

Prominent Roles of Impurities in Ionic Liquid for Catalytic Conversion of Carbohydrates

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Published online: 7 February 2012
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Abstract Impurities present in commercially available ionic liquids display prominent catalytic functions toward carbohydrate conversion. Little conversion was observed at 180 °C with high purity [EMIM]Cl ionic liquid whereas significant conversion was observed for ionic liquids of lower purity levels. Addition of metal halides to high purity [EMIM]Cl catalyze cellulose conversion with drastically different product selectivities dependent on the metal ions. CuCl₂ is an active catalyst for hydrolyzing cellulose and further degrading the products. CrCl₂ is an active and a selective catalyst for the formation of 5-hydroxymethyl-furfural (5-HMF). CrCl₂ also helps stabilize the 5-HMF product. FeCl₂ does not show catalytic activity. Metal impurities in ionic liquid correlate to the activities observed when similar metals were added to high purity ionic liquids.

Keywords Ionic liquid · 1-ethyl-3-methyl-imidazolium chloride · Cellulose · Cellulose conversion · Purity · Impurities · Catalysis · Catalyst

1 Introduction

In the last two decades, ionic liquids have emerged as new and versatile solvents, and many of them are also catalysts

for a broad range of catalytic reactions [1]. Certain ionic liquids have been found to possess the unique capability of dissolving cellulosic biomass [2, 3]. The potential of such ionic liquids as solvents to enable catalytic conversion of cellulosic polymers was first explored and demonstrated by Zhao et al. [4]. This field of research has since experienced a rapid growth [5].

Most ionic liquids have negligible vapor pressure and excellent thermal stability over a wide temperature range. For example, ionic liquids composed of 1-ethyl-3-methyl-imidazolium (EMIM⁺) cation and Cl⁻ anion are reported to be stable up to 285 °C, while salts of the same cation with other anions such as BF₄⁻ and PF₆⁻ are thermally stable above 380 °C under an inert atmosphere [6]. It is well known that presence of impurities in ionic liquids typically causes changes in physical properties, e.g. decreasing melting point and viscosity [7]. Addition of Lewis acid metal chlorides, e.g. AlCl₃, to 1-alkyl-3-methylimidazolium chloride [AMIM]Cl, is an exothermic reaction and considerably reduces the melting point by forming [AMIM]AlCl₄ or [AMIM]Al₂Cl₇ that have much lower melting points than the parent [AMIM]Cl [8]. While most early research on catalysis involving ionic liquids with metallohalide anions were conducted using stoichiometric ratios of anions to organic cations, e.g. [AMIM]⁺ [9], the use of pure ionic liquids as a solvent to carry out reactions with a catalytic amount of a metal halide as catalyst allow the solvent property of such ionic liquids to be displayed [4]. In such a reaction system, catalytic amounts of metal halides were used to catalyze the conversion of glucose and cellulose [4, 11, 12]. The concentration of metal chloride as catalyst was on the order of 10⁻³ M. The presence of an additional metal chloride in the ionic liquid, even on the order of 10⁻⁵ M concentration, was found to have a dramatic synergistic effect [11].

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Thus, the catalytic performance of metal halides for conversion of carbohydrates in the ionic liquid systems can be highly sensitive to the presence of impurities. This work presents findings on the role of impurities present in some commercially available ionic liquids used for the conversion of cellulose.

2 Experimental

Three 1-ethyl-3-methylimidazolium chloride [EMIM]Cl, ionic liquids of different purity were studied for the conversion of cellulose. A high purity [EMIM]Cl (99.5%), was purchased from Solvent-Innovation (designated as [EMIM]Cl-HP). A medium purity [EMIM]Cl, (98%), was purchased from BASF ([EMIM]Cl-MP). A low purity [EMIM]Cl, (93%), was purchased from Sigma-Aldrich ([EMIM]Cl-LP). These ionic liquids were used without further purification (the purity of the ionic liquids are only nominal numbers).

