

SO₃H-functionalized acidic ionic liquids as catalysts for the hydrolysis of cellulose

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ABSTRACT

The conversion of cellulose into valuable chemicals to deal with the depletion of fossil fuel has got much attention. Completing the hydrolysis of cellulose under mild conditions is the key step. In this study, six kinds of SO₃H-functionalized acidic ionic liquids were used as acid catalyst to promote the hydrolysis of cellulose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl). All of them were efficient for the hydrolysis of cellulose, with the maximum total reducing sugars (TRS) yields over 83% at 100 °C. Acidic ionic liquids with analogous structures showed similar catalytic activities. Triethyl-(3-sulfo-propyl)-ammonium hydrogen sulfate (IL-5 in this study) was the optimum ionic liquid for cellulose hydrolysis, with the maximum TRS yield at 100 °C up to 99% when the dosage used was 0.2 g. In addition, the water in [BMIM]Cl had negative effect on cellulose hydrolysis. Therefore, controlling the content of water in a comparatively low level is quite necessary.

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1. Introduction

In the past decade, more attentions have been paid on the conversion of renewable biomass into valuable chemicals to deal with the crisis of fossil fuels. The use of renewable biomass, instead of fossil fuels, also caters to the concept of green chemistry for the decrease of exhausting carbon dioxide (Ragauskas et al., 2006; Yat, Berger, & Shonnard, 2008). To reduce the pressure of the food supply, inedible cellulose is a promising feedstock. The critical step is to complete the hydrolysis of cellulose into monosaccharides (Onda, Ochi, & Kazumichi, 2008). However, the tight hydrogen-bonding network and van der Waals interactions greatly stabilize cellulose (Nishiyama, Sugiyama, Chanzy, & Nagan, 2003), which makes cellulose recalcitrant to hydrolyze. So a pretreatment process to reduce the crystallinity of cellulose is highly required. The traditional chemical pretreatments include alkali and acid pretreatments, organic solvents pretreatment, etc. (Kumar, Barrett, Delwiche, & Stroev, 2009). Due to the output of a lot of waste acid and the emission of volatile organic solvents, all of them are environmentally detrimental. Hence, more efficient and environment friendly pretreatment procedures are required for the conversion of cellulose to monosaccharides.

Since Swatloski, Spear, Holbrey, and Rogers (2002) showed that ionic liquid [BMIM]Cl was a powerful solvent for cellulose, up to 25 wt% of cellulose could be dissolved in IL, more attentions have been paid on the hydrolysis of cellulose using ILs (Fu and Mazza, 2011; Kim, Dwiattmoko, & Choi, 2010). According to the nature

of IL, it can be used as the solvent or catalyst. After the dissolution of cellulose in ILs, dilute acid, solid acid and cellulase can be used to promote the hydrolysis of cellulose (Dwiattmoko, Choi, Suh, Suh, & Kung, 2010; Li, Wang, & Zhao, 2007; Li, Filpponen, & Argyropoulos, 2010; Rinaldi, Palkovits, & Schuth, 2008; Sievers, Valenzuela-Olarte, Marzalletti, Agrawal, & Jones, 2009; Watanabe, 2010). Each of the hydrolysis process above has its advantages and disadvantages. Dilute acid in IL is an efficient system for the hydrolysis of lignocellulosic biomass under mild conditions. However, the disposal of waste acid remains a difficult task. The depolymerization of cellulose in IL over solid catalysts has been performed successfully. Unfortunately, excessive catalyst loading is required and solid catalysts are difficult to be separated from the solid residues. Although the enzyme hydrolysis can be performed in mild conditions, the negative effects on enzyme from IL residues cannot be ignored (Turner, Spear, Huddleston, Holbrey, & Rogers, 2003; Zhao et al., 2009). In general, these processes above have significant drawbacks such as corrosion of reactors, difficulty in separation of catalysts, high loading of catalysts and high cost of enzymes. Acidic ionic liquid, which combines the advantages of mineral acid and ionic liquid, can behave as both the solvent and catalyst in the process of biomass conversion.

In recent years, many kinds of acidic ionic liquids have been used as solvent or acid catalyst for the conversion of saccharides into valuable chemicals. Amarasekara and Owereh (2009) reported the first application of acidic ionic liquids for the dissolution and hydrolysis of cellulose under moderate reaction temperatures, and the highest total reducing sugar (TRS) yield of 62% was attained in 1 h of preheating at 70 °C and 30 min of heating at 70 °C after adding water. Then the group (Amarasekara and Wiredu, 2011) investigated the hydrolysis of cellulose in dilute aqueous

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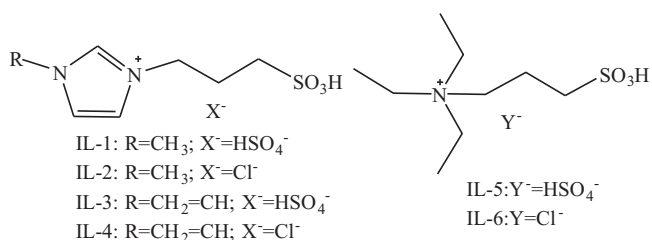


Fig. 1. Acidic ionic liquids used in this study.

solutions of 1-(1-propylsulfonic)-3-methylimidazolium chloride ([C₃SO₃Hmim]Cl) and produced TRS yield of 28.5% after heating at 170 °C for 3.0 h. Jiang, Zhu, Ma, Liu, and Han (2011) investigated several kinds of acidic ionic liquids bearing –COOH, –SO₃H as the catalysts for direct conversion of cellulose to glucose and 5-hydroxymethylfurfural (HMF) in [BMIM]Cl. The acidic ionic liquids functionalized with –SO₃H greatly increased the reaction rate of the cellulose hydrolysis, with TRS yields up to 85% in 1 h. Tao, Song, and Chou (2011a) used the ionic liquid [C₄SO₃Hmim] HSO₄ as the catalyst to dehydration of fructose, high fructose conversion of 100% with HMF yield of 94.6% was obtained at 120 °C for 180 min reaction time. Then the group (Tao, Song, & Chou, 2011b) chose sixteen kinds of SO₃H-functionalized acidic ionic liquids for the production of HMF and furfural from cellulose, the results showed that MnCl₂-containing ionic liquids were efficient catalysts for the selectivities of HMF. Acidic ionic liquid, which combines the advantages of mineral acid and ionic liquid, has higher catalytic activity for the fracture of glycosidic bonds and can be reused conveniently.

At present, most of the acidic ionic liquids used in the literatures were based on imidazoles and pyridine. In this study, six kinds of acidic ionic liquids (Fig. 1) based on 1-methylimidazole, 1-vinylimidazole, triethylamine were applied as catalysts to catalyze the hydrolysis of microcrystalline cellulose (MCC) in [BMIM]Cl. The main factors influencing the hydrolysis of cellulose were examined, involving the hydrolysis temperature, the dosage of acid catalyst, the structure of acidic ionic liquid and the purity of solvent [BMIM]Cl.

2. Materials and methods

2.1. Materials

1-Methylimidazole (99.0%) and 1-vinylimidazole were purchased from Yancheng Calechem Co. Ltd. (Jiangsu, China); triethylamine was purchased from Tianjin chemical reagent company (Tianjin, China); microcrystalline cellulose (average particle size 50 μm) was purchased from Acros (NJ, USA); 1-chlorobutane (98%) was purchased from Guangfu Fine Chemical Research Institute (Tianjin, China).

2.2. Typical procedure for synthesis of ionic liquids

[BMIM]Cl used for the study was prepared according to the method described in the literature (Huddleston, Willauer, Swatloski, Visser, & Rogers, 1998).

2.3. Synthesis of SO₃H-functionalized ionic liquids

The acidic ionic liquids used in this study were synthesized according to the literatures (Cole et al., 2002; Qian and Liu, 2011). The acidic ionic liquid IL-1 (1-(1-propylsulfonic)-3-methylimidazolium hydrogen sulfate) was prepared as follows: 1,3-propanesulfone (12.21 g, 0.1 mol) was dissolved in acetone and

a stoichiometric amount of 1-methylimidazole (8.21 g, 0.1 mol) was added dropwise. The mixture was stirred for 3 h at ambient temperature to get the white solid zwitterion. Then the zwitterion was washed with acetone repeatedly and dried in vacuum for 5 h. Equimolar amount of concentrated sulfuric acid was added slowly and the mixture was stirred for 6 h at 80 °C to get viscous liquid. Then the viscous liquid was washed three times with ethyl acetate and dried in vacuum to form IL-1. Its NMR spectral characteristic was shown as:

¹H NMR (300 MHz, D₂O): δ 2.039–2.097 (m, 2H), 2.661 (t, 2H), 3.654 (s, 3H), 4.120 (t, 2H), 4.694 (t, 1H), 7.213 (d, 1H), 7.284 (d, 1H), 8.518 (s, 1H).

The synthesis of ionic liquids IL-2 to IL-6 followed the same protocol as was used for the preparation of IL-1. Their NMR spectral characteristics were shown as follows:

IL-2: ¹H NMR (300 MHz, D₂O): δ 1.848–1.877 (m, 2H), 2.461 (t, 2H), 3.453 (s, 3H), 3.912 (t, 2H), 4.792 (t, 1H), 7.011 (d, 1H), 7.075 (d, 1H), 8.288 (s, 1H).

IL-3: ¹H NMR (300 MHz, D₂O): δ 2.146–2.175 (m, 2H), 2.747–2.762 (m, 2H), 4.229 (t, 2H), 4.667 (t, 1H), 5.248–5.634 (t, 2H), 6.967 (s, 1H), 7.446 (s, 1H), 7.611 (s, 1H), 8.907 (s, 1H).

IL-4: ¹H NMR (300 MHz, D₂O): δ 2.114–2.144 (m, 2H), 2.717–2.747 (m, 2H), 4.199 (t, 2H), 4.688 (t, 1H), 5.218–5.606 (t, 2H), 6.939 (s, 1H), 7.417 (s, 1H), 7.585 (s, 1H), 8.878 (s, 1H).

IL-5: ¹H NMR (300 MHz, D₂O): δ 1.069 (t, 9H), 1.887–1.950 (m, 2H), 2.769 (t, 2H), 3.112 (m, 8H), 4.679 (s, 1H).

IL-6: ¹H NMR (300 MHz, D₂O): δ 1.035 (t, 9H), 1.852–1.915 (m, 2H), 2.734 (t, 2H), 3.079 (m, 8H), 4.689 (s, 1H).

2.4. Typical procedure for hydrolysis of cellulose into TRS

MCC (0.1 g) in [BMIM]Cl (2.0 g) was heated with stirring at 100 °C to form a transparent solution. Followed by the addition of the acidic IL and 0.1 ml H₂O, the mixture was stirred at a given temperature. At different time intervals, certain amount of sample was extracted and quenched immediately by 5 ml distilled water. The supernatant was subjected to TRS analysis.

2.5. Analysis method

The amount of TRS was measured using the DNS method (Miller, 1959). The DNS reagent was prepared according to an IUPAC method. 1 ml of supernatant was transferred to a test tube, then 3 ml of DNS reagent was added, the resulting solution was heated at 100 °C for 10 min. Then the absorbance was measured at 490 nm using UV–Vis spectrophotometer. The concentration of the TRS was calculated by employing a standard curve prepared using glucose.

3. Results and discussion

3.1. The influence of reaction temperature on the hydrolysis of MCC

The first step of the study was designed to obtain the optimum temperature condition for the hydrolysis of MCC in [BMIM]Cl with acidic ionic liquid as the catalyst. Most researchers set the hydrolysis temperature at 100 °C. To confirm the effect of hydrolysis temperature on the yield of TRS, we studied the hydrolysis of MCC at 80 °C and 100 °C, respectively. Fig. 2 shows the effect of IL-1 on the TRS yield under different temperatures. Obviously, the hydrolysis rate at 100 °C was higher than the rate at 80 °C. 62.49% of TRS yield was obtained in 1 h at 100 °C, while 36.85% of TRS yield was produced at 80 °C. From the tendency of the given curve at 80 °C, a maximum TRS yield of ~67% was achieved after 5 h. The

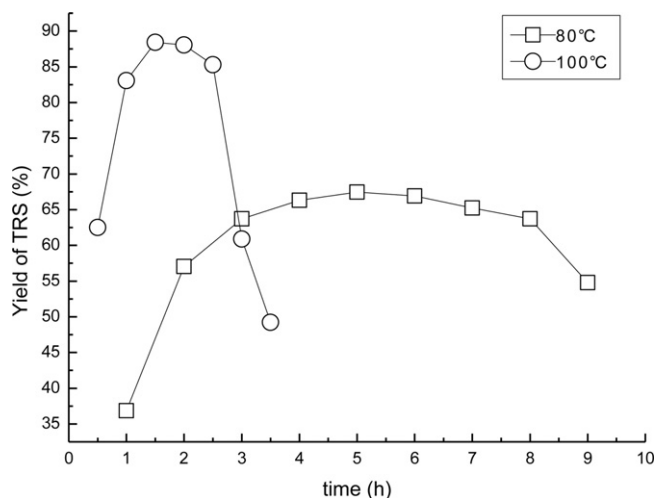


Fig. 2. TRS yield of cellulose hydrolysis catalyzed by IL-1 at different temperatures in [BMIM]Cl (0.1 g MCC, 2.0 g [BMIM]Cl, 0.2 g IL-1, 0.1 ml H₂O).

TRS yields kept nearly constant and had a slowly decrease from the 8th hour due to the dehydration of glucose. Compared to 80 °C, it only took 1.5 h to reach the peak TRS yield of 88.4% and had a sharply decline after 2 h at 100 °C. In addition, the other five kinds of acidic ionic liquids followed the similar pattern as IL-1. Fig. 3 shows the maximum TRS yields of cellulose hydrolysis catalyzed by all the acidic ionic liquids used in our study. It can be seen that all the acidic ionic liquids used are effective to promote the hydrolysis of cellulose. The maximum TRS yields at 100 °C were all above 83%, much higher than the TRS yields at 80 °C. There is no doubt that reaction temperature has a great effect on the hydrolysis of cellulose and the dehydration of glucose. A higher hydrolysis temperature can shorten the reaction time and get higher TRS yield. Meanwhile, the degradation of glucose begins earlier, the downward trend curve is more obvious.

3.2. Effect of the acidic liquid dosage on the hydrolysis of cellulose

The effect of acidic ionic liquid dosage on the hydrolysis of cellulose cannot be ignored. From Fig. 3, we can see that IL-5 is one of the best catalysts for the hydrolysis of cellulose. In our research,

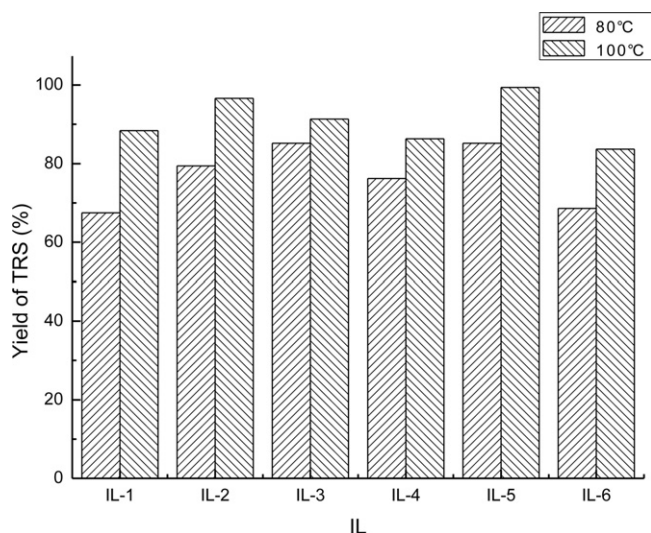


Fig. 3. The maximum TRS yield of MCC hydrolysis catalyzed by kinds of acidic ILs at 80 °C and 100 °C, respectively.

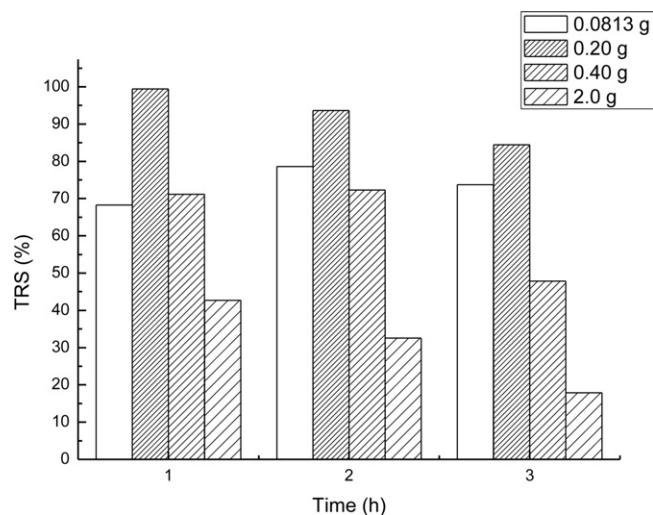


Fig. 4. Effect of IL-5 dosage on MCC hydrolysis (0.1 g MCC, 2.0 g [BMIM]Cl, 0.1 ml H₂O, T = 100 °C).

IL-5 was chosen as the catalyst to study the effect of IL dosage on MCC hydrolysis. The amount of IL-5 used was 0.0813 g, 0.2 g, 0.4 g and 2.0 g, respectively. As it was depicted in Fig. 4, when the dosage of IL-5 increased from 0.0813 g to 0.20 g, the yield of TRS increased obviously, from 68% to 99% in 1 h. When the amount increased from 0.2 g to 0.4 g, the TRS yield in 1 h decreased from 99% to 72%. When the amount of IL-5 was 2.0 g, only 42% of TRS yield was obtained after 1 h. It also showed that with the reaction time getting longer, the differences of TRS yields got smaller, which was attributed to the dehydration of more monosaccharides. In summary, the TRS yields decreased with the dosage of IL-5 increasing (above 0.2 g) and the react time prolonging due to the dehydration rate of glucose monomer increasing, which led to less accumulation of TRS and the increase of dehydration products. In our study, choosing the amount of IL-5 at 0.2 g was more reasonable.

3.3. Hydrolysis of MCC with different ionic liquids

The acidity and structure of ionic liquids had great effects on MCC hydrolysis. The acidic liquids used in this study involved three kinds of cations and two kinds of anions. Fig. 5 shows the hydrolysis

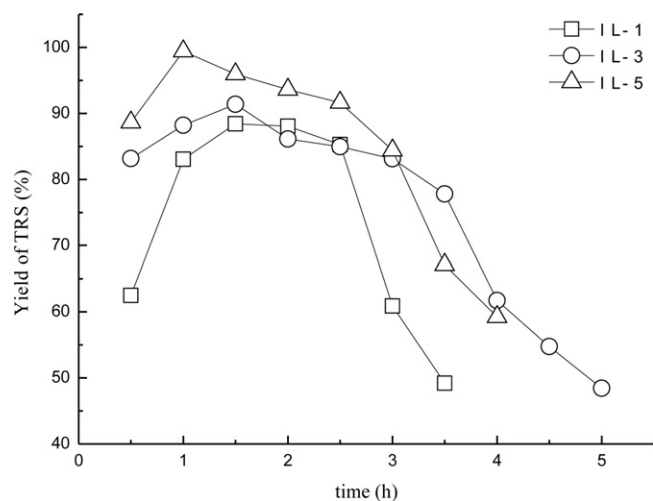


Fig. 5. Hydrolysis of MCC catalyzed by IL-1, IL-3, and IL-5, respectively (0.1 g MCC, 2.0 g [BMIM]Cl, 0.2 g acidic ionic liquid, 0.1 ml H₂O, T = 100 °C).

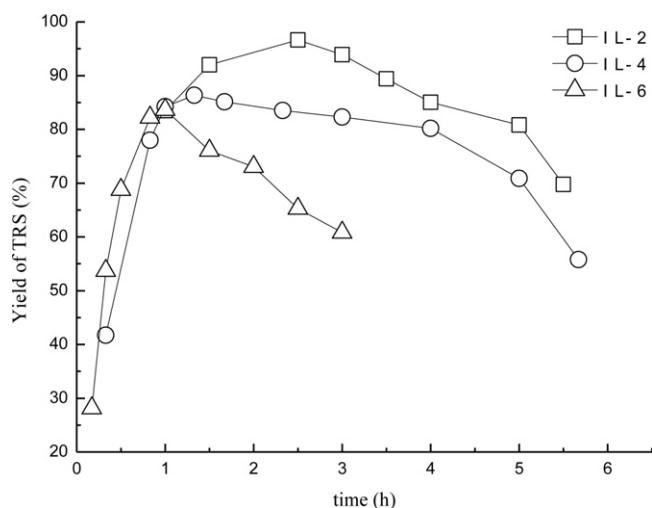


Fig. 6. Hydrolysis of MCC catalyzed by IL-2, IL-4, and IL-6, respectively (0.1 g MCC, 2.0 g [BMIM]Cl, 0.2 g acidic ionic liquid, 0.1 ml H₂O, T = 100 °C).

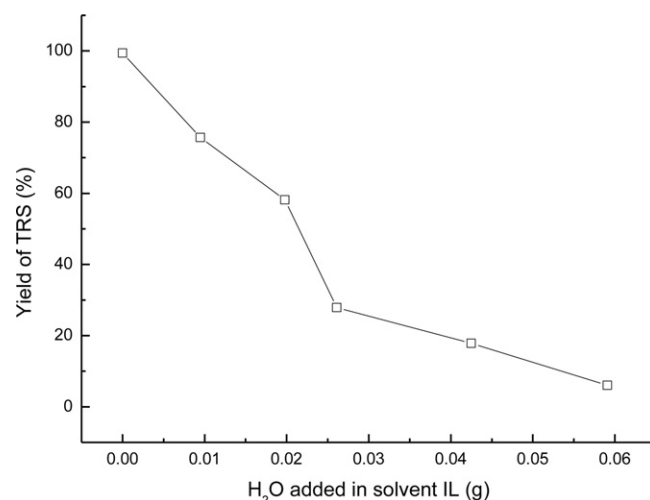


Fig. 7. Effect of H₂O added in [BMIM]Cl on the hydrolysis of MCC catalyzed by IL-5.

of MCC catalyzed by ionic liquids with HSO₄[−] (IL-1, IL-3 and IL-5) at 100 °C. As seen in Fig. 5, compared to IL-1 and IL-3, IL-5 performed steadily well, the TRS yields were above 90% from the reaction time of 1–2.5 h. The hydrolysis of MCC catalyzed by ionic liquids with anion Cl[−] (IL-2, IL-4 and IL-6) were shown in Fig. 6. It showed that the best result was achieved with IL-2 as the catalyst, and then was IL-4. There is no doubt that the catalytic activity of acidic ionic liquid is affected by the nature of anion as well as the cation. Fig. 5 showed that IL-1 and IL-3 performed similar TRS yields tendency due to the same anion and similar cations. There was a decrease in TRS yields after a maximum yield period. In our study, the acid-catalyzed hydrolysis of cellulose is a homogeneous reaction and the conversion rate of cellulose is nearly 100%, in the follow-up stage of the reaction, the degradation of glucose is the dominant reaction. The consumption of large amounts of glucose led to the reduction of TRS. As shown in Fig. 6, compared to the ILs with HSO₄[−] as anion, the influences of cations on the hydrolysis of MCC were distinctive for the ILs with Cl[−] as anion. The hydrolysis curves catalyzed by IL-2 and IL-4 had analogous tendency due to their same anion (Cl[−]) and similar cations. With IL-2 and IL-4 as catalyst, the TRS yields changed little from 1 h to 4 h. Obviously, the dehydration of glucose into HMF is relatively slow. It might have great relationship with the nature of IL-2 and IL-4, such as fewer active acid sites and larger viscosities. The performance of IL-6 based on triethylamine was different from IL-2 and IL-4, the maximum TRS yield (83.6%) was lower and the TRS yields decreased sharply after 1 h. We speculated that less active acid sites caused the lower TRS yield and the lower viscosity of IL-6 led to the sharply decline of TRS yield. In addition, the different interactions between acidic ionic liquids and solvent IL might be another critical factor. Although IL-5 had the same cation with IL-6, IL-5 showed better result, with the TRS yield up to 99% in 1 h at 100 °C, which was attributed to more active acid sites accelerating the fracture of glycosidic bonds. In summary, for the acidic ionic liquids used in our study, the structure of ionic liquids had effects on MCC hydrolysis due to their different acidities, active acid sites and viscosities. Especially the active acid site and viscosity, both of them greatly affected the catalytic activity of IL. More active acid sites could accelerate the fracture of glycosidic bonds and produced more TRS. However, the dehydration of glucose got faster as well and the TRS yields had a sharply decline. To some extent, larger viscosity had negative effects on the attacks from H⁺ to the β-1,4-glycosidic bonds, but the TRS yield could remain invariable for a long time. All the factors are interactional and the mechanism is very complicated.

3.4. Effect of the purity of [BMIM]Cl on the hydrolysis of cellulose

After the dissolution of the cellulose in [BMIM]Cl completely, the β-1,4-glycosidic bonds of carbohydrate dissolved in the IL could be easily attacked by the sulfonic acid groups of the acidic ionic liquids, which promotes the hydrolysis of cellulose. Impurities in the solvent [BMIM]Cl can impair the dissolution capacity of IL. Considering the synthesis process and the hygroscopicity of [BMIM]Cl, impurities in [BMIM]Cl can be residue reactant, side-reaction products or water. In our study, it was found that the water in [BMIM]Cl had great effects on the hydrolysis of cellulose. The water in [BMIM]Cl is a hamper for the dissolution of cellulose in [BMIM]Cl and it has been shown that 1 wt% of water in [BMIM]Cl is sufficient to prevent cellulose dissolution (Rogers et al., 2002). As it was shown in Fig. 7, with the increasing of deionized water added in [BMIM]Cl, the TRS yield declined sharply. 0.0261 g H₂O added in [BMIM]Cl led to the decline of TRS yield from 99% to 27.9%. We speculated that water impaired the dissolution capacity of IL by forming competitive hydrogen-bonding to the cellulose hydroxyl groups, which caused the incomplete dissolution of cellulose. When the amount of H₂O added increased to 0.0591 g, only 6% TRS yield was obtained. In addition, we found that when the cellulose was dissolved in [BMIM]Cl completely, after adding deionized water and acidic ionic liquid, a kind of intractable gel might form. This gel was hard to be broken out. To some extent, increasing the amount of acid catalyst would change the condition, but the TRS yield was quite low. Binder and Raines (2010) had reported the similar phenomenon that a 5 wt% solution of cellulose in [EMIM]Cl formed an intractable gel when the solution was diluted to 10 wt% water. In general, the water in solvent IL had negative effect on the dissolution of cellulose and led to the decrease of the β-1,4-glycosidic bonds of carbohydrate dissolved in the IL. Therefore, strict purification procedures for [BMIM]Cl are required to ensure the hydrolysis of cellulose effectively.

4. Conclusions

In this study, six kinds of acidic ionic liquids based on 1-methylimidazole, 1-vinylimidazole, triethylamine were applied as catalysts to promote the hydrolysis of MCC in [BMIM]Cl. All of them were efficient acid catalyst, with the maximum TRS yields over 83%. Especially the acidic ionic liquid based on triethylamine (IL-5), the TRS yield in 1 h at 100 °C was up to 99% when the dosage of IL-5 was 0.2 g. In addition, the amount of catalyst used had great effect on the hydrolysis products. When the dosage of acid catalyst was

higher, the dehydration rate of monosaccharides increased, which led to less accumulation of TRS and the increase of further dehydration products. Moreover, the structure of ionic liquids had effects on MCC hydrolysis due to their different acidities, active acid sites and viscosities. In addition, it should be noted that the presence of water in [BMIM]Cl had conspicuous effect on the hydrolysis of cellulose, 0.0261 g H₂O added in [BMIM]Cl led to the decline of TRS yield from 99% to 27.9%. So strict purification procedures for the synthesis and recycling of [BMIM]Cl were required.

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