Journal of Molecular Catalysis A: Chemical 334 (2011) 8–12

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Direct conversion and NMR observation of cellulose to glucose and 5-hydroxymethylfurfural (HMF) catalyzed by the acidic ionic liquids

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ARTICLE INFO

Article history:
Received 14 May 2010
Received in revised form 30 August 2010
Accepted 4 October 2010
Available online 8 December 2010

Keywords:
Hydrolysis of cellulose
Ionic liquids
In situ ^{13}C NMR
Acidic catalysis
Apparent activation energy

ABSTRACT

The hydrolysis of cellulose was catalyzed over a variety of acidic ionic liquids (ILs). It is found that the hydrolysis activity is directly associated with the acidity of catalysts, as evidenced by IR spectroscopy. ^{13}C NMR characterization results confirm the majority product of cellulose hydrolysis is glucose, and the resulting carbohydrates undergo further degradation, possibly also catalyzed by the acidic ILs, to 5-hydroxymethylfurfural (HMF). Moreover, *in situ* ^{13}C NMR measurements clearly exhibit that the evolution of products is dependent on the reaction process. We attempt to study the kinetics of cellulose hydrolysis over the most active catalyst of $[C_4SO_3Hmim]HSO_4$ at different temperatures (80–120 °C) to obtain the important kinetic parameters such as apparent activation energies of consecutive reaction steps.

1. Introduction

Cellulose constitutes the major components of the so-called biomass that has attracted worldwide attention as a potentially widespread approach for sustainable energy production [1], but there are very few practical processes for converting cellulosic biomass directly into more value-added products. The reason for this difficulty is related with their strong hydrogen-bond networks in the cellulose crystalline forms, leading to the low efficiency and environmental unfriendliness at the hydrolysis process in which the bulk cellulose are transformed to their monomers or fermentable sugars. Therefore, a novel, green and cost-effective process under mild reaction conditions is urgently required for cellulose utilization.

The application of ionic liquids (ILs) as solvents for the dissolution of cellulose was firstly reported by Rogers and co-workers [2]. The unique reaction performances were attributed to the interaction of the chloride in the studied IL of $[C_4mim]Cl$ with the hydrogen-bonding networks of cellulose, resulting in the decrystallization. The characteristic properties of the ionic liquids such as low vapor pressure and good thermal stability offer promising future to circumvent the cost and scalability hurdles as encountered in the traditional gasification and pyrolysis processes for the biomass transformation. Moreover, the components of cation and anion in the ILs can be fine-tuned to adjust the physicochemical properties, such as hydrophobicity/hydrophilicity, of the resulting ILs, thus affecting their performance in the interaction with the cellulose [3]. Furthermore, hydrolysis of cellulose to the sugars such as monosaccharides and disaccharides was observed when liquid acids or solid acids were added to the reaction system with ILs as solvents [4–6]. The separation of the products (from ILs) can be achieved by extraction, e.g., supercritical CO_2, or the so-called nanofiltration by the membrane [7]. It is interesting to note that the product of resulting monosaccharides could be subsequently converted to other valuable products, e.g., 5-hydroxymethylfurfural (HMF), which could be used for the future liquid fuel [8]. The acidities of the employed acids undoubtedly played crucial roles for those transformations, but the detailed studies of the reaction mechanisms have been scarce in the literature.

The acidic ionic liquids can be prepared by modifying the ILs with acidic groups, and such materials were used as catalysts for the acid-catalyzed reactions [9–11]. In this report, we investigate the hydrolysis of cellulose over several acidic ILs in the solvent of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). Infrared spectroscopy is used to study the acidity of the catalysts with pyridine as the probe molecule to correlate the acidity and hydrolysis activity. Moreover, *in situ* ^{13}C NMR spectroscopy is applied to identify the reaction products and to monitor the hydrolysis process to under-

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doi:10.1016/j.molcata.2010.10.006

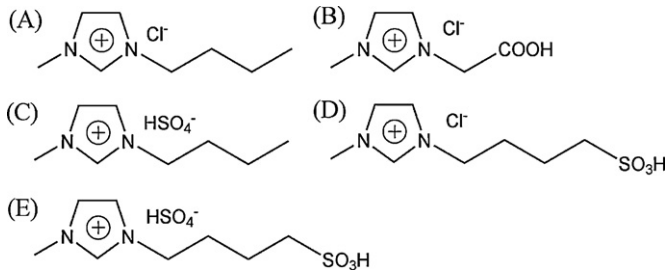

Fig. 1. Ionic liquids used in the experiments. (A) [Bmim]Cl, (B) [C_1COOHmim]Cl, (C) [Bmim]HSO_4, (D) [C_4SO_3Hmim]Cl, and (E) [C_4SO_3Hmim]HSO_4.

stand the underlying reaction mechanism. Based on the knowledge of the characterization results, we propose a simplified reaction model, and perform kinetic studies to obtain important reaction parameters. To our knowledge, it is the first time to report *in situ* study of ^{13}C NMR to monitor the hydrolysis process of cellulose with the acidic ionic liquids as catalysts.