A cellulose (fibrous, long, Catalog No. C6663-1 KG) was purchased from Sigma-Aldrich. CuCl_2 (99.9%) was obtained from Sigma-Aldrich, and CrCl_2 (99.9%) and FeCl_2 (99.9%) from Strem Chemicals.

In a typical test, 500 mg [EMIM]Cl was loaded into 4 mL vials (15.5 mm diameter \times 50 mm). When used as catalysts, the metal chloride was added to the [EMIM]Cl-HP at concentration of 6 mol% with respect to the glucose concentration calculated from the cellulose feed. This concentration level is much higher than those of metal impurities found in [EMIM]Cl-MP and [EMIM]Cl-LP, mainly to allow unambiguous verification of the metal chloride catalytic performance. The vials were sealed and inserted into a high-throughput batch reactor (Symyx Technologies, Inc., Sunnyvale, CA), where they were heated to 150 °C and shaken at 600 rpm for 30 min. After the reactor had cooled to room temperature, 50 mg of cellulose (10 wt% with respect to ionic liquid) was added to each vial. The vials were sealed and reinserted into the high-throughput reactor. During the dissolution process, the vials were heated to 100 or 120 °C and shaken at 600 rpm for 1 h. The reactor was cooled to room temperature, and 50 μL of H_2O was added to each vial to initiate the depolymerization. The added water was a large excess of the amount needed for full hydrolysis of the cellulose. The vials were sealed and reinserted into the high-throughput reactor which was heated to a specified temperature for a specified time period while shaken at 600 rpm. Exactly two milliliters of water was added to each vial after the reactor had cooled to room temperature. The vials were sealed and centrifuged at 2,000 rpm for 30 min. A single liquid layer was formed and the liquid products were analyzed by HPLC. All results were replicated at least five times.

Elemental analysis of the ionic liquid samples was performed using inductive coupling plasma analysis.

3 Results and Discussion

The initial high-throughput catalyst screening tests compared the conversion of dissolved cellulose for several purities of ionic liquid. The experiment was conducted at 180 °C for five minutes, without added metal chloride. Surprisingly, the three ionic liquids exhibited different activities as shown in Fig. 1. [EMIM]Cl-HP showed little activity, while reactions in MP and LP [EMIM]Cl ionic liquids produced considerably higher amount of products, mainly glucose (47%) in [EMIM]Cl-LP, from cellulose hydrolytic depolymerization, and 5-hydroxymethylfurfural (5-HMF, 29%) in [EMIM]Cl-MP from conversion of glucose. The high catalytic activity of [EMIM]Cl-LP and [EMIM]Cl-MP can be attributed to the presence of impurities in the ionic liquids, as evidenced by the lack of activity of the [EMIM]Cl-HP. The striking difference in the selectivity of [EMIM]Cl-MP for 5-HMF from that of [EMIM]Cl-LP for glucose suggests that the impurities in the two ionic liquids are different. Water as an impurity in the as-received ionic liquids is not considered to play a differentiating role among the ionic liquid systems since excess water was added to all ionic liquids prior to reaction. In previously published work, varying the amount of water to a pure [EMIM]Cl ionic liquid containing various metal chlorides affected the conversion but had little effect on the selectivity [11]. The direct production of 5-HMF from dissolved cellulose polymer is particularly

