration process of the fructose to HMF through a series of cyclic furan intermediates, and the synergetic effect of both acidic sites also enhances IL catalytic performance (Scheme 2). The metal chlorides had a decisive influence on the catalytic performance of ILs (Entries 7, 11 and 13). IL $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.55$) showed the best catalytic performance (Entry 13). These results may be due to the different role on the stability to HMF. $CrCl_2$ has a good stability for HMF [8], which avoids the hydration and decarboxylation of HMF to produce levulinic acid and formic acid. Among all the chlorochrominate ILs (Entries 12-14), HMF yield raised with increasing molar fraction of $CrCl_2$ (x). When x value was 0.55, the dehydration of fructose was effectively catalyzed. This can be explained by that, when the molar fraction of metal chloride (x) is more than 0.5, IL is Brönsted and Lewis acidic, and by increasing the x value, the strength of IL Lewis acidity also increases, which enhances the catalytic activity of IL. However, further increasing its value, the result was not improved. It is indicated that too high a Lewis acid strength is adjective for the dehydration to form HMF.

Table-1:   Effects of catalysts on the reaction results [a]

Entry	catalyst	H_0	Yield /%
1	Blank	-	0
2	$[C_4mim]Cl$	-	8.57
3	$[C_4mim]Cl-CrCl_3$ ($x = 0.55$)	-	63.9
4	30% H_2SO_4	-1.53	83.2
5	$[HO_3S-(CH_2)_3-NEt_3]Cl$	2.91	80.1
6	$[HO_3S-(CH_2)_3-NEt_3]Cl-ZnCl_2$ ($x = 0.33$)	3.21	82.5
7	$[HO_3S-(CH_2)_3-NEt_3]Cl-ZnCl_2$ ($x = 0.55$)	2.81	88.5
8	$[HO_3S-(CH_2)_3-NEt_3]Cl-ZnCl_2$ ($x = 0.60$)	2.62	87.1
9	$[HO_3S-(CH_2)_3-NEt_3]Cl-FeCl_2$ ($x = 0.33$)	2.84	81.0
10	$[HO_3S-(CH_2)_3-NEt_3]Cl-FeCl_2$ ($x = 0.55$)	2.70	91.1
11	$[HO_3S-(CH_2)_3-NEt_3]Cl-FeCl_2$ ($x = 0.60$)	2.64	91.6
12	$[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.33$)	2.75	81.7
13	$[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.55$)	2.56	93.4
14	$[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.60$)	2.46	92.9

a: fructose 2 g, n-butanol 15 g, catalyst 1.2 g, T = 180 °C, t = 15 min.

Effects of Reaction Conditions on the Dehydration

The effects of reaction conditions on the dehydration were showed in Table-2. IL dosage was very important for the dehydration. With increasing of IL $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.55$) dosage from 0.4 g to 1.6 g, the yield of HMF increased from 76.5% (Entry 1) to 93.6% (Entry 4). When increasing of solvent n-butanol dosage from 10 g to 20 g, the yield of HMF increased from 83.5% (Entry 5) to 93.8% (Entry 6). This result can be explained by the

different dissolubility of fructose and HMF in the reaction mixture. The reaction temperature and time were also important for the dehydration. At 170 °C, HMF yield was only 84.3% (Entry 7). But when the temperature reached to 180 oC, HMF yield was 93.4% (Entry 3), and after that it did not increase further (Entry 9). This is because that too high reaction temperature facilitates the hydration and decarboxylation of HMF to produce levulinic acid and formic acid. With increasing reaction time from 10 min to 15 min, the yield of product HMF increased from 79.6% to 93.4% (Entries 3 and 9). However, HMF yield decreased to 91.7% at 20 min (Entry 10). It is seen that both too high a reaction temperature and too long a reaction time are unfavorable to the yield of HMF.

Table-2: Effects of reaction conditions on the dehydration results.

Entry	IL /g	Solvent /g	T /°C	t /min	Yield /%
1	0.4	15	180	15	76.5
2	0.8	15	180	15	83.6
3	1.2	15	180	15	93.4
4	1.6	15	180	15	93.6
5	1.2	10	180	15	83.5
6	1.2	20	180	15	93.8
7	1.2	15	170	15	84.3
8	1.2	15	190	15	90.7
9	1.2	15	180	10	79.6
10	1.2	15	180	20	91.7

Reusability of Catalyst

The reusability of $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.55$) was investigated, and the results were given in Table-3. The results showed that HMF yield was almost unchanged after $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$ ($x = 0.55$) was used repeatedly five times. It is indicated that Brönsted-Lewis acidic IL was of excellent reusability. The good reusability may be explained by the following two points. First, in the structure of IL $[HO_3S-(CH_2)_3-NEt_3]Cl-CrCl_2$, the alkyl sulfonic acid group is covalently tethered in IL cation, and IL anions $[CrCl_3]^-$ and $[Cr_2Cl_5]^-$ are inert and stable to water and Brönsted acid. Therefore, the acidity of IL is not easily lost. Second, the use of $CrCl_2$ increases the density of the IL, which gives an easier separation of IL from the reaction mixture, and the IL is not easily lost in this process. Therefore, its activity is stable and its reusability is good.

Table-3:   Reusability of the IL catalyst.

Cycle	Yield /%
1	93.4
2	93.6
3	93.2
4	93.0
5	93.2
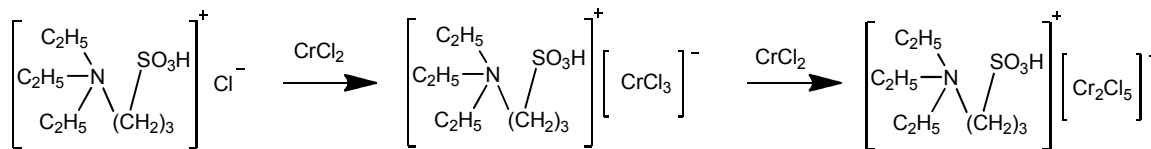
Scheme-2:   Synthesis of IL $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}CrCl_2$ ($x = 0.67$)

Conclusion

The dehydration of fructose was investigated using Brönsted-Lewis acidic ILs as catalysts. IL (3-sulfonic acid)-propyl-triethylammonium chlorochrominate $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}CrCl_2$ ($x = 0.55$) was of good catalytic property and the yield of product was 93.4%. The type of acidity of ILs played a significant role in the efficiency of the dehydration reaction. It was also found that the Brönsted-Lewis acidic sites of IL can selectively catalyze the protonation, dehydration, and deprotonation dehydrogenation in the reaction, and a synergetic effect of Brönsted and Lewis acid sites enhanced the catalytic performance of the IL.

Acknowledgments

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