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WCl₆ catalyzed cellulose degradation at 80 °C and lower in [BMIM]Cl



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ABSTRACT

Degradation of cellulose to reducing sugar is the key step for the conversion of cellulose to valuable chemicals. Cellulose was degraded by WCl₆ in 1-butyl-3-methyl imidazole chloride at 80 °C and lower. 83% and 85.5% yield of total reducing sugar was gotten at 70 and 80 °C, respectively. Compared with inorganic acid, heteropoly acid, acidic ionic liquid and other metal chlorides, WCl₆ has shown better catalytic performance for degradation of cellulose to reducing sugar. The effect of reaction temperature, reaction time, WCl₆ amount and cellulose concentration were investigated. Degradation of cellulose by WCl₆ in 1-butyl-3-methyl imidazole chloride is a zero reaction. WCl₆ also showed excellent catalytic performance for the degradation of nature cellulose and lignocellulose. Catalyst can be reused at least 5 times without decrease of reducing sugar yield. The mechanism of degradation of WCl₆ was also suggested.

1. Introduction

Degradation of biomass to chemicals is a practical way to replace fossil resources, which face the crisis of exhausting and cause the rising of atmospheric temperature (Hobson, 2008), for the energy and chemicals requirements. Inexpensive, abundant, and renewable non-food cellulose has been a cosset to chemists in recent years. However, the complex hydrogen bonded network structures in cellulose make it hard to be dissolved in traditional solvents (Notley, Pettersson, & Wagberg, 2004). Cellulose hydrolysis is commonly carried out in inorganic acids aqueous solution at high temperature and high pressure, which consume a lot of energy and need overpressure resistant equipments (Rinaldi & Schüth, 2009a, 2009b). In 2002, Rogers et al. found that cellulose can be dissolved in [BMIM]Cl (Swatloski, Spear, Holbrey, & Rogers, 2002). Because ionic liquids almost have no vapour pressure, homogeneous degradation of cellulose at atmosphere pressure can be realized.

Cellulose degradation in ionic liquids can be catalyzed by inorganic acids, metal chlorides, acid functional ionic liquids and solid acids (Li, Wang, & Zhao, 2008; Lima et al., 2009; Rosa, Campos-Martin, & Fierro, 2012; Su et al., 2011). Inorganic acids were firstly used as the catalysts for cellulose degradation in ionic liquids. Li et al. (2008) hydrolyzed lignocelluloses by different inorganic acids in different ionic liquids at

100 °C. The results showed that HCl was the best catalyst and 81% vield of reducing sugar was got by HCl in C4mimCl at 100 °C. However, HCl is volatile, which is easy to be lost in this heating system. H₂SO₄ was also used for the hydrolysis of lignocellulose in ionic liquids. Dee and Bell (2011) degraded cellulosic and hemicellulosic components of miscanthus by H₂SO₄ in [Emim]Cl at 378 K and got 84% yield of sugar. Sievers et al. (2009) hydrolyzed pine wood by trifluoroacetic acid in [Bmim]Cl and got reducing sugar, furfural and 5-HMF. Although inorganic acids showed good catalytic activity for cellulose degradation in ionic liquids, the disadvantages cannot be ignored. The reaction temperature was high and the inorganic acids were corrosive to the equipments. Besides the corrosive properties of acids, reducing sugars also have side reactions in the presence of strong acids, which produced byproducts, humin. Acidic ionic liquids were synthesized to replace inorganic acids for the cellulose degradation. Amarasekara and Owereh (2009) decomposed sigmacell cellulose in acidic functional ionic liquids and water, 62% yield of reducing sugars was gotten at 70 °C. They also tried to degrade sigmacell cellulose in aqueous solution of acidic functional ionic liquids (Amarasekara & Wiredu, 2011). Only about 25% yield of reducing sugars was gotten at 170 °C. Jiang, Zhu, Ma, Liu, and Han (2011) hydrolyzed cellulose by acid functional ionic liquids in [BMIM]Cl and got about 90% yield of reducing sugars at 80-100 °C. Other kinds of acidic functional ionic liquids were also used for the

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Abbreviations: HMF, 5-hydroxymethylfurfural; TRS, total reducing sugar