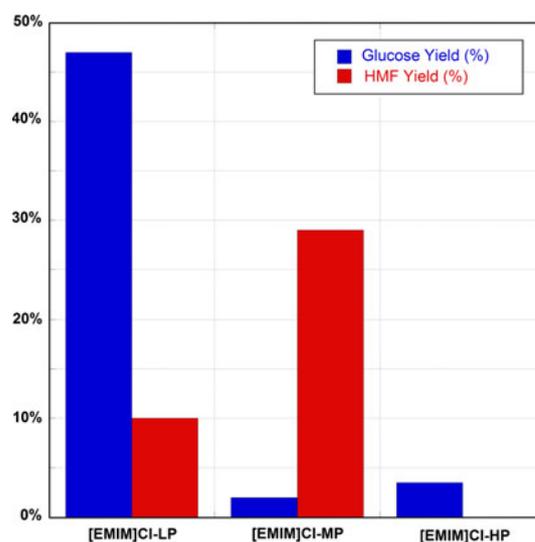


Fig. 1 Effect of ionic liquid purity on cellulose depolymerization. Reaction was conducted at 180 °C for 5 min. [EMIM]Cl-HP: 99.5%; [EMIM]Cl-MP: 98%; [EMIM]Cl-LP: 93%

remarkable as 5-HMF is a highly desirable platform chemical [10].

The analytical results of metal speciation and content in all three ionic liquids are shown in Table 1. There is negligible amount of sulfur in all samples. The main difference between [EMIM]Cl-LP and the [EMIM]Cl-MP is the amount of organic impurities present, which are not quantified as they are not expected to catalyze cellulose depolymerization. It was shown in published work that CrCl_2 in 3% of CuCl_2 largely enhanced the activity of CuCl_2 for cellulose conversion at temperature as low as $120\text{ }^\circ\text{C}$ [11]. The presence of Cr at concentration of 1/3 of that of Cu in the [EMIM]Cl-LP vs. a non-detected Cr in [EMIM]Cl-HP may have attributed to the difference in the performance of the two ionic liquids. Although the impurity level is very low, the high reaction temperature at $180\text{ }^\circ\text{C}$ largely amplifies their activities. The metal concentrations are significantly higher in [EMIM]Cl-MP than in [EMIM]Cl-HP, particularly for Fe, Cr, and Ni. It should be noted that the individual and total concentrations of these impurities are less than ten part per million. Reactions with cellulose carried out at $120\text{ }^\circ\text{C}$ containing metal chlorides such as CrCl_2 or CuCl_2 in [EMIM]Cl-HP showed little activity even at a considerably higher concentration (6,000 ppm) [11, 12].

It is known that 5-HMF and other carbohydrate products are not stable at high reaction temperatures. Therefore, in well characterized catalytic systems, temperatures of $120\text{ }^\circ\text{C}$ or lower are preferred [4]. For the ionic liquids studied in this work without added metal chlorides, testing at higher temperatures was necessary to examine the effect of impurities present at lower concentrations. To minimize the product decomposition at high temperature, the reaction time was reduced. The effect of reaction time on product distribution was investigated at $160\text{ }^\circ\text{C}$ for all three [EMIM]Cl-LP, [EMIM]Cl-MP, and [EMIM]Cl-HP ionic liquids. The results are shown in Figs. 2, 3 and 4.

The product labeled as “unknown” in Figs. 2, 3 and 4 has a mass of 162.14, which is identical to levo-glucosan.

Table 1 Concentration (part per million) of main impurities in the three [EMIM]Cl ionic liquids

Element	[EMIM]Cl-HP	[EMIM]Cl-MP	[EMIM]Cl-LP
Cr	0.000	1.170	0.011
Cu	0.051	0.057	0.033
Fe	0.014	4.990	0.035
Mn	0.004	0.072	0.004
Mo	0.000	0.040	0.001
Na	0.181	0.198	0.130
Ni	0.005	0.710	0.026

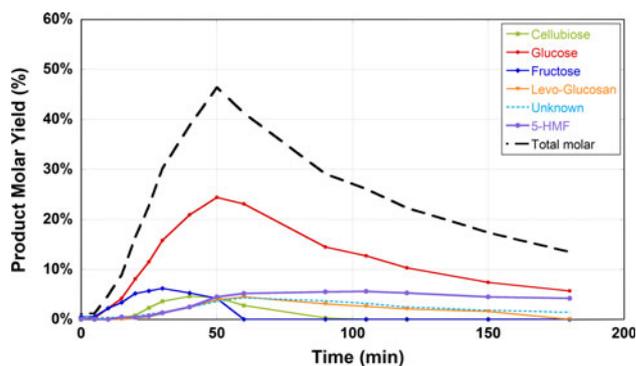


Fig. 2 Product yield from cellulose conversion in [EMIM]Cl-LP at $160\text{ }^\circ\text{C}$