2. Experimental

2.1. Materials

The structures of the ionic liquids used for this study are displayed in Fig. 1. 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-carboxyethyl-3-methylimidazolium chloride ([C_1COOHmim]Cl), 1-butyl-3-methylimidazolium hydrogensulfate ([Bmim]HSO_4), 1-butyl sulfonic acid-3-methylimidazolium chloride ([C_4SO_3Hmim]Cl), 1-butyl sulfonic acid-3-methylimidazolium hydrogensulfate ([C_4SO_3Hmim] HSO_4) were provided from Meisibei company, China, and purities of all ILs were ca. 98%. We speculate that [C_1COOHmim]Cl and [Bmim]HSO_4 belong to the weakly acidic ILs since it is well known that the function group of –COOH and HSO_4^- are relatively weak acids, whereas [C_4SO_3Hmim]Cl and [C_4SO_3Hmim]HSO_4 are suggested to be relatively strong ILs because $-SO_3H$ group are widely used to modify the acidity of the polymers, leading to the strong acidic catalysts. To remove the water content in the ILs, the ILs have been kept in the vacuum drying oven at 50 °C, and reactant of microcrystalline cellulose (AR, ACROS) is dried at 100 °C oven overnight before use.

2.2. Hydrolysis reaction

The cellulose hydrolysis was carried out in a round bottom flask that was heated in the oil-bath in the range from 80 °C to 120 °C. Typically, 0.4 g microcrystalline cellulose was added into 8.0 g [Bmim]Cl solvent that was preheated under vigorous stirring, followed by the addition of desired 1 ml acidic ionic liquid catalyst, 0.08 g H_2O and 2 ml co-solvent of dimethylformamide (DMF) at the reaction temperature. Blank experiment was also performed without the addition of the acidic IL catalyst for comparison. The reaction was then vigorously stirred until a transparent solution was obtained. At different time intervals, 0.11 g samples (0.1 ml) were extracted, and quenched immediately with 0.9 ml NaOH solution (0.03 mol/l). The solution was centrifuged at 15,000 rpm for 10 min and further employed for the product analysis. The analysis of total reducing sugar (TRS) was based on the adsorption spectroscopy, and the details are elaborated in the literature [12]. In a typical measurement, 0.5 ml resultant solution was mixed with 0.5 ml predetermined 3,5-dinitrosalicylic acid (DNS) reagent, heated for 10 min at 100 °C and cooled to room temperature. 4 ml deionized water was then added to the sample, and the mixture was subjected for the quantitative analysis on a JASCO V-550 spectrophotometer at 520 nm with a slit width of 0.1 mm.

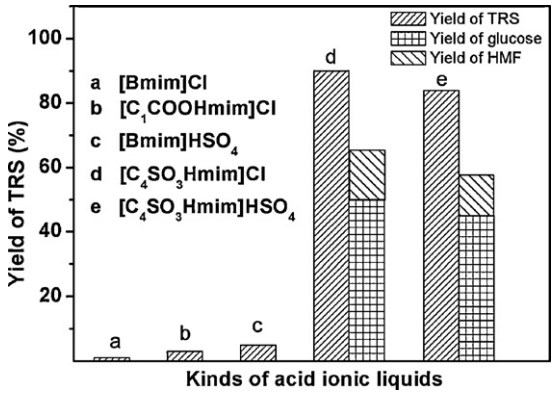

Fig. 2. Yield of TRS/glucose/HMF at 100 °C (1 h) with different acid ionic liquids as catalysts in the solvent of [Bmim]Cl. (a) Blank, (b) [C_1COOHmim]Cl, (c) [Bmim]HSO_4, (d) [C_4SO_3Hmim]Cl, and (e) [C_4SO_3Hmim]HSO_4.

2.3. Characterization

2.3.1. IR

The interaction of pyridine molecule with the acidic sites of studied ionic liquids was studied by infrared spectroscopy at room temperature. The probe molecule of pyridine was mixed with the ionic liquids with the ratio of 1:5, and the mixture was spreaