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Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst

Zhen-Dong Ding, Jin-Cai Shi, Jing-Jing Xiao, Wen-Xiu Gu, Chang-Ge Zheng, Hai-Jun Wang*

School of Chemical and Material Engineering, Jiangnan University, Wuxi, Jiangsu 214122, China

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ABSTRACT

Efficient catalytic conversion of microcrystalline cellulose (MCC) to 5-hydroxymethyl furfural (HMF), is achieved using acidic ionic liquids (ILs) as the catalysts and metal salts as co-catalysts in the solvent of 1-ethyl-3-methylimidazo-lium acetate ([emim][Ac]). A series of acidic ILs has been synthesized and tested in conversion of MCC to HMF. The effect of reaction conditions, such as reaction time, temperature, catalyst dosage, metal salts, water dosage, Cu^{2+} concentration and various acidic ILs are investigated in detail. The results show that $CuCl_2$ in 1-(4-sulfonic acid) butyl-3-methylimidazolium methyl sulfate ([C_4SO_3Hmim][CH_3SO_3]), is found to be an efficient catalyst for catalytic conversion of MCC to HMF, and 69.7% yield of HMF is obtained. A mechanism to explain the high activity of $CuCl_2$ in [C_4SO_3Hmim][CH_3SO_3] is proposed. To the best of our knowledge, this report first proposes that the Cu^{2+} and [C_4SO_3Hmim][CH_3SO_3] show better catalytic performance in catalytic conversion of MCC to HMF.

1. Introduction

With the rapid development of society, energy demand is increasing, and it is projected to grow by more than 50% by 2025 (Ragauskas et al., 2006). However, the exhaustible fossil fuels represent ~80% of the total world energy supply. For constant production and consumption, the presently known reserves of oil will last around 36 years, natural gas 59 years and coal 150 years. It can be speculated that fossil fuels cannot be considered as the world's main source of energy for more than one hundred years. Besides, the use of fossil fuels presents serious environmental problems, particularly global warming. In addition, their production costs will increase as reserves approach exhaustion and as more expensive technologies are used to explore and extract fewer attractive resources (Goldemberg, 2007). Therefore, it can be concluded that a sustainable energy in future depends on an increased share of renewable energy. One of the best ways to achieve such a goal is to convert renewable biomass to valuable fuels and products. Key global biomass resources come from agricultural residues, wood and herbaceous energy crops. Cellulose, the most abundant biomass resource, is a key component of grass, agricultural and wood waste, and has a highly crystalline linear polymer of D-an-hydroglucopyranose units join together in long chains by β-1,4-glycosidic bonds (Zhang & Lynd, 2004). Moreover, it has the potential to become a promising alternative to fossil resources for the sustainable production of HMF, a versatile and key intermediate in the bio-fuel chemistry and petrochemical industry. But it is practically difficult to dissolve cellulose in most common organic solvents, because of their stiff molecules and close chain packing via numerous intermolecular and intramolecular H-bonds (Zhang, Wu, Zhang, & He, 2005). The tight H-bond network and van der Waals interactions greatly stabilize it, which makes it notoriously resistant to hydrolysis.

Recently, some researchers have investigated the dissolution and hydrolysis of cellulose. For the dissolution of cellulose, ILs have been received attention as green solvents for cellulose. Prior to the studies by Robin Rogers demonstrated 1-butyl-3-methylimidazolium salts as good solvents for cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002), and the dissolution mechanism of cellulose in ILs was also investigated by NMR spectroscopy (Mikkola et al., 2007). From then on, the dissolution of cellulose has attracted much attention. It has been reported that some hydrophilic ILs can dissolve cellulose. For example, 1-allyl-3-methylimidazolium chloride ([amim][Cl]) (Kosan, Michels, & Meister, 2008), 1-ethyl-3-methyli-midazolium acetate ([emim][Ac]) (Fukaya, Sugimoto, & Ohno, 2006) and 1-allyl-3-methyli-midazolium formate ([amim][Fo]) (Fu, Mazza, & Tamaki, 2010). Due to the increased interest and demand for industrial application, substantial effort has been devoted to the development of appropriate hydrolysis schemes, including catalysis using mineral acids, enzyme-drivenreactions and heteropolyacid. However, there are many disadvantages of these processes, such as the use of mineral acids is efficient at high temperature (170–240 °C), the corrosion of equipments is very serious, and the generation of large

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* Corresponding author.
E-mail address: wanghj329@hotmail.com (H.-J. Wang).

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amounts of acid waste water; In enzymatic hydrolysis, the obvious disadvantages are the low activity, high cost of enzymes; In heteropoly acids hydrolysis, the inherent advantages are their high catalytic activity, reusability, fewer side reactions, strong Brønsted acidity and so on. Moreover, a remarkably high yield of glucose (82.4%) is obtained (Cheng et al., 2011), but the disadvantage is the low selectivity of HMF. Therefore, the development of a new, green and economical process for the conversion of cellulose into HMF under mild conditions with high selectivity is essential. Raines's group reported that N,N-dimethylacetamide containing lithium chloride is a privileged solvent that enables the synthesis of HMF in a single step, producing HMF from cellulose to obtain with a yield of 50% (Binder & Raines, 2009). Zhao, Holladay, Brown, and Zhang (2007) first reported metal chlorides in IL converts sugars to 5-HMF, the yield nearly 70% can be obtained. Zhang et al. studied the conversion of lignocellulose into furans in the presence of $CrCl_3$ under microwave irradiation, the yield of HMF could be up to 45–52% (Zhang & Zhao, 2010). Chou's group investigated the hydrolysis of cellulose by using catalytic amounts of $FeCl_2$ in ILs, and the HMF yield of 34% was achieved (Tao, Song, & Chou, 2010). Tao, Song, and Chou (2011), Tao, Song, Yang, and Chou (2011) also indicated that the catalytic hydrolysis of cellulose to HMF in $MnCl_2$–IL system, HMF yield was up to 37%. It can be speculated that the metal ion in IL is demonstrated to be an efficient catalyst system for the conversion of cellulose to HMF.

The catalytic conversion of cellulose to HMF consists of hydrolysis of cellulose to β-glucose, isomerization of β-glucose to fructose, and fructose dehydration to HMF. Furthermore, metal ions mainly act as the catalyst for promoting rapid conversion of the α-glucose to the β-glucose and isomerization of β-glucose to fructose (Zhao et al., 2007), while cellulose hydrolysis and fructose dehydration can be simply achieved at acidic condition. Herein, we investigate the conversion of MCC to HMF with several acidic ILs and metal salts in the solvent of [emim][Ac] under mild conditions, and the highest yield of HMF can be obtained when the optimal conditions of catalytic conversion of cellulose to HMF in [emim][Ac] are selected.

2. Methods

2.1. Materials

MCC (AR, average particle size 90 μm) is a commercial product from J&K Chemical Company. N-methylimidazole is obtained from Changzhou Chemical Factory and further purified by distillation. 1,4-Butyl sultone is obtained from Shanghai Chemical Factory. Bromoethane and ethyl acetate are distilled and then are stored over molecular sieves in tightly sealed glass bottles, respectively. N-methyl-2-pyrrolidone (99%), methane sulfonic acid (99%) and other chemicals (AR) are commercially available and used without further purification unless otherwise stated.

2.2. Synthesis procedure and characterization data of ILs

The ILs used in this study (Fig. 1) are synthesized as described in the literatures (Ellis, 1996; Junming, Jianchun, Zhiyue, & Jing, 2010; Tao, Song, & Chou, 2011; Tao, Song, & Yang, et al., 2011; Yang, Zhang, Wang, & Tong, 2006; Zhang et al., 2009).

2.2.1. Preparation of [emim][Ac]

[emim][Ac] was prepared following the reported procedures: [emim][Br] was synthesized by refluxing the N-methylimidazole with excess bromoethane at 50 °C for 48 h. The excess bromoethane was removed by evaporation and the crude product was recrystallized twice by ethyl acetate. The resulting precipitate was brownish and was dried in vacuum for 24 h under reduced pressure. Then 0.2 mol [emim][Br] and 0.1 mol $Pb(Ac)_2 \cdot 3H_2O$ were separately dissolved in solutions of methanol–water (4:1, v/v). Upon mixing the two solutions, a precipitate of $PbBr_2$ was produced, which was removed by filtration after cooling at −20 °C overnight. The solvent was removed from the filtrate by rotary evaporation, and the product [emim][Ac] was obtained by being dried in vacuum for 2 days at 80 °C. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 1.46–1.52 (m, 3H), 1.89–1.94 (t, 3H), 3.88–3.90 (t, 3H), 4.18–4.26 (m, 2H), 7.42–7.43 (d, 1H), 7.49–7.50 (d, 1H), 8.72 (s, 1H).

2.2.2. Preparation of [C_4SO_3Hmim][HSO_4]

Methylimidazole (0.11 mol) and 1,4-butane sulfone (0.10 mol) were dissolved in toluene (20 mL) and stirred for 3 h at 80 °C under a nitrogen atmosphere. A white precipitate formed which was filtered, washed with diethyl ether three times, and then dried in a vacuum. The resulting white precipitate (0.06 mol) was added to an aqueous solution of H_2SO_4 (0.06 mol), and then the mixture was stirred at room temperature for 2 h. Water was removed in vacuum to give the product. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 1.74–1.78 (m, 2H), 1.99–2.06 (m, 2H), 2.93–2.96 (q, 2H), 3.89 (s, 3H), 4.23–4.26 (t, 2H), 7.44 (t, 1H), 7.49–7.50 (t, 1H), 8.73 (s, 1H).

2.2.3. Preparation of [NMP][CH_3SO_3]

Under vigorous stirring, benzene (30 mL) was mixed with N-methyl-2-pyrrolidone (0.1 mol) in a 50 mL flask. Then, methane sulfonic acid (0.1 mol) was dropped slowly into the flask within 30 min in an ice-bath. The reaction lasted for another 4 h at room temperature. Benzene was removed under reduced pressure and was further dried at 90 °C in vacuum for 1 h, giving [NMP][CH_3SO_3] as a light yellow viscous liquid. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 2.0–2.08 (m, 2H), 2.42–2.48 (t, 2H), 2.78 (s, 3H), 2.83 (s, 3H), 3.48–3.54 (t, 2H).

