Carbohydrate Polymers 115 (2015) 49–53

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Hydrolysis of cellulose catalyzed by novel acidic ionic liquids

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ARTICLE INFO

Article history:
Received 24 June 2014
Received in revised form 6 August 2014
Accepted 10 August 2014
Available online 2 September 2014

Keywords:
Acidic ionic liquid
Cellulose
Hydrolysis
Catalyst

ABSTRACT

The conversion of cellulosic biomass directly into valuable chemicals becomes a hot subject. Six novel acidic ionic liquids (ILs) based on 2-phenyl-2-imidazoline were synthesized and characterized by UV–VIS, TGA, and NMR. The novel acidic ionic liquids were investigated as catalysts for the hydrolysis of cellulose in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The acidic ionic liquids with anions HSO_4^- and Cl^- showed better catalytic performance for the hydrolysis of cellulose than those with $H_2PO_4^-$. The temperature and dosage of water affect significantly the yield of total reducing sugar (TRS). When the hydrolysis of cellulose was catalyzed by 1-propyl sulfonic acid-2-phenyl imidazoline hydrogensulfate (IL-1) and the dosage of water was 0.2 g, the TRS yield was up to 85.1% within 60 min at 100 °C. These new acidic ionic liquids catalysts are expected to have a wide application in the conversion of cellulose into valuable chemicals.

1. Introduction

As the crisis of fossil fuel intensified, there is an urgent demand for a new energy source to replace the fossil fuel gradually. Cellulose as a widespread renewable resource (Liu, Xiao, Xia & Ma, 2013; Xu, Wang & Wang, 2010) has attracted wide attention, and the conversion of cellulosic biomass directly into renewable bioenergy has become an attractive field. However, there are few practical processes to produce reducing sugars from cellulose. Therefore, a green, economic, and efficient process for hydrolysis of cellulose under mild reaction conditions remains to be developed.

Recently, the degradation of cellulose in ionic liquids (ILs) has been studied intensively. 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) as a solvent has good performance for the dissolution of cellulose because of the formation of hydrogen-bonding networks between hydroxyl groups of cellulose and chloride ions (Dong & Zhang, 2012; Swatloski, Spear, Holbrey & Rogers, 2002). The hydrolysis of cellulose can be catalyzed by enzymes (Yeh, Huang & Chen, 2010), solid acid catalysts (Hara, 2010), and metal salts (Zhao, Holladay, Brown & Zhang, 2007) in ILs to produce reducing sugars, then the resulting sugars can be further converted to other valuable products, such as 5-hydroxymethyl-2-furldehyde (HMF), which would be an important fuel resource in the future (Xiao, Liu, Wang, Fang & Zhang, 2014).

Acidic ionic liquids attracted the attention because of their distinct advantages, such as strong plasticity and good thermal stability. In 2002, Bronsted acidic ionic liquids were used for the first time as novel acid catalysts for esterification (Cole et al., 2002), then a measuring method of acidity scale of Bronsted acidic ionic liquids was established based on Hammett acidity function (Thomazeau, Olivier-Bourbigou, Magna, Luts & Gilbert, 2003). Later, more and more researchers focused on acidic ionic liquids as acid catalysts for some chemical reactions, such as Pechmann reaction (Gu, Zhang, Duan & Deng, 2005), transesterification (Elsheikh, Man, Bustam, Yusup & Wilfred, 2011; Wu, Chen, Han, Wang & Wang, 2007), and etherification (Liao et al., 2012). In addition, due to their unique structure, acidic ionic liquids have better catalytic activity, and thus been widely used in the fields of cellulose degradation. Amarasekara and Owereh reported the application of acidic ionic liquids for the dissolution and hydrolysis of cellulose for the first time in 2009 (Amarasekara & Owereh, 2009). Then the group investigated the hydrolysis of cellulose catalyzed by 1-(1-propylsulfonic)-3-methylimidazolium chloride ($[C_3SO_3Hmim]Cl$) in H_2O medium and by imidazolium-based acidic ionic liquid modified silica in [Bmim]Cl medium, with the highest total reducing sugars yields of 67% and 28.5%, respectively (Amarasekara & Owereh, 2010; Amarasekara & Wiredu, 2011). Jiang et al. choosed several imidazole-based acidic ionic liquids as catalysts for the hydrolysis of cellulose in [Bmim]Cl and applied *in situ* ^{13}C NMR spectroscopy to monitor the hydrolysis process of cellulose (Jiang, Zhu, Ma, Liu & Han, 2011). Tao et al. and Ding et al. studied the

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http://dx.doi.org/10.1016/j.carbpol.2014.08.078
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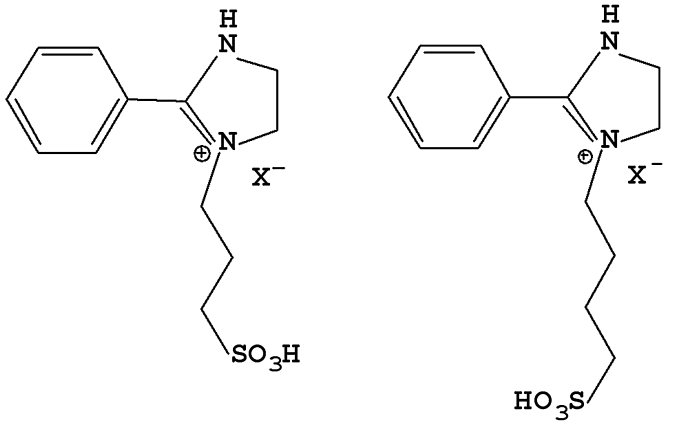

Fig. 1. Chemical structures of the ionic liquids used in this work.

conversion of cellulose to HMF using acidic ionic liquids as the catalysts and metal salts as co-catalysts under mild conditions (Tao, Song & Chou, 2011; Ding et al., 2012). Liu et al. used six kinds of SO_3H-functionalized acidic ionic liquids as acid catalysts to promote the hydrolysis of cellulose in [Bmim]Cl (Liu et al., 2013).

Up to now, most of the acidic ionic liquids as catalysts for hydrolysis of cellulose were based on imidazole, pyridine, triethanolammonium, and triethylamine. However, imidazoline-based acidic ionic liquids have not been reported. 2-Phenyl-2-imidazoline cation has a large conjugated system which is different from the cation in the above traditional acidic ionic liquids. This unique structure makes this class of ionic liquids have some special properties, such as acidities, active acid sites and viscosities (Liu et al., 2013), which may affect their catalytic performance. Hence, we synthesized a series of imidazoline-based acidic ionic liquids, and investigated their catalytic performance for the hydrolysis of cellulose in [Bmim]Cl. To our knowledge, it is the first time to report the synthesis of the propyl/butyl sulfonic acid-2-phenyl imidazoline-based acidic ionic liquids and application in the hydrolysis of cellulose.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC, average particle size of 50 μm), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, CP, >99%), 1, 3-propanesultone, 1,4-butylenesulfone (CP, >99%), 2-phenyl-2-imidazoline (CP, >99%), and 3,5-dinitro-2-hydroxybenzoic acid (DNS, CP, >99%) were purchased from J&K Chemical Company (Beijing, China).

2.2. Synthesis of acidic ionic liquids

Chemical structures of the acidic ionic liquids synthesized in this work were shown in Fig. 1. IL-1 (1-propyl sulfonic acid-2-phenyl imidazoline hydrogensulfate) was synthesized as follows: 1,3-propanesultone (1.221 g, 0.01 mol) was dissolved in chloroform, and the equimolecular 2-phenyl-2-imidazoline (1.462 g, 0.01 mol) was added at room temperature. The mixture was stirred at 40 °C for 48 h, and then the obtained white solid (zwitterion) was washed with chloroform for three times through Buchner funnel and dried in a vacuum for 6 h. Equimolar concentrated sulfuric acid was mixed with the zwitterion, and heated to 50 °C for 24 h under stirring. Pasty IL-1 was washed with ether and dried in a vacuum. IL-2 and IL-3, light yellow viscous liquids, were prepared as the above method for IL-1. Their ^{1}H NRM spectral characteristics were shown as follows:

IL-1: ^{1}H NMR (400 MHz, D_2O): δ 1.86–1.93 (m, 2H), 2.67 (t, 2H), 3.29 (t, 2H), 3.97–4.01 (d, 4H), 7.40–7.69 (m, 5H).

IL-2: ^{1}H NMR (400 MHz, D_2O): δ 1.83–1.91 (m, 2H), 2.64 (t, 2H), 3.27 (t, 2H), 3.95–3.99 (d, 4H), 7.38–7.67 (m, 5H).

IL-3: ^{1}H NMR (400 MHz, D_2O): δ 1.86–1.94 (m, 2H), 2.67 (t, 2H), 3.30 (t, 2H), 3.98–4.02 (d, 4H), 7.41–7.70 (m, 5H).

IL-4 (1-butyl sulfonic acid-2-phenyl imidazoline hydrogensulfate) was prepared as follows: equimolar 1,4-butylenesulfone (1.362 g, 0.01 mol) and 2-phenyl-2-imidazoline (1.462 g, 0.01 mol) were dissolved in chloroform. The mixture was stirred at 40 °C for 72 h and evaporated to remove the solvent by reduced pressure distillation. The product was washed using methylene chloride to remove impurities and then dried in a vacuum at 50 °C for 24 h to get white solid. A stoichiometric amount of concentrated sulfuric acid was added slowly and the mixture was stirred at 50 °C for 24 h. Pasty IL-4 was washed with ether repeatedly and dried in a vacuum. The synthesis of IL-5 and IL-6, light yellow viscous liquids, was as the above method for IL-4. Their ^{1}H NRM spectral characteristics were shown as follows:

IL-4: ^{1}H NMR (400 MHz, D_2O): δ 1.45–1.52 (m, 2H), 1.55–1.62 (m, 2H), 2.63 (t, 2H), 3.16 (t, 2H), 3.96–3.97 (d, 4H), 7.39–7.68 (m, 5H).

IL-5: ^{1}H NMR (400 MHz, D_2O): δ 1.38–1.46 (m, 2H), 1.49–1.55 (m, 2H), 2.57 (t, 2H), 3.11 (t, 2H), 3.90–3.91 (d, 4H), 7.33–7.62 (m, 5H).

IL-6: ^{1}H NMR (400 MHz, D_2O): δ 1.38–1.45 (m, 2H), 1.48–1.56 (m, 2H), 2.56 (t, 2H), 3.10 (t, 2H), 3.89–3.90 (d, 4H), 7.32–7.61 (m, 5H).

2.3. Determination of Hammett function of acidic ionic liquids

4-Nitroaniline was used as the indicator in this work (Kore & Srivastava, 2013), and the concentrations of acidic ionic liquids and 4-nitroaniline in deionized water were 0.05 mol/L and 9 mg/L, respectively. The values of the Hammett acidity (H_0) of all the acidic ionic liquids were determined under 380 nm using a PGeneral TU-1900 UV-spectrophotometer.

2.4. Thermal gravimetric analysis of acidic ionic liquids

The thermal analysis data were acquired using a thermal analyzer of Netzsch (STA 409 PC), and the measurements were carried out under N_2 with a temperature ramp of 10 K/min between 0 and 700 °C.

2.5. Hydrolysis of cellulose

MCC was dried in a vacuum oven at 50 °C for 24 h. A pretreatment was adopted in solvents. MCC (0.1 g) and [Bmim]Cl (2.0 g) were added into a 25 mL round bottom flask, and the mixture was heated to 100 °C under stirring for 1 h to form a transparent and homogeneous solution. An as-prepared acidic ionic liquid (0.2 g) and H_2O (0.02 g) were added to the reaction system, and the reaction was carried out under stirring at 80, 100, and 120 °C, respectively. A certain amount of the sample was extracted from the reaction system and quenched immediately with 1 mL NaOH solution (0.03 mol/L) at specific time intervals. The sample was centrifuged using a centrifugal machine (Shanghai Anting Scientific Instrument Factory, China) at 14,000 rpm for 10 min, and the supernatant was transferred to a colorimetric tube for further

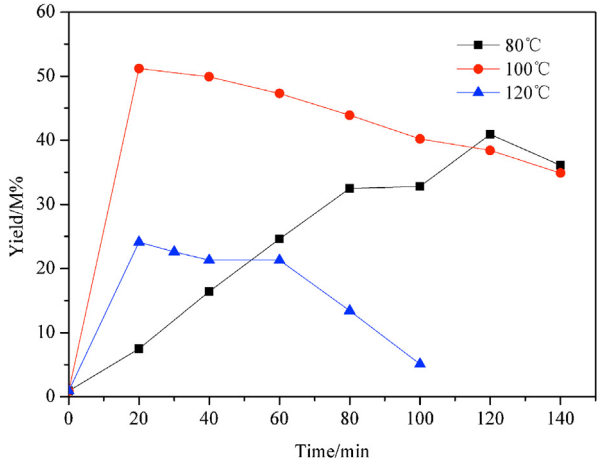

Fig. 2. Hydrolysis of cellulose catalyzed by IL-1 at 80, 100 and 120 °C (2.0 g [Bmim]Cl, 0.1 g MCC, 0.02 g H_2O, 0.2 g IL-1).

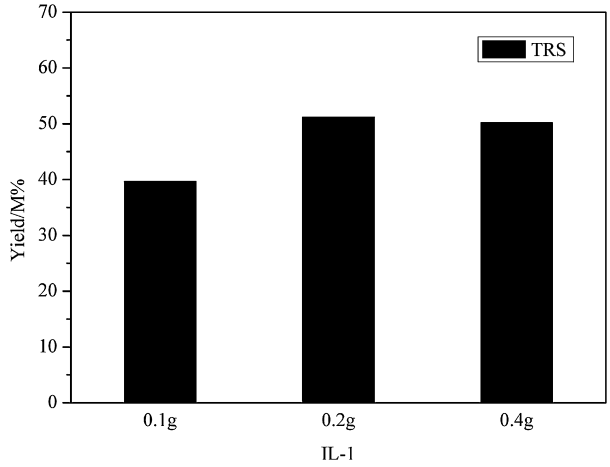

Fig. 3. Hydrolysis of cellulose catalyzed by IL-1 from 0.1 g to 0.4 g at 100 °C for 20 min (2.0 g [Bmim]Cl, 0.1 g MCC, 0.02 g H_2O).

analysis. The reaction without acidic ionic liquids was also carried out as the blank experiment for comparison.

2.6. Determination of total reducing sugars (TRS)

The DNS method was used for the determination of total reducing sugars (TRS) (Miller, 1959). The supernatant was transferred to a test tube and 0.5 mL DNS reagent was added into the sample; the solution was heated in boiling water for 10 min and then diluted with deionized water to 10 mL at room temperature. The absorbance was tested by a PGeneral TU-1900 UV-spectrophotometer at 520 nm, and the concentration of TRS was calculated based on a standard curve obtained with glucose.

3. Results and discussion

3.1. Effect of temperature on the hydrolysis of MCC

Temperature is a very important parameter in chemical reaction process. The thermal decomposition temperature of the acidic ionic liquids used in our study is higher than 300 °C. IL-1 was selected as a catalyst to study the dependence of hydrolysis products on temperature in the hydrolysis process of cellulose. The reaction temperatures are 80, 100, and 120 °C, respectively. As shown in Fig. 2, the higher the reaction temperature, the earlier the maximum of TRS yield appears. The yield of TRS was up to 51.2% at 100 °C within 20 min, and then declined to 34.9% at 140 min. However, the yield of TRS kept increasing and reached the maximum of 40.9% at 80 °C within 120 min, and then the yield had a slowly decrease. The yield of TRS only reached a maximum of 24.1% at 120 °C. The results showed that TRS had the highest yield at 100 °C. The first increase and then decrease of the TRS yield may be due to the conversion of the produced reducing sugars to HMF and other products. The reaction temperature was chosen at 100 °C to investigate catalytic performance of the as-prepared ILs for the hydrolysis of MCC.

3.2. Effect of acidic ionic liquid dosage on the hydrolysis of MCC

IL-1 was chosen as the catalyst to investigate the effect of ionic liquid dosage on the hydrolysis of cellulose. As shown in Fig. 3, when the dosage of IL-1 was 0.1 g, 0.2 g, and 0.4 g, the yield of TRS was 39.7%, 51.2%, and 50.2%, respectively. This shows that the excess catalyst could lead to a drop of the TRS yield due to the catalytic dehydration of the reducing sugars. That means the catalyst made more contribution to the dehydration rate of the reducing sugars. In our study, 0.2 g of ionic liquid dosage was chosen for the hydrolysis of cellulose.