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degradation of cellulose, such as SO₃H, COOH and OH functionalized imidazole based ionic liquids and acidic ionic liquids with HSO4⁻ and Cl⁻ as anions. All these acidic functional ionic liquids showed good catalytic activity (Khan et al., 2018; Parveen, Patra, & Upadhyayula, 2016; Tao, Song, & Chou, 2011a, 2011b; Zhou, Liang, Ma, Wu, & Wu, 2013; Zhuo et al., 2015). However, the results showed that reducing sugars were unstable in this system, the yield of reducing sugar decreased quickly with the extending reaction time and acid functional ionic liquids are also corrosive. The complex synthesis processes of acid functional ionic liquids also hinder their application. A series of solid acid catalysts were also developed to avoid these advantages for cellulose degradation and high yields of reducing sugar were gotten (Chutinate, Watthanaphanit, Saitoe, & Damrongsakkul, 2017; Hu, Lin, Wu, Zhou, & Liu, 2015; Peng, Lee, Wu, & Wu, 2012; Rinaldi & Schüth, 2009a, 2009b; Rinaldi, Palkovits, & Schüth, 2008; Shen, Guo, Bai, Qiu, & Qi, 2018; Suganuma et al., 2008; Yuan, Guan, Peng, Zhu, & Jiang, 2017; Zhang, Shan, Liu, & Sun, 2018). However, the reaction temperatures were higher than 100 °C, at which reducing sugars and other products were unstable and further reacted to byproducts. To avoid the further degradation of reducing sugar, cellulose degradation in ionic liquids should be performed at lower temperature than 100 °C.

Metal chlorides were also used for the degradation of cellulose in ionic liquids. Su et al. (2011) used CuCl₂/PdCl₂ catalytic system for the degradation of cellulose and got 61% yield of reducing sugars. However, the high cost of Pd is the main obstacle for the application. Our previous research also showed that the degradation products were really unstable in the presence of CuCl₂ (Zhou et al., 2015). Other metal chlorides were also used for the degradation of cellulose, such as MnCl₂, CrCl₃, AlCl₃, LiCl, ZrCl₄, InCl₃, RuCl₃, ZnCl₂, IrCl₃ and AuCl₃ (Binder & Raines, 2009; De, Dutta, & Saha, 2011; Kim et al., 2011; Liu, Zhang, & Zhao, 2013; Tao et al., 2011a, 2011b; Tao, Song, & Chou, 2012; Li et al., 2013; Wang, Yu, Zhan, & Wang, 2011; Wei, Li, Thushara, Liu, & Ren, 2011; Yang, Hu, & Abu-Omar, 2012; Yuan, Xu, Cheng, & Leitch, 2011). All these researches mainly focused on the conversion of cellulose to HMF and furfural and were performed at temperature higher than 100 °C. Hence, new catalytic systems for the cellulose degradation at low temperature are needed. In our previous study, cellulose can be degraded to reducing sugars very quickly by WCl₆ in [BMIM]Cl. However, reducing sugars were further transformed to humin at 120 °C (Zhou et al., 2015). We were curious for the catalytic properties of WCl₆ at low temperature for the degradation of cellulose. WCl₆ has been used in halo-de-hydroxylation, dihalo-de-oxo-bisubstitution reactions and metathesis of olefin (Firouzabadi & Shiriny, 1996; Patton & McCarthy, 1987), which suggested that W⁶⁺ can react with aldehyde groups. This property might be positive for the degradation of cellulose.

In this research, cellulose degradation by WCl₆ at low temperature in [BMIM]Cl has been studied. WCl₆ showed good catalytic performance for the decomposition of cellulose in [BMIM]Cl at 80 °C and lower. The kinetics and mechanism of this process were also studied to find out the reason of WCl₆ excellent catalytic activity. This system was also used for the degradation of lignocelluloses. The influence factors of cellulose degradation have also been analyzed. This finding is promising to produce stable reducing sugars from cellulose and reduce energy cost in cellulose degradation process.

2. Materials and methods

2.1. Materials and instruments

Heteropolyacids (H₃PW₁₂O₄₀, H₃PMo₁₂O₄₀ and H₄SiW₁₂O₄₀), microcrystalline cellulose (MCC, DP: 215–245), N-methylimidazole (AR), 1-chlorobutane (CP), CrCl₃·6H₂O (\geq 99%), SnCl₄ and WCl₆ (99.5%) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). CuCl₂·2H₂O (\geq 99%) was obtained from Guangfu Fine Chemical Research Institute (Tianjin, China). 1,3-Propanesultone (AR) was purchased from Shandong Yinghuan Chemical Co. Ltd. (Shandong, China).

Sulfuric acid was purchased from Juhua Group Corporation (Zhejiang, China). Microcrystalline cellulose was dried in blast oven at 100 °C for 1 h before use. All other chemicals were supplied by local suppliers and used without further purification.

DF-101S constant temperature magnetic stirrer was purchased from Zhengzhou Greatwall Scientific Industrial and Trade Co., Ltd. (Zhengzhou, China). TU-1810 Model UV-vis spectrophotometer was obtained by Purkinje General Co. Ltd. (Beijing, China). FT-IR spectrometer (Nicolet NEXUS670) which was used to analyze the leftover of the reaction was purchased from Nicolet Co. Ltd. (USA).

2.2. Synthesis of ionic liquid

Ionic liquid [BMIM]Cl was prepared by the reported procedures (Tao et al., 2011a, 2011b). N-methylimidazole and acetonitrile were added in three-necked flask, and then it was heated to 80 °C. The 1-butyl chloride was slowly dropped in N-methylimidazole by top funnel with mole ratio of 1.1:1. The mixture was heated to reflux for 48 h at 80 °C. When the reaction was finished, the mixture was cooled to room temperature and washed by ethyl acetate, which was twice the volume of mixture, for three times. Half volume of mixture acetonitrile and a little [BMIM]Cl crystal were added into it. Then the mixture was airproof, still and crystallized for 12 h. The white crystal was washed by ethyl acetate for 3 times. The pure [BMIM]Cl was prepared at last.

[PSMIM]HSO₄ was prepared by the following procedure (Zhou et al., 2013). Some 1,3-propanesultone was added into three-necked flask and dissolved by 150 mL methylbenzene. N-methylimidazole was dropped into flask in mole ratio of 1:1. Then the temperature was increased to 80 °C and reacted for 2 h. Reaction product was white solid-[PSMIM]. The product was washed by acetic ester for 3 times and dried at 100 °C for 5 h. Some [PSMIM] was dissolved in deionized water and the same mole sulfuric acid was dropped into the solution. When all the sulfuric acid was added, reaction temperature was increased to 80 °C and reacted for 6 h. The mixture was cooled to room temperature, washed by ether for more than 3 times and dried at 100 °C for 24 h. [PSMIM]HSO₄ was prepared at last.

2.3. Typical procedure for microcrystalline cellulose degradation

0.05 g MCC was added into 1.0 g [BMIM]Cl, and the mixture was heated to 70 °C. After the mixture became clear which means all of MCC was dissolved into [BMIM]Cl, the temperature was increased to the target temperature, and WCl₆ was added into this solution, then reacted for some time. The WCl₆ loading amount was 0.02 g. For the test of catalysts loading amount, The WCl₆ loading amounts used in this catalytic system were 0.01, 0.02, 0.03, 0.04 and 0.05 g, respectively. The loading amounts of other catalysts compared with WCl₆, such as CrCl₃, CuCl₂, SnCl₄, H₂SO₄, [PSMIM]HSO₄, H₃PW₁₂O₄₀, H₃Si₁₂O₄₀ and H₃Mo₁₂O₄₀ used in this research were all 0.02 g. At different time intervals, two samples were withdrawn, weighted and quenched immediately with cold water each time, one for TRS detection (recorded as M_1) and the other for HMF detection (recorded as M_2). Every reaction was repeated 3 times.

2.4. TRS analysis

Total reducing sugar was detected by DNS method. The samples were taken periodically, and diluted with deionized water 150 times, added 1 mL DNS regent, then heated for 20 min in boiling water, and cooled by cold water. The colour intensity of the mixture was measured in a TU-1810 Model spectrophotometer at 498 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose. The yield of TRS was calculated as follows: $Y_{TRS} = (C_{TRS} \times M_1 \times 1500)/(M_{cellulose} \times 1.11 \times M_1/M_0)$, where C_{TRS} is the concentration of total reducing sugars, M_0 is the mass of the reaction solution, $M_{cellulose}$ is the mass of cellulose in the reaction, and M_1 is

the mass of sample withdrawn from the reaction mixture. The standard errors of the experiments results were controlled in 4%.

2.5. HMF analysis

Samples were dissolved in 1500 times volume of deionized water, and centrifuged at 4000 r/h for 5 min. The colour intensity of supernatant fluid was measured in a TU-1810 Model spectrophotometer at 284 nm with a slit width of 0.06 mm (De et al., 2011). The concentration of furans was calculated based on a standard curve obtained with HMF. The yield of furans was calculated as follows: $Y_{furan} = (C_{FURANS} \times M_2 \times 1500)/(M_{cellulose} \times 0.778 \times M_2/M_0)$, where C_{FURANS} is the concentration of furans, M_0 is the mass of the reaction solution, $M_{cellulose}$ is the mass of cellulose in the reaction, and M_2 is the mass of sample withdrawn from the reaction mixture.

2.6. FT-IR analysis

The FT-IR spectra of [BMIM]Cl, WCl₆-[BMIM]Cl, cellulose-[BMIM]Cl and WCl₆-cellulose-[BMIM]Cl were collected by the following ways. 0.02 g WCl₆ was dissolved in 1.0 g [BMIM]Cl. The solution was dropped on the KBr pellets, and then the FT-IR spectrum was collected. The FT-IR spectra of cellulose-[BMIM]Cl and WCl₆-cellulose-[BMIM]Cl and WCl₆-cellulose-[BMIM]Cl and WCl₆-cellulose-[BMIM]Cl were 0.1 g cellulose in 1.0 g [BMIM]Cl, 0.1 g cellulose and 0.02 g WCl₆ in 1.0 g [BMIM]Cl, respectively. The solid leftover was separated, washed by deionized water and submitted for FT-IR analysis. All the FT-IR spectra were collected on an FT-IR spectrometer (Nicolet NEXUS670) with a resolution of 4 cm⁻¹ and 32 scans in the region of 4000–400 cm⁻¹.

3. Results and discussion

3.1. Selection of catalysts

The TRS yields were selected the highest one among ones from different reaction times.

The common catalysts used for the hydrolysis of cellulose in [BMIM]Cl were investigated, such as H_2SO_4 , $CrCl_3$, WCl_6 , $SnCl_4$, $CuCl_2$, $H_3PW_{12}O_{40}$, $H_3SiW_{12}O_{40}$, $H_3PM_{012}O_{40}$ and [PSMIM]HSO₄. As can be seen in Table 1 and Figures S1–S11, heteropoly acid showed better catalytic performance than metal chlorides and acidic ionic liquid at 120 °C. Cellulose was almost completely degraded to reducing sugar in the presence of $H_3PW_{12}O_{40}$ and $H_3SiW_{12}O_{40}$ in half an hour. While, only 74% yield of reducing sugar was gotten in $H_3PM_{012}O_{40}$ -[BMIM]Cl system. The reason may be that the acidity of $H_3PM_{012}O_{40}$ was lower than $H_3PW_{12}O_{40}$ and $H_3SiW_{12}O_{40}$. 100% yield of reducing sugars was gotten in 8 h in the presence of H_2SO_4 . No residue was found in the solution of H_2SO_4 -[BMIM]Cl system, which also suggested the completely hydrolysis of cellulose. For heteropoly acids, some solid residues were found after reaction. These residues were washed and dried. The

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Degradation of cellulose to reducing sugars by different catalysts in [BMIM]Cl.

Entry	Catalyst	Solvent	Time (h)	Temperature (°C)	TRS yield (%)
1	WCl ₆	[BMIM]Cl	1	120	89
2	CrCl ₃	[BMIM]Cl	6	120	82
3	CuCl ₂	[BMIM]Cl	3	120	32
4	SnCl ₄	[BMIM]Cl	10	120	37
5	H_2SO_4	[BMIM]Cl	8	120	100
6	[PSMIM]HSO ₄	[BMIM]Cl	1	120	48
7	$H_3PW_{12}O_{40}$	[BMIM]Cl	0.5	120	99
8	$H_3SiW_{12}O_4$	[BMIM]Cl	0.5	120	99
9	$\mathrm{H_{3}PMo_{12}O_{40}}$	[BMIM]Cl	4	120	74

FT-IR spectra of these solid showed that its heteropoly salts which formed from the reaction between heteropoly acids and [BMIM]Cl, $[BMIM]_3PW_{12}O_{40}$, $[BMIM]_3PM_{12}O_{40}$, $[BMIM]_3PW_{12}O_{40}$, $[BMIM]_3PW_{12}O_{40}$, $[BMIM]_3SiW_{12}O_{40}$ (Fig. 6). The byproduct of this reaction was HCl, which was could be easily removed during the heating process. It demonstrates that heteropoly acids are not suitable for the hydrolysis of cellulose in ionic liquids. For H₂SO₄, although it showed high catalytic efficiency, TRS yield decreased with the reaction time prolonging. The acidic ionic liquid, only 48% yield of TRS was gotten in [PSMIM]HSO₄-[BMIM]Cl system, with the prolonging of reaction time, TRS yield decreased obviously, which suggested the low stability of sugars in this system.

WCl₆ showed the best catalytic performance among the metal chlorides been used. 89% vield of TRS was gotten in 1 h at 120 °C (Table 1). However, TRS yield also decreased with the prolonging of reaction time due to the side reactions of reduce sugars (Fig. 6). 82% yield of TRS was gotten in CrCl₃-[BMIM]Cl in 6 h. In our previous research, CrCl₃ is active for the conversion of cellulose to 5-HMF, which was generated from the dehydration of glucose (Zhao, Holladay, Brown, & Zhang, 2007). Low yields of TRS were gotten in CuCl₂-[BMIM]Cl (32%) and SnCl₄-[BMIM]Cl (37%). The solid residue in CuCl₂-[BMIM]Cl was black and mainly humin (Zhou et al., 2015), while the residue in SnCl₄-[BMIM]Cl was white, which was mainly cellulose. It suggests that cellulose in CuCl2-[BMIM]Cl was totally degraded and further transformed to byproducts, while the catalytic activity of SnCl₄ was too low. Although WCl₆ showed better catalytic performance than CrCl₃, CuCl₂, SnCl₄, [PSMIM]HSO₄ and H₃PMo₁₂O₄₀, the catalytic efficiency of WCl₆ is lower than H₂SO₄, H₃PW₁₂O₄₀ and H₃PMo₁₂O₄₀.

It seems that WCl₆ does not show the outstanding catalytic performance at high reaction temperature. We wondered if the hydrolysis of cellulose in [BMIM]Cl could be carried out by these catalysts at lower temperature. Degradation of cellulose by WCl₆, CrCl₃, CuCl₂, H₂SO₄ and H₃PW₁₂O₄₀ was performed at 70 °C. The results were shown in Fig. 1. WCl₆ showed the best catalytic performance among these catalysts. 63.5% yield of TRS was obtained in WCl₆-[BMIM]Cl in 2 h. The TRS yield reached 81.2% in 6 h, and then slightly decreased to 77.5% when the reaction time reached 10 h. TRS was also detected in the system without catalysts. 9.4% yield of TRS was obtained from cellulose in [BMIM]Cl after 2 h heating and stirring at 70 °C. TRS yield decreased to 8.2% when reaction time reached 10 h. The results match the previous published research (Liang, Wang, Zhou, Wu, & Wu, 2013). Compared with the blank control group, H₂SO₄, H₃PW₁₂O₄₀ and CuCl₂ were seemed to show no catalytic activity at 70 °C. 22.1% yield of TRS was obtained in CrCl₃-[BMIM]Cl after 2 h reaction at 70 °C, which was much worse than WCl₆. All these results demonstrate that cellulose can be hydrolyzed by WCl₆ in [BMIM]Cl at really low temperature.



Fig. 1. Degradation of cellulose by different catalysts at 70 °C.



Fig. 2. Degradation of cellulose by WCl₆ in [BMIM]Cl at different temperatures.

3.2. Influence of reaction temperature and time

Temperature is a key factor influencing the hydrolysis of cellulose, which would influence the reaction rate, yield of byproducts, viscosity of ionic liquids and mass transfer rate. So the reaction temperature was evaluated at first. As seen in Fig. 2a, with the increase of reaction temperature, the hydrolysis rate increase obviously. It takes 180 min, 110 min, less than 30 min and less than 10 min at 70, 100 and 110 °C to get 75% TRS yield, respectively. There may be two reasons which accelerated the reaction rate. The increase of reaction temperature can increase the energy of system to break the β -1,4-glucosidic bonds. The increase of temperature also can decrease the viscosity of the reaction system and speed up the mass transfer rate. The results also showed that the increase of temperature could increase TRS yield. The highest TRS yields gotten at 70, 80, 90, 100, 110 and 120 °C were 80.4%, 85.8%, 76.8%, 82.1%, 93.7%, and 88.7%, respectively. However, when reaction temperature reached 90 °C, TRS yield decreased quickly due to the side reactions of glucose. HMF was the main byproducts in this reaction were produced from the dehydration of glucose (Zakrzewska, Bogel-Łukasik, & Bogel-Łukasik, 2011). It was also the reactant for the production of humin. The results showed that with the increase of reaction temperature, HMF production rate and yield all raised obviously (Fig. 1a). It demonstrates that glucose can be more easily translated to byproducts at high temperature than at low temperature. When reaction was performed at temperature higher than 100 °C, not only TRS yield decreased, but also HMF decreased with the prolonging of reaction time. It suggests that TRS was stable in the system when temperature was lower than 90 °C.

3.3. Influence of catalyst amount

To test the efficiency of WCl₆, WCl₆ amount was evaluated in the experiments. When 0.01 g WCl₆ was added in the reaction system, it took 7 h to reach the highest TRS yield (41.8%). With the catalyst amount increasing to 0.02 g, 85.8% yield of TRS was gotten in 5 h. The highest HMF yield was also achieved with 0.02 g catalysts. When the catalyst amount further increased, both TRS and HMF yield decreased, while the amount of humin increased obviously. It suggests that too many catalysts would lead to the further degradation of TRS and HMF. The results showed that the most suitable catalyst is amount 0.02 g/ (1.0 g [BMIM]Cl, 0.05 g cellulose) (Fig. 3).

3.4. Degradation of cellulose with different concentration of cellulose

Cellulose concentration in [BMIM]Cl is a main factors influence the catalytic performance. The cellulose concentration was varied to test the effect of cellulose concentration on catalytic performance. As can be seen in Fig. 4, 100% yield of TRS was gotten when cellulose concentration was 2%. With the cellulose concentration increasing to 10%, TRS yield decreased to 36.3%. To find the reasons behind these data,

the degraded cellulose mole amount was calculated by following method. The degraded molar quantities of cellulose monomer, glucose, were calculated by the following formula: N(glucose) = m(cellulose)/180 \times Yield of TRS, where *m*(cellulose) is the mass of cellulose, Yield of TRS was the yield of TRS, 180 is the molar mass of monomer of cellulose (C₆H₁₀O₆). The degraded molar quantities of cellulose with different cellulose concentration (2%, 4%, 5%, 6%, 8%, 10%) in 2 h were 1.235×10^{-4} . 2.239×10^{-4} , 2.373×10^{-4} , 2.244×10^{-4} 2.252×10^{-4} and 2.241×10^{-4} mol, respectively. The results demonstrate that except the first one, the same amount of TRS was produced with different cellulose concentration at the same time. So the reaction rate based on TRS per mole WCl₆ was the same, about $1.126 \text{ mol g}^{-1} \text{ h}^{-1}$. The results showed that the cellulose concentration has no influence on the reaction rate, and the hydrolysis of cellulose is an apparent zero order reaction ($r = 1.126 \text{ mol g}^{-1} \text{ h}^{-1}$).

3.5. Degradation of different cellulose

The polymerization degree of microcrystalline cellulose used in previous experiments was 215-245, which was much smaller than the nature cellulose and lignocellulose. In order to test the catalytic performance of WCl6 for nature cellulose, WCl6-[BMIM]Cl system was used for the degradation of cotton (cellulose content: about 98%; polymerization degree: 6000-11,000), filter paper (cellulose content: 98%; polymerization degree: 3000-6000) and poplar wood (cellulose and hemicelluloses content: 82%; polymerization degree: about 10,000) at 90 °C. Because of large polymerization degree, cotton or filter paper was dissolved in [BMIM]Cl and formed high viscosity colloid. After the addition of WCl₆, the colloid became lilac and transformed to solution in 20 min, and then the lilac solution became brown slowly which suggested the generation of coloured products, such as HMF and furfural. This phenomenon suggests that the first step to degrade cellulose may be cutting the long chains of cellulose to short chains. For poplar wood, the dissolution process took 5 h and formed brown colloid. The results showed that the highest TRS yield was gotten from filter paper (88.5%). The TRS yields of cotton and polar wood were 83.1% and 82.8%, respectively. The cellulose and hemicelluloses content of polar wood is 82%, which suggested that all the cellulose and hemicelluloses were degraded to TRS. TRS yield of cotton was lower than filter paper, which has the similar cellulose content, while the polymerization degree of cotton was larger than that of filter paper. It demonstrates that the low polymerization degree is positive for the degradation of cellulose in ionic liquids. The cellulose hemicelluloses content of polar wood is 82%, while TRS yields of polar wood was 82.8%. It suggests that almost all the cellulose and hemicelluloses in polar wood were degraded to TRS in our experiments. These results showed that lignocelluloses and other nature cellulose can be decomposed to TRS by WCl₆ in [BMIM]Cl at temperature lower than 100 °C (Fig. 5).



Fig. 3. Reduce sugar and HMF yield of degradation of cellulose by different amount of WCl₆ at 80 °C.



Fig. 4. TRS yield from degradation of cellulose with different cellulose concentration at 90 \degree C (WCl₆ 0.02 g; [BMIM]Cl 1 g; 2 h).



Fig. 5. Degradation of different kinds of cellulose by WCl₆ for 2 h at 90 °C.

3.6. Degradation residue of cellulose by WCl_6 and $H_3PW_{12}O_{40}$

To investigate the degradation process of cellulose by WCl₆ in [BMIM]Cl, the residues of cellulose were characterized by FT-IR (Fig. 6). The characteristic bands of cellulose emerged at 3350.9 [*vs* (O–H)], 2977 [*vs*(C–H)], 1640 [*vs*(C=O)], 1371 [*vs*(C–O–C)], 1162 [*vs*(C–C)] and 1056.7 [*vs*(C–O–H)] cm⁻¹ (Zhou et al., 2013). After degradation by WCl₆, FT-IR spectrum of solid residue was different from the one of cellulose. The characteristic bands of cellulose (1056–1461 cm⁻¹) were disappeared or weakened. The vibration band of O–H at 3350 cm⁻¹ was weakened. The results showed that constitutes of residue were the polymerized products of glucose, HMF and furfural, which was commonly called humin. For the spectrum of solid



Fig. 6. FT-IR spectra of cellulose and residue of cellulose degradation at 120 $^\circ C$ for 2 h.

residue from H₃PW₁₂O₄₀-[BMIM]Cl system, the characteristic bands of Keggin structure were shown at 1109 [vs(P-O_a)], 955 [vs(W-O_d)], 894 [vs(W-O_c-W)], 794 [vs(W-O_d-W)], which suggested the presence of PW12040³⁻ in residue (Ghanbari-Siahkali, Philippou, Dwyer, & Anderson, 2000). The vibration bands of N-H in NH₄⁺ (2933, 1471 cm⁻¹), iminazole ring (1572, 1166 cm⁻¹) and C–H in iminazole ring (3100 cm^{-1}) were also found in this spectrum (Xie et al., 2018). All these vibration bands can be assigned to the bands in [BMIM]₃PW₁₂O₄₀ (Xie et al., 2014). It suggests that $H_3PW_{12}O_{40}$ reacted with [BMIM]Cl. The characteristic bands of cellulose were also emerged at 1056, 1461, 2977 and 3350 cm^{-1} . It suggests that there is some cellulose in residue. The vibration band emerged at 1638 cm^{-1} which can be assigned to vs (C=O) was much stronger than it in the spectrum of cellulose. It demonstrates that there was also humin formed in H₃PW₁₂O₄₀-[BMIM]Cl system. The FT-IR spectra showed that the TRS was easily transformed to humin in the presence of WCl₆ and H₃PW₁₂O_{40at} high temperature. H₃PW₁₂O₄₀ can reacted with [BMIM]Cl and fromed [BMIM]₃PW₁₂O₄₀.

3.7. Recycle of the catalytic system

It is important that catalysts can be recovered after cellulose degradation and can be reused for the reaction. WCl₆ was added in cellulose ionic liquids solution and reacted for 3 h at 80 °C. After the reaction, deionized water was added into the cellulose degradation system, and then the solid was separated. The solid was added into cellulose ionic liquid solution. RS yield of the first recycle was 76.5% at 80 °C. However, after the first cycle, the time for degradation of cellulose increased obviously. When reaction temperature increased to 100 °C, 76.5% yield of RS was gotten in 1 h. So beside the first cycle, the



Fig. 7. Reducing sugar and HMF yield of WCl₆ recycled for different times (cellulose 0.05 g, [BMIM]Cl 1 g, WCl₆ 0.02 g).

rest cycles of cellulose degradation were performed in 1 h at 100 °C. The catalyst was recycled for 5 times and RS yield has no obviously decreased. It indicates that the catalysts can be recovered after degradation and can be reused for the reaction. However, HMF yield decreased from 8.5% to 1.8% after the first cycle. When water was added into the reaction system, WCl₆ might be hydrolyzed to WO₃*n*H₂O. To find out if WO₃*n*H₂O has been the catalysts for the secondary and the rest cycles, WO₃*n*H₂O was added into cellulose ionic liquid solution to degrade cellulose at 100 °C. The results showed that similar RS yield (82.1%) was gotten with the secondary cycle. While HMF yield was only 1.3% which demonstrates that WO₃*n*H₂O was the real catalyst for the secondary and the rest cycles. The decrease of HMF yield in the secondary and the rest cycles may be due to the generation of WO₃*n*H₂O. However, the mechanism of cellulose in [BMIM]Cl degraded by WO₃*n*H₂O need further research (Fig. 7).

3.8. Mechanism of degradation of cellulose

To find out the mechanism of degradation of cellulose by WCl₆ in [BMIM]Cl, FT-IR spectra of cellulose, WCl₆ and cellulose-WCl₆ dissolved in [BMIM]Cl was performed. In the spectrum of [BMIM]Cl, the vibration band emerged at 3381 cm⁻¹ can be adscripted to O-H, which demonstrated the presence of H₂O in [BMIM]Cl. It can explain why cellulose can be hydrolyzed in this system. The vibration bands of [BMIM]Cl were shown at 3054 cm⁻¹ [vs(C-H) in iminazole ring], 1565 and 1169 cm⁻¹ (skeletal vibration of iminazole ring). The vibration bands of C-H in CH2 and CH3 were also detected at 2740-2993, 1459 cm⁻¹. After the addition of WCl₆, two new peaks appeared at 902 and 819.8 cm^{-1} , which can be assigned to vibration bands formed from the interaction between W⁶⁺ and [BMIM]Cl. After cellulose was dissolved into [BMIM]Cl, the characterization vibration bands of cellulose can be found at 1059 and 1034 cm^{-1} , which can be assigned to C-O in cellulose. No other vibration bands of cellulose was found in the spectra of cellulose-[BMIM]Cl solution, which suggested that cellulose was well dissolved in [BMIM]Cl. A new vibration band emerged at 445.7 cm⁻¹, which can be assigned to the vibration bands formed from the interaction between W⁶⁺ and C=O (Firouzabadi & Shiriny, 1996; Patton & McCarthy, 1987). This vibration band became stronger with the increase of reaction time (Figure S14). It suggested that cellulose was degraded by WCl₆ through the combination of W⁶⁺ with aldehyde carbonyl groups which formed the 1,4-glucosidic bonds. After the system was heating for 10 min, the vibration band at 902 cm^{-1} was disappeared, and the vibration bands at 819.8 and 445.7 cm^{-1} became stronger (Figure S14). It suggested that the W⁶⁺ strongly interacted with aldehyde carbonyl group became stronger under the calefaction. It further proved the degradation of cellulose by WCl6 in [BMIM]Cl was



Fig. 8. FT-IR spectra of [BMIM]Cl, [BMIM]Cl-WCl₆, [BMIM]Cl-cellulose and [BMIM]Cl-cellulose-WCl₆.

through the interaction between W⁶⁺ and aldehyde carbonyl groups.

According to the previous studies and FT-IR spectra (Fig. 8, S14), the mechanism of degradation by WCl₆ in [BMIM]Cl was suggested. After cellulose being dissolved in [BMIM]Cl, the crystal of cellulose is destroyed. Then cellulose chain is dispersed in [BMIM]Cl and [BMIM]Cl forms hydrogen bonds with hydroxyl group in cellulose (Fort et al., 2007). W⁶⁺ has good ability in combination with aldehyde O (Firouzabadi & Shiriny, 1996; Jung & Murphy, 2007; Patton & McCarthy, 1987), so in the reaction of cellulose's degradation it can attack glycosidic bonds which exist between two glucose units in cellulose more easily than other cations. When WCl₆ is added in the reaction system, it ionizes into W^{6+} and Cl^- . Then W^{6+} attacks the O in glycosidic bonds (aldehyde O), and glycosidic bonds are broken down. Water existing in [BMIM]Cl combines with glycosidic bonds which have been broken down to form TRS. Long chains of cellulose were broken down into short chains. Then short chain of cellulose was further degraded into TRS. As reactions continue, TRS was dehydrated to furans. W⁶⁺ also can interact with the aldehyde carbonyl groups, so furans are further polymerized to humin. To find out whether WCl₆ combines with aldehyde O or O in OH, formaldehyde and methanol were added into the reaction system, respectively. When formaldehyde was added in reaction system, TRS yield has decreased clearly (only 40% yield of TRS was produced at 80 °C for 3 h). However, when the same amount of methanol was added, TRS yield only decreased a little (78% yield of TRS was produced at 80 °C for 3 h). It is due to the competition of the aldehyde group on formaldehyde with which on cellulose combination with W^{6+} (Fig. 9).

4. Conclusions

Compared with inorganic acid, heteropoly acids, acidic ionic liquids and other metal chlorides, WCl₆ showed excellent activity for the degradation of cellulose in [BMIM]Cl at temperature lower than 80 °C and atmosphere pressure. More than 80% TRS yield can be obtained in 4 h at 70 °C. Reducing sugars are stable with WCl₆ at low temperature $(\leq 80 \degree C)$, while too high temperature (> 90 °C) would lead to the quick decrease of reducing sugar and generated humin as byproduct. The good catalytic activity was due to the good combination ability with aldehyde O in cellulose to break β -1,4-glucosidic bonds, which was proved by FT-IR. Degradation of cellulose by WCl₆ in [BMIM]Cl is a zero order reaction. Lignocelluloses and other nature cellulose also can be almost totally degraded to reducing sugar by WCl₆ in [BMIM]Cl at 90 °C. The most suitable catalysts loading amount and reaction time at 80 °C is 0.04 g/g cellulose 2 g [BMIM]Cl and 2 h. Catalyst can be recycled for 5 times without the decrease of catalytic activity. This research shows an efficient way for the degradation of cellulose at low temperature.



Fig. 9. Mechanism of degradation of cellulose by WCl₆ in [BMIM]Cl.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.carbpol.2019.02.050.

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