2.2.4. Preparation of [Hmim][HSO_4]

[Hmim][HSO_4] was obtained by mixing 1-methylimidazole with concentrated sulfuric acid at 0–5 °C and stirring for 2 h at room temperature. The liquid was washed with ether several times and dried for 5 h in vacuum. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 1.46–1.52 (m, 3H), 1.89–1.94 (t, 3H), 3.88–3.90 (t, 3H), 4.18–4.26 (m, 2H), 7.42–7.43 (d, 1H), 7.49–7.50 (d, 1H), 8.72 (s, 1H).

2.2.5. Preparation of [C_4SO_3Hmim][CH_3SO_3]

Methylimidazole (0.11 mol) and 1,4-butane sulfone (0.10 mol) were dissolved in toluene (20 mL) and stirred for 3 h at 80 °C under a nitrogen atmosphere. A white precipitate formed, which was filtered, washed with diethyl ether three times, then dried in a vacuum. The resulting white precipitate (0.06 mol) was dissolved in water, and equal mole methane sulfonic acid was dropped slowly at room temperature. After dropping, the reaction mixture was slowly heated up to 90 °C and was stirred for 2 h, and then the water was removed under vacuum at 90 °C, giving [C_4SO_3Hmim][CH_3SO_3] as a light yellow viscous liquid. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 1.74–1.78 (m, 2H), 1.99–2.06 (m, 2H), 2.93–2.96 (q, 2H), 3.89 (s, 3H), 4.23–4.26 (t, 2H), 7.44 (t, 1H), 7.49–7.50 (t, 1H), 8.73 (s, 1H).

2.2.6. Preparation of [NMP][HSO_4]

[NMP]HSO_4 was obtained by mixing N-methyl-2-pyrrolidone (0.1 mol) with concentrated sulfuric acid (0.1 mol) at 0–5 °C and stirring for 4 h at room temperature. The liquid was then washed with ethyl acetate (3× 10 mL) and dried at 80 °C in vacuum. The IL was obtained in quantitative yield. ^1H NMR (400 MHz, D_2O): δ_H (ppm) = 2.01–2.09 (m, 2H), 2.42–2.48 (t, 2H), 2.84 (s, 3H), 3.50–3.54 (t, 2H).

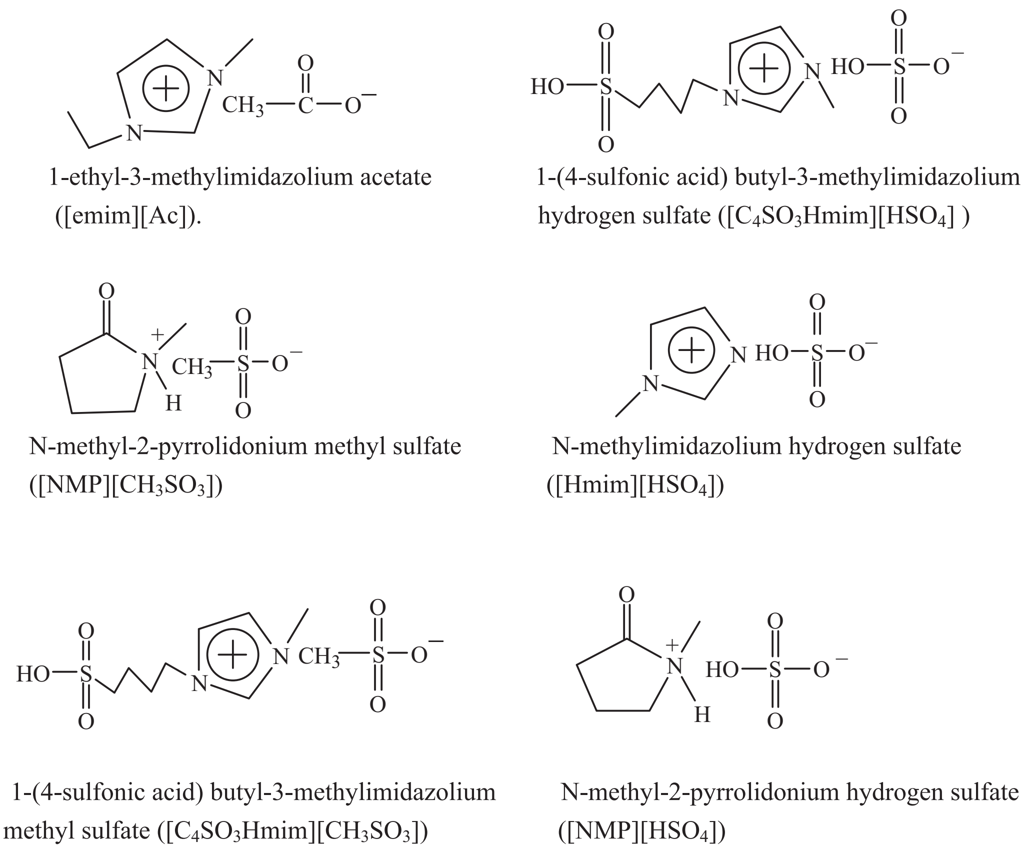


Fig. 1. Structures of ILs prepared and used in this paper.

2.3. Thermo gravimetric analyzer (TGA) of ILs

Considering that the thermal stability of ILs in cellulose hydrolysis temperature ranges (130–180 °C). So the thermal decomposition curves of the ILs were determined using a precisa TGA/DSC1/1100 SF thermo gravimetric analyzer. Each sample was analyzed in a platinum pan with nitrogen as the purge gas. In all experiments, the temperature was increased from 25 to 600 °C at a constant rate of 20 °C min^{-1}.

2.4. Catalytic conversion of MCC to HMF

The catalytic conversion of MCC to HMF was carried out in a round bottom flask that was heated in the oil-bath in the range from 130 °C to 180 °C. Typically, 0.5 g MCC was added into 10.0 mL [emim][Ac] solvent that was preheated under vigorous stirring until a transparent solution was obtained, followed by the addition of the desired 0.05–0.30 mol/L acidic IL catalyst and H_2O at the reaction temperature. At different time intervals, 0.5 mL samples were extracted, and quenched immediately with NaOH solution. The solution was centrifuged at 15,000 rpm for 10 min and further employed for the product analysis.

2.5. HMF analysis

The catalytic conversion of MCC to HMF by the acidic ILs is an extremely complex process in which a variety of reactions can take place together and many products will be formed. Based on our observation that the products detected is only HMF. The HMF was analyzed by high performance liquid chromatography (HPLC) on a Waters Alliance 2695 series chromatograph equipped with UV detector and a ODS-EP C_{18} reversed-phase column (250 mm × 4.6 mm, 5 μm). The mobile phase was water-acetonitrile (15:85, v/v) at a flow rate of 0.6 mL/min. HMF was detected at 280 nm, and the volume for each injection was 20 μL. The concentration of HMF was calculated based on the standard curve obtained with known concentrations of the standard substance. The yield of HMF was calculated from the equation: yield (wt%) = (weight of HMF)/(weight of cellulose put into the reactor) × 100.

3. Results and discussion

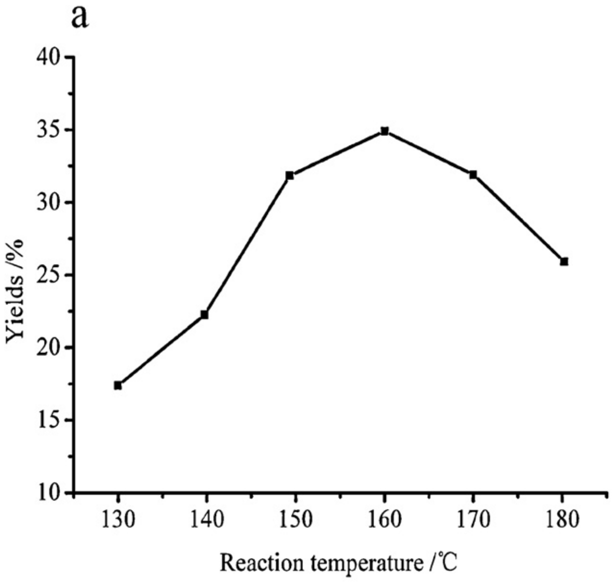
3.1. The thermal stability of ILs

The thermal decomposition curves of the ILs were determined using TGA. Neglecting small initial drops in weight occurring near 100 °C due to evaporation of retained moisture, a single pronounced decomposition event followed by slow loss of mass was observed in all cases. The maximum decomposition rate temperature ($T_{\max}$) computed from the TGA traces of the ILs. It is found that the ranges of $T_{\max}$ values of [emim][Ac], [C_4SO_3Hmim][CH_3SO_3], [C_4SO_3Hmim][HSO_4], [NMP][CH_3SO_3], [NMP]HSO_4 and [Hmim][HSO_4] are about 230–310 °C, 330–390 °C, 310–390 °C, 150–280 °C, 190–280 °C and 340–400 °C, respectively. Clearly, these ILs have good thermal stability in the temperature ranges of 130–180 °C.

3.2. Influence of reaction conditions on catalytic conversion of MCC to HMF

3.2.1. Effect of reaction temperature and time

The reaction temperature is a key parameter to determine the yield of HMF, the results on the effect of temperature are presented



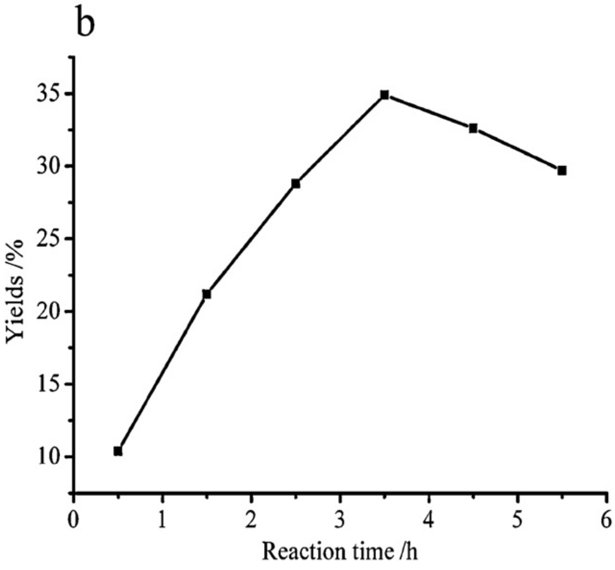


Fig. 2. (a) Effect of the reaction temperature: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.4 mL), $[C_4SO_3Hmim][HSO_4]$ (2 mL), t = 5.5 h. (b) Effect of the reaction time: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.4 mL), $[C_4SO_3Hmim][HSO_4]$ (2 mL), T = 160 °C.