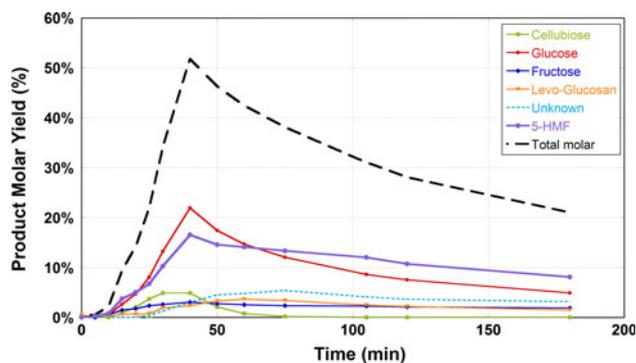


Fig. 3 Product yield from cellulose conversion in [EMIM]Cl-MP at $160\text{ }^\circ\text{C}$

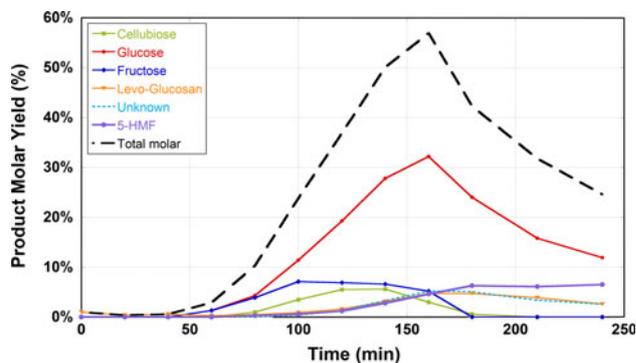


Fig. 4 Product yield from cellulose conversion in [EMIM]Cl-HP at $160\text{ }^\circ\text{C}$

This product could be a mannosan derived from isomerization and dehydration through a fructose intermediate. Although the exact determination of the by-product is not known, its identity does not affect the conclusions of this paper as the minor product was observed in all experiments.

As Figs. 2, 3 and 4 show, the induction time for the reaction in [EMIM]Cl-MP (10 min) and [EMIM]Cl-LP (5 min) are considerably shorter than for the reaction in

[EMIM]Cl-HP (60 min). It was not anticipated that the reaction would occur in [EMIM]Cl-HP even after an extended induction time. This delayed activity for [EMIM]Cl-HP could be due to a number of possible causes, including trace amount of etched metals from the glass vial, or autocatalysis by a small amount of product formed at a slow rate which upon reaching a required concentration catalyzes the reaction. An unambiguous conclusion for the cause has not been reached.

Consistent with the results shown in Fig. 1, the impurities in [EMIM]Cl-MP catalyzed the formation of 5-HMF as a main product. The maximum total product yield was also higher in [EMIM]Cl-MP than in [EMIM]Cl-LP and the maximum yield was reached after 40 min for [EMIM]Cl-MP, as compared to 50 min for [EMIM]Cl-LP. These observations coincide with a higher metal content in the [EMIM]Cl-MP (Table 1). Therefore a higher activity is displayed by the metal impurities in this ionic liquid than in the [EMIM]Cl-LP. Even though the iron concentration is highest in the [EMIM]Cl-MP, it is not responsible for the observed high 5-HMF yield. In earlier work, iron was not found to be an effective catalyst. Further experimental evidence on the inactive nature of iron for cellulose conversion is presented and discussed below.

The strong catalytic activity of trace amounts of metal impurities in the [EMIM]Cl-MP system may also be synergistically influenced by the presence of multiple metal impurities. In previous work, such synergism was established when a trace amount of CrCl_2 or PdCl_2 was introduced into a CuCl_2 /[EMIM]Cl-HP ionic liquid system [11, 12].

To verify the role of metal chloride catalysts in the [EMIM]Cl solvent, CuCl_2 , CrCl_2 , and FeCl_2 were tested for their performance in the [EMIM]Cl-HP (Table 1). Higher concentrations of selected metal chlorides are used to unambiguously determine their catalytic functions at the same concentration level. The selectivity patterns of the metal chlorides are the focus. The starkly different catalytic performances of the metal chlorides are presented in Figs 5, 6 and 7.

From Fig. 5, it is immediately evident that CrCl_2 is highly active and selective for the catalytic formation of 5-HMF. The long induction period observed in [EMIM]Cl-HP is drastically reduced in the presence of CrCl_2 catalyst. The main product is 5-HMF (Fig. 5), a result of the higher concentration of CrCl_2 in the [EMIM]Cl-HP than that in [EMIM]Cl-MP (Fig. 3). Formation of other products is considerably reduced, as compared to the reaction in [EMIM]Cl-MP likely due to a higher concentration of CrCl_2 . The fructose yield during the reaction time is low, consistent with the proposed mechanism that fructose is an intermediate in the conversion of glucose to 5-HMF [4]. At the higher temperature of 160 °C, the formation of fructose

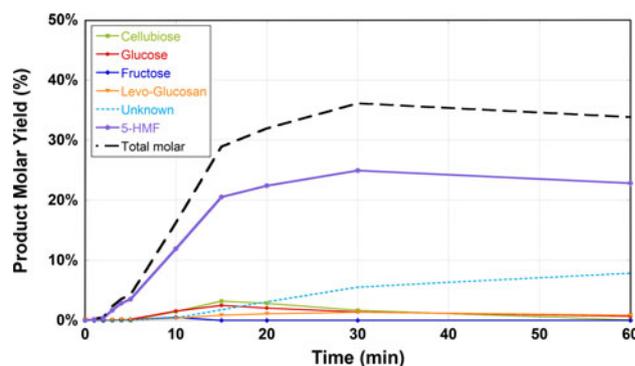


Fig. 5 Product yield from cellulose conversion catalyzed by CrCl_2 in [EMIM]Cl-HP at 160 °C

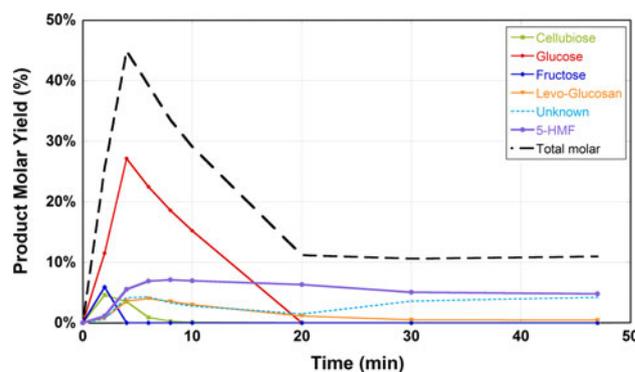


Fig. 6 Product yield from cellulose conversion catalyzed by CuCl_2 in [EMIM]Cl-HP at 160 °C

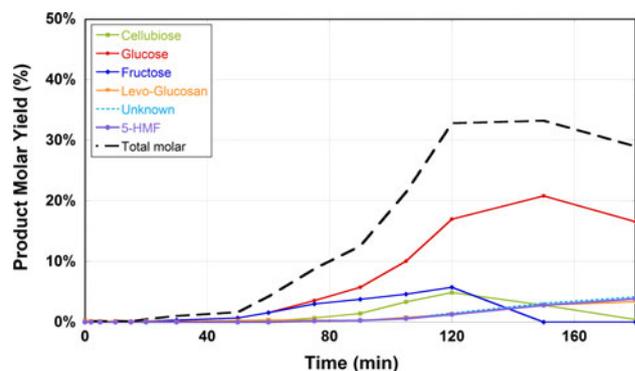


Fig. 7 Product yield from cellulose conversion catalyzed by FeCl_2 in [EMIM]Cl-HP at 160 °C