3.3. Effect of various acidic ionic liquids on the hydrolysis of MCC

The acidity and structure of ionic liquids have remarkable effects on their catalytic performance. The hydrolysis of MCC catalyzed by various acidic ionic liquids was investigated in this work. Fig. 4 shows the results of hydrolysis catalyzed by all as-prepared acidic ionic liquids. As shown in Fig. 4, the TRS yields were up to 51.2% and 45.5% when acidic ionic liquids with anion HSO_4^- (IL-1 and IL-4) were used as catalysts, respectively. When MCC were catalyzed by IL-2 and IL-5, the yields of TRS only reached 2% and 1.5%, respectively, indicating that ILs with $H_2PO_4^-$ as anion had very low catalytic ability because of their weaker acidity. Compared to the ionic liquids with anion HSO_4^- (IL-1, IL-4), IL-3 and IL-6 with anion Cl^- led to different change tendencies of yields. Using IL-3 and IL-6, the highest yields of TRS reached, respectively, 46.9% and 40.1% at the reaction time of 40 min (see Fig. 5), and appeared later than those using IL-1 and IL-4.

The value of H_0 can be calculated as follow: $H_0 = pK(I_{aq}) + \log([I]/[IH^+])$, where I represents the indicator. 4-Nitroanline was used as the indicator in this work. When the acidic ionic liquid was added to the solution, the combination of the protons with the indicator causes the lowering of the UV-absorbance. The H_0

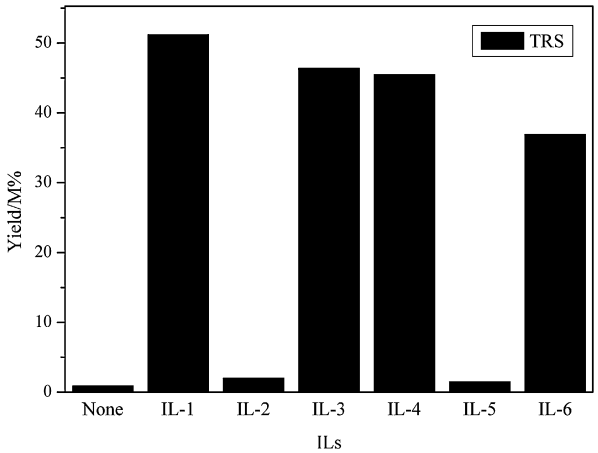

Fig. 4. Hydrolysis of cellulose catalyzed by various ILs in 20 min at 100 °C (2.0 g [Bmim]Cl, 0.1 g MCC, 0.02 g H_2O, 0.2 g ILs).

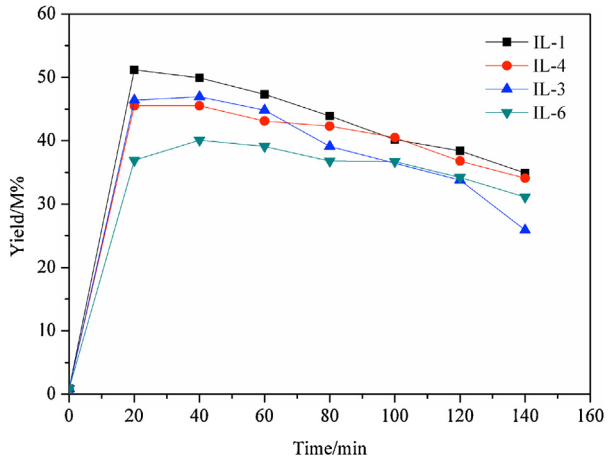

Fig. 5. Hydrolysis of cellulose catalyzed by various ILs at 100 °C (2.0 g [Bmim]Cl, 0.1 g MCC, 0.02 g H_2O, 0.2 g ILs).

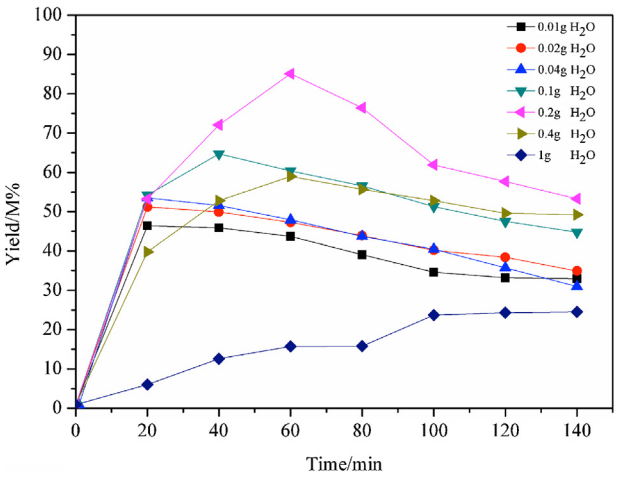

Fig. 6. Hydrolysis of cellulose with different H_2O dosage catalyzed by IL-1 at 100 °C (2.0 g [Bmim]Cl, 0.1 g MCC, 0.2 g IL-1).

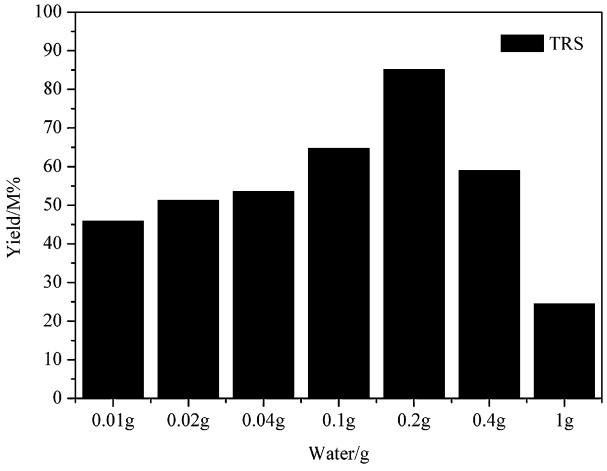

Fig. 7. The highest yield of TRS with different H_2O dosage catalyzed by IL-1 at 100 °C (2.0 g [Bmim]Cl, 0.1 g MCC, 0.2 g IL-1).

values of all acidic ionic liquids were determined and are given in Table 1. As seen in Table 1, the acidity order of the ionic liquids was observed: IL-1 > IL-4 > IL-3 > IL-6 > IL-2 > IL-5. The ionic liquids with HSO_4^- anion (IL-1 and IL-4) showed higher acidity than the others, and the ionic liquids with the shorter side-chain [$(CH_2)_3$] at C-1 on the imidazoline ring (IL-1, IL-2, and IL-3) had higher acidity than the ionic liquids with the longer side chain [$(CH_2)_4$] (IL-4, IL-5, IL-6). As shown in Fig. 4 and Table 1, the TRS yields mainly depended on the acidity of ionic liquids. And the stronger acidity can lead to the faster breakage of glycosidic bonds, meanwhile the dehydration of glucose into HMF also got faster. Perhaps this is the most important reason why the TRS yield in the reaction catalyzed by IL-4 is higher than that catalyzed by IL-3. To some degree, the appropriate acidity of ILs was beneficial to the yield of TRS for hydrolysis of cellulose.

3.4. Effect of water dosage on the hydrolysis of MCC

In our study, the highest TRS yield was obtained when IL-1 was used as the catalyst for the hydrolysis of MCC, and thus IL-1 was selected as the catalyst to explore the effect of water dosage on the hydrolysis of cellulose. In Figs. 6 and 7, the amount of water was from 0.01 g to 1 g in the hydrolysis reaction. The highest yield of TRS increased obviously from 46.4% to 85.1% when the dosage of water increased from 0.01 g to 0.2 g. However, when water dosage increased from 0.2 g to 0.4 g, the highest TRS yield decreased from 85.1% to 59%, and then when the water dosage was 1 g, the highest TRS yield was only 24.5%. The decline of the yield is due to the decrease of the solubility of MCC in [Bmim]Cl medium with the excessive water. As shown in Fig. 6, the more water, the later the highest yield appeared, which is attributed to the decrease in the dehydration rate of TRS. These results showed that the yield of TRS can be controlled by water dosage.

When some acidic ionic liquids or inorganic acids were used as the catalyst for hydrolysis of cellulose in solvent ILs/water, the

Table 1
Hammett acidity functions of all acidic ionic liquids in water.[a]

ILs	A_{max}	[I] (%)	[IH^+] (%)	H_0
None	1.00	100	0	
IL1	0.65	65	35	1.26
IL2	0.88	88	12	1.86
IL3	0.75	75	25	1.47
IL4	0.67	67	33	1.30
IL5	0.90	90	10	1.94
IL6	0.77	77	23	1.51

[a] 4-Nitroanline: 9 mg/L; ILs: 50 mmol/L.

Table 2
Yields of TRS obtained from hydrolysis of cellulose catalyzed by various acidic ionic liquids/inorganic acids.

Entry	Catalyst	Solvent	Temp (°C)/time (min)	TRS (%)
1	IL-1 (this work)	[Bmim]Cl	100/60	85.1
2	$[C_3SO_3Hmim]HSO_4$[a]	[Bmim]Cl	100/90	88.4
3	$[C_4SO_3Hmim]HSO_4$[b]	[Bmim]Cl	100/60	85
4	$[Et_3(C_3SO_3H)N]Cl$[a]	[Bmim]Cl	100/60	83.6
5	$[C_3SO_3Hmim]Cl$[c]	$[C_3SO_3Hmim]Cl$	70/30	12
6	$[C_4SO_3Hmim]Cl$[c]	$[C_4SO_3Hmim]Cl$	70/30	7
7	$[C_3SO_3Hmim]Cl$[d]	H_2O	170/300	35.5
8	$[C_3SO_3Hmim]Cl$-SiO_2[e]	[Bmim]Cl	70/360	67
9	BC-SO_3H-IL[f]	[Bmim]Cl	90/120	64.6
10	BC-SO_3H-IL[f]	H_2O	90/120	33.4
11	H_2SO_4[d]	H_2O	170/300	33
12	H_2SO_4[e]	[Bmim]Cl	70/360	24
13	H_2SO_4[g]	[Bmim]Cl	100/28	66
14	HCl[g]	[Bmim]Cl	100/11	65
15	HNO_3[g]	[Bmim]Cl	100/10	50
16	H_3PO_4[g]	[Bmim]Cl	100/420	54

[a] Liu et al. (2013).
[b] Jiang et al. (2011).
[c] Amarasekara and Owereh (2009).
[d] Amarasekara and Wiredu (2011).
[e] Amarasekara and Owereh (2010).
[f] Zhang et al. (2012).
[g] Li and Zhao (2007).

yields of TRS were collected from the literature and are given in Table 2. The data indicate that Bronsted acidic ionic liquids with $-SO_3H$ generally demonstrate higher catalytic activity than inorganic acids (H_2SO_4, HCl, HNO_3, and H_3PO_4) in [Bmim]Cl/H_2O. Compared with some acidic ionic liquids reported in the literature ([C_3SO_3Hmim]HSO_4, [C_4SO_3Hmim]HSO_4, and [$Et_3(C_3SO_3H)N$]Cl), IL-1 also exhibits excellent catalytic performance for hydrolysis of cellulose in [Bmim]Cl, because all of them have the same active group, $-SO_3H$. However, less time was needed to get the highest yield of TRS using IL-1 as the catalyst than using [C_3SO_3Hmim]HSO_4. Moreover, compared with our results, the yields of TRS were low when [C_3SO_3Hmim]Cl and [C_4SO_3Hmim]Cl were used as both catalysts and solvents, [C_3SO_3Hmim]Cl-SiO_2 as the catalyst in [Bmim]Cl, and BC-SO_3H-IL as the catalyst in [Bmim]Cl/water.

4. Conclusions

Six novel SO_3H-functionalized acidic ionic liquids based on 2-phenyl-2-imidazoline were synthesized, and were used as catalysts for the hydrolysis of cellulose in solvent [Bmim]Cl. Compared with some acidic ionic liquids/inorganic acids reported in the literature, the acidic ionic liquids with the shorter side-chain [$(CH_2)_3$] at C-1 on the imidazoline ring and HSO_4^- as anion (IL-1) also has excellent catalytic performance. The yield of TRS for hydrolysis of cellulose was dependent on acidity of the ionic liquids, dosage of water, and reaction conditions including reaction temperature and time. The novel acidic ionic liquids would become a new potential candidate of catalysts for the conversion of cellulose to a new widespread renewable energy resource. To improve the yield of TRS, the effect of these factors on the yield remains to be explored in the future work.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (Nos. 21173070, 21303044) and the Plan for Scientific Innovation Talent of Henan Province (No. 124200510014) are gratefully acknowledged.

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