in Fig. 2(a). It can be seen that the yield of HMF increases fast from 130 °C to 160 °C. However, the HMF yield decreases gradually when the temperature is further elevated to the higher range. These results show that the optimal temperature is 160 °C in the acidic IL $[C_4SO_3Hmim][HSO_4]$ catalytic conversion of MCC to HMF. To show the relationship between reaction time and the yield of HMF, the effect of reaction time is shown in Fig. 2(b). It is found that the yield of HMF increases gradually during the reaction from 0.5 h to 3.5 h. When the time is extended to 3.5 h or even longer, the yield of HMF decreases, which indicates that the conversion to byproducts is probably more rapid than the generation of HMF. It is consistent with the reported results that the HMF can be converted to levulinic acid, formic acid and furfural (Tao et al., 2010). The highest HMF yield of 34.9% can be obtained at 160 °C for 3.5 h.

3.2.2. Effect of the catalyst dosage

The performance of acid catalyst $[C_4SO_3Hmim][HSO_4]$ is examined under reaction conditions, such as 0.35 g MCC and 0.5–2.5 mL catalyst at 160 °C for 3.5 h in 0.4 mL distilled water. It can be seen from Fig. 3 that without catalyst, the MCC cannot be hydrolyzed into HMF under such reaction conditions, and the conversion of MCC to HMF can be promoted by using acid catalysts. With increasing the dosage of catalyst 0.5–2.5 mL, the yield of HMF increases from 20.5% and 35.3%. This increase can be attributed to an increase in the availability of the number of catalytically active sites. As mentioned by Shimizu, Furukawa, Kobayashi, Itaya, and Satsuma (2009), the acid catalyst with stronger Brønsted acidity could result in the higher relative rate of acid-catalyzed cellulose hydrolysis. It should be noted that the HMF yield shows little additional increase within higher catalyst dosage over 1.5 mL, which implies that there are sufficient catalytic active sites available for the substrate MCC in the system under the experimental conditions. Therefore, considering the cost of the experiment, we chose 1.5 mL as the dosage of $[C_4SO_3Hmim][HSO_4]$.

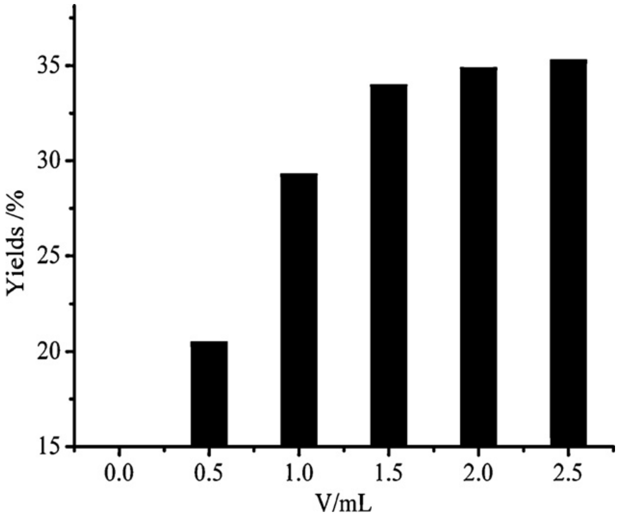


Fig. 3. Effect of the catalyst dosage: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.4 mL), T = 160 °C, t = 3.5 h.

3.2.3. Effect of metal salts

Knowing that the metal salts in IL was demonstrated to be an efficient catalyst system for the conversion of cellulose to HMF (Binder & Raines, 2009; Zhao et al., 2007). In present work, some metal salts are investigated and we first chose $CuCl_2$ in our present system. As shown in Fig. 4, the existence of metal salts can improve the yield of HMF. Compared with other metal salts, the promoting effect of copper salt is remarkable. In the presence of Cu^{2+}, the yield of HMF increases about 30%. The reason for the promotional effect of the copper salt may be due to the Cu^{2+} coordination interaction. In addition, the Cu^{2+} could play an important role in promoting rapid conversion of the α-glucose to the β-glucose and isomerization of β-glucose to fructose, which improves the yield of HMF (Zhao et al., 2007). Moreover, the comparison of the promoting catalytic activity of $CuCl_2$ and $FeCl_2$ indicates that the yield of HMF is higher when $CuCl_2$ is used as co-catalyst, therefore we conclude that the promoting effect of Cu^{2+} is larger than Fe^{2+} in catalytic conversion of MCC.

3.2.4. Effect of water dosage

Shimizu, Uozumi, and Satsuma (2009) found in the conversion of fructose to HMF under acidic condition, full removal of water decreased the HMF yield while mild evacuation could improve the HMF yield. Considering that water dosage may affect conversion of cellulose to HMF, in this study several special experiments are designed in order to investigate the influence of water on the conversion of cellulose to HMF. As listed in Fig. 5, it is shown that the optimal dosage of H_2O is 0.2 mL, we obtain the maximal yield of HMF reached 62.6%. While the dosage of H_2O is 0.6 mL, the yield of

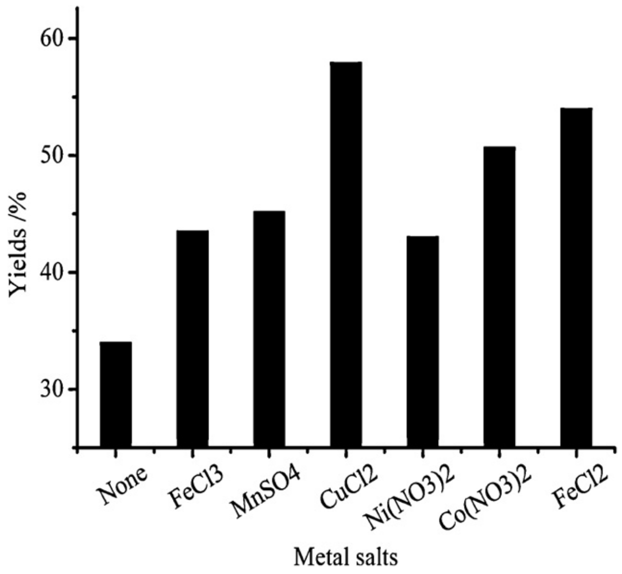


Fig. 4. Effect of metal salts: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.4 mL, $C = 0.2$ mol/L), [C_4SO_3Hmim][HSO_4] (1.5 mL), $T = 160\,^{\circ}C$, $t = 3.5$ h.

HMF is only 47.9%. The results confirm that the presence of a small amount of water in the reaction system does promote the reaction, but more water has a negative effect on the conversion of cellulose to HMF and results in the decomposition of HMF to levulinic acid, which is consistent with the previous reports by Hu et al. (2008). In addition, with the water content increasing, the selectivity of the HMF decreases, the results are also in a good agreement with previous reported by Qi, Watanabe, Aida, and Smith (2008).

3.2.5. *Effect of Cu^{2+} concentration*

Conversion of MCC to HMF by varying the concentration of Cu^{2+} from 0.05 to 0.30 mol/L was investigated under reaction conditions: 1.5 mL of catalyst, 0.2 mL of water and at 160 °C for 3.5 h (Fig. 6). It can be seen that the HMF yield increases first, and then decreases with increasing concentration of Cu^{2+}. The HMF yield reaches a maximum of 64.9%, when concentration of Cu^{2+} was 0.1 mol/L.

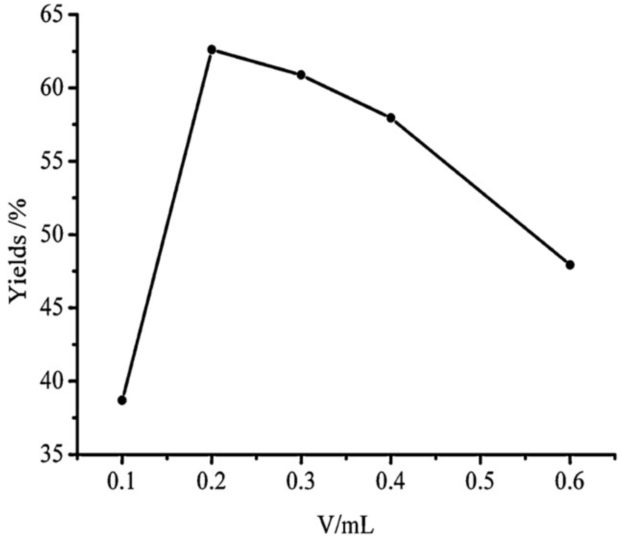


Fig. 5. Effect of H_2O dosage: MCC (0.35 g), [emim][Ac] (10 mL), $T = 160\,^{\circ}C$, $t = 3.5$ h, $C_{(Cu^{2+})} = 0.2$ mol/L, [C_4SO_3Hmim][HSO_4] (1.5 mL).

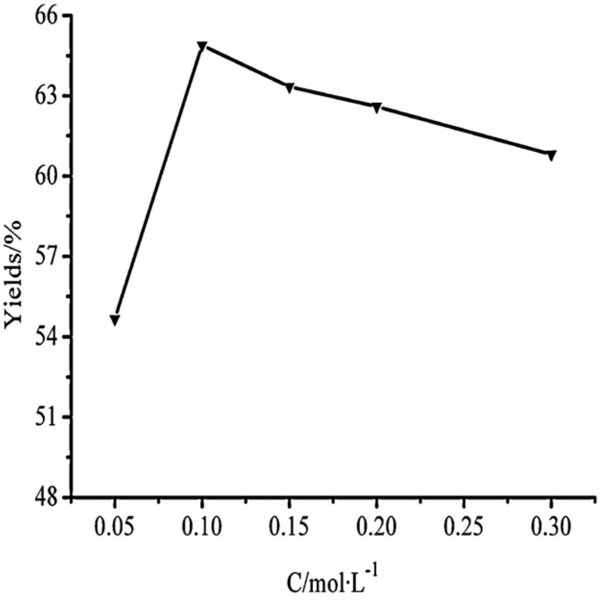


Fig. 6. Effect of Cu^{2+} concentration: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.2 mL), $T = 160\,^{\circ}C$, $t = 3.5$ h, [C_4SO_3Hmim][HSO_4] (1.5 mL).

3.2.6. *Effect of various acidic ILs*

The results of conversion of cellulose to HMF by the various acidic ILs catalysts with co-catalyst of 0.1 mol/L $CuCl_2$ are exhibited in Fig. 7. With various acidic ILs as catalysts, the present system is effective on the MCC conversion to HMF. It is remarkable that the presence of SO_3H-functionalized ILs shows better catalytic performance than other ILs and results in higher yield of HMF. In case of [C_4SO_3Hmim][HSO_4] and [C_4SO_3Hmim][CH_3SO_3], the yield of HMF is 64.9%, 69.7%, respectively. It should be noted that [C_4SO_3Hmim][HSO_4] and [C_4SO_3Hmim][CH_3SO_3] have same cation [C_4SO_3Hmim]$^+$, but the anions are HSO_4^-, $CH_3SO_3^-$, respectively. This implies that the anions can influence the catalytic activity of such as SO_3H-functionalized ILs. Moreover, the ILs have the same cation but containing $CH_3SO_3^-$ anion exhibits better catalytic performance than those containing HSO_4^- under the same conditions.

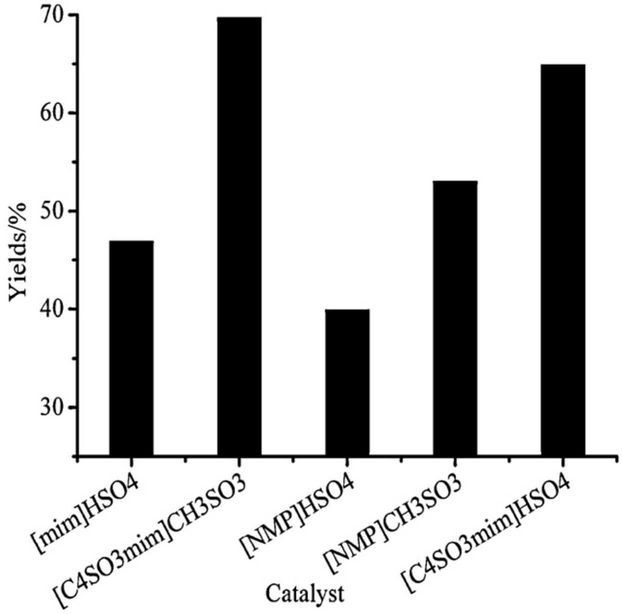


Fig. 7. Effect of various acidic ILs: MCC (0.35 g), [emim][Ac] (10 mL), H_2O (0.2 mL), $C_{(Cu^{2+})} = 0.1$ mol/L, $T = 160\,^{\circ}C$, $t = 3.5$ h.

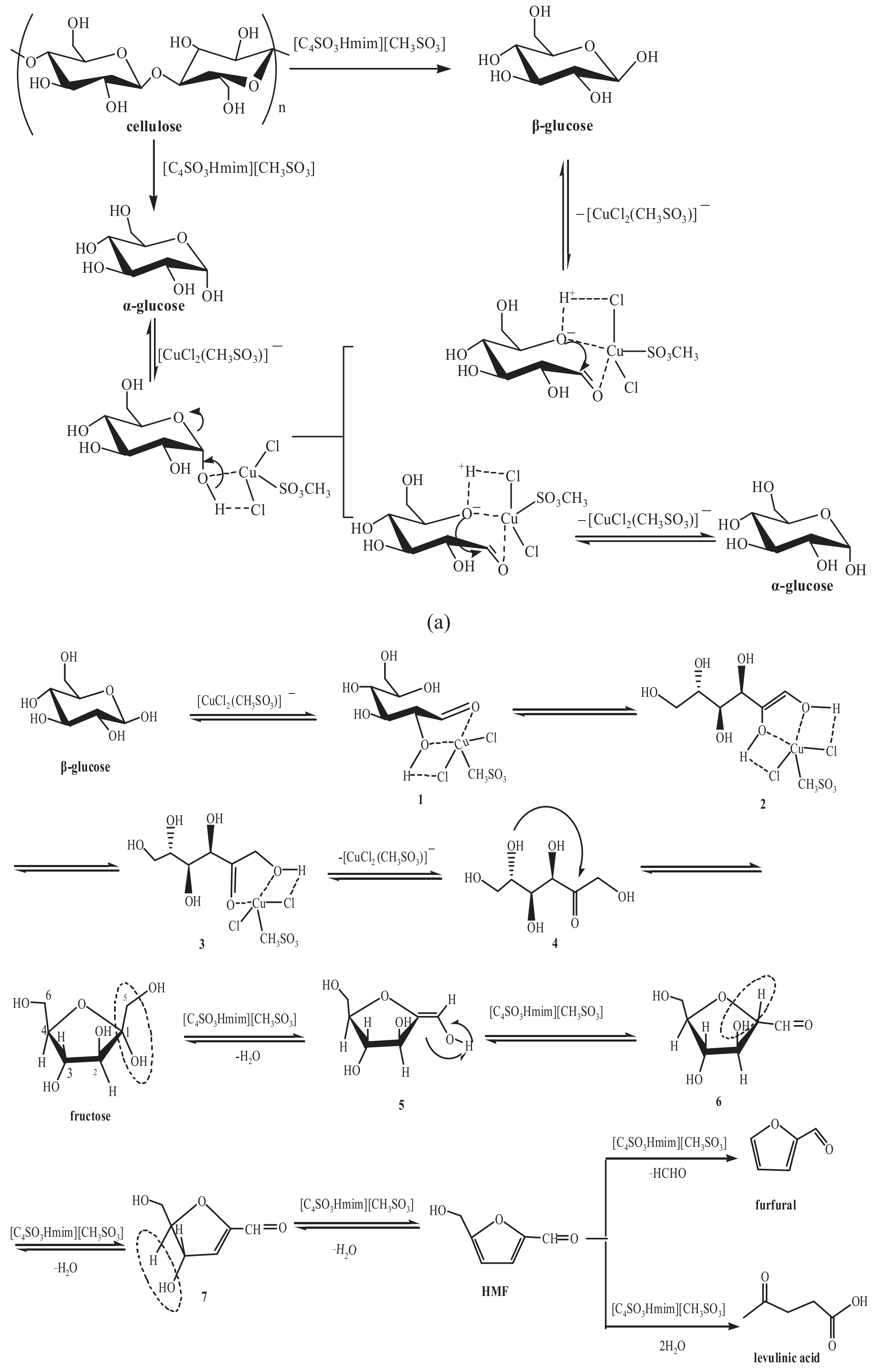


Fig. 8. (a) Putative mechanism of $CuCl_2$ and $[C_4SO_3Hmim][CH_3SO_3]$ promote conversion of cellulose into β-glucose. (b) Putative mechanism of $CuCl_2$ and $[C_4SO_3Hmim][CH_3SO_3]$ promote conversion of β-glucose into HMF.

It can be concluded that the acidity and structure of ILs had large effects on the conversion of MCC to HMF.

3.3. Mechanism of cellulose transforming to HMF

As we know, the glycosidic bonds in cellulose are weakened by Brønsted acid attack. A Lewis acid can also weaken the glycosidic bonds through binding with a glycosidic oxygen atom in a similar manner to protic acid, leading to the dehydration of polysaccharide to produce monosaccharides (Guan, Cao, Guo, & Mu, 2011). To explain the results of conversion of MCC to HMF, we propose a mechanism in which $CuCl_2$ in $[C_4SO_3Hmim]CH_3SO_3$ forms $[CuCl_2(CH_3SO_3)_n]^{n-}$ complexes in a similar manner to $LnCl_3$ as reported by Hines et al. (2008). We suggest that $[CuCl_2(CH_3SO_3)]^-$ plays a role in proton transfer, and facilitates mutarotation of α-glucose. These complexes would promote rapid conversion of the α-glucose to the β-glucose through hydrogen bonds between the chloride anions and the hydroxyl groups (as shown in Fig. 8(a)). The putative mechanism of $CuCl_2$ and $[C_4SO_3Hmim]CH_3SO_3$ promote conversion of β-glucose into HMF is shown in Fig. 8(b). Intermediate 1 is generated through the interactions between the hydroxyl groups in β-glucose and Cu atom in $[CuCl_2(CH_3SO_3)]^-$, characterized by binding of —CHO group in the open form of glucose to $[CuCl_2(CH_3SO_3)]^-$, then intermediate 1 is transformed into 1,2-enediol intermediate 2, which involves the formation of a five-membered-ring chelate between the two neighboring hydroxyl groups in glucose and Cu atom, the next step occurs with the conversion of the enolate 2 into intermediate 3, which can finally release the $[CuCl_2(CH_3SO_3)]^-$ moiety and convert into fructose via a ring closure. Then loses a water molecule and change to enediol intermediate 5 and rapidly isomerizes into its aldehyde form 6, and then $[C_4SO_3Hmim][HSO_4]$ interacts with the oxygen atoms connected with C_2 and aldehyde group leading to the formation of intermediate 7, Subsequently releases a water molecule to produce the $C_1{=}C_2$ in 7, follows by the removal of a water molecule to give the $C_3{=}C_4$ in the product HMF. Then with the effect of $[C_4SO_3Hmim][HSO_4]$, the HMF is combined with water to generate levulinic acid or lost formaldehyde to produce furfural.

4. Conclusion

Preparation of HMF through the conversion of MCC is one of the most important approaches to utilize biomass as promising substitutes for petroleum-based chemicals, and efficient catalytic conversion of cellulose to HMF has been achieved using small amounts of acidic ILs as catalysts and metal salts as co-catalysts under mild conditions. $[C_4SO_3Hmim][CH_3SO_3]$ shows higher catalytic activity among different ILs. Moreover, Cu^{2+} could play an important role in the conversion of cellulose to HMF as co-catalyst. 69.7% yield of HMF was obtained for 3.5 h at 160 °C in the presence of 1.5 mL $[C_4SO_3Hmim][CH_3SO_3]$ and 0.2 mL H_2O ($C_{(Cu^{2+})} = 0.1$ mol/L). The effective catalyst system may be proved valuable in facilitating the conversion of cellulose into HMF. To better understand the catalysis of Cu^{2+}, the influence of different copper salts on the reaction will be studied in our future work. In addition, the effect of MCC dosage and ILs recycling on the conversion of MCC is remaining subjects in future studies.

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