becomes a rate limiting step. It is also important to note that the 5-HMF is relatively stable in the CrCl_2 /[EMIM]Cl-HP system, even at higher temperatures. It has been observed previously that CrCl_2 stabilizes 5-HMF [4]. The reason for this stabilization effect of CrCl_2 remains unclear.

CuCl_2 is the most active catalyst for both depolymerization of cellulose, as shown in Fig. 6, and also the rapid degradation of products formed. The maximum total product yield appeared in only five minutes. The absence

of an induction time is characteristic of the CuCl_2 catalyst system.

Comparison of the product distribution for FeCl_2 /[EMIM]Cl-HP system (Fig. 7) and for the [EMIM]Cl-HP system (Fig. 4) reveals that FeCl_2 exhibits little catalytic effect for the reaction. Note that the maximum product yield (33%) for the FeCl_2 /[EMIM]Cl-HP system is even lower than that for [EMIM]Cl-HP system (56%), suggesting that FeCl_2 may be an inhibitor for the reaction.

Conversion of glucose to 5-HMF in general proceeds via fructose intermediate [4, 13]. The results of this work also indicate a similar mechanism. For the [EMIM]Cl-MP that contains a higher concentration of Cr ions than [EMIM]Cl-LP and [EMIM]-HP, a high selectivity to 5-HMF was observed (Fig. 3). However, for [EMIM]Cl-LP and [EMIM]Cl-HP, close inspection of the product profiles indicates that the 5-HMF formation profile lags considerably the fructose profile beyond the induction period in each case, as shown in Figs. 2 and 4. This observation is likely due to the low metal concentrations in both [EMIM]Cl-LP and [EMIM]Cl-HP. Because Brønsted acidity is known to readily catalyze the conversion of fructose to 5-HMF [14–16], the observed lag in fructose conversion to 5-HMF in both [EMIM]Cl-LP and [EMIM]Cl-HP, particularly at the high temperature, suggests low Brønsted acidity in both systems. The higher yield to 5-HMF in [EMIM]Cl-MP can thus be attributed to higher metal ion impurities that can be expected to display Lewis acidity. When the concentrations of active metal chlorides, like CuCl_2 and CrCl_2 , are high, the fructose is rapidly converted as shown in Figs. 5 and 6, so that fructose formation becomes a rate limiting step. For an inactive metal chloride, such as FeCl_2 , it is interesting to note that fructose formation after a long induction period, is not rate limiting.

4 Conclusion

While pure [EMIM]Cl is not active for cellulose depolymerization, the presence impurities promote reactions. Trace metal ion impurities in [EMIM]Cl, particularly Cu and Cr ions, correlate to similar reactivity observed when the same metals were added to high purity [EMIM]Cl, suggesting a that at least part of the reactivity could be due to trace metals in very low amounts. The [EMIM]Cl-MP

containing a low concentration of Cr ions produced 5-HMF as a main product that is characteristic of CrCl_2 and CrCl_3 added to pure [EMIM]Cl that were evaluated at a lower temperature. CuCl_2 is the most active catalyst in [EMIM]Cl at a higher reaction temperature like in this work. CuCl_2 not only catalyzes cellulose depolymerization reaction, but also catalyzes the degradation of depolymerization products. FeCl_2 has little activity, and even shows inhibition in [EMIM]Cl for the reaction.

Acknowledgments This work was supported by the Laboratory Directed Research and Development Program at the Pacific Northwest National Laboratory (PNNL), a multiprogram national laboratory operated by Battelle for the U.S. DOE under contract no. DE-AC06-76RL01830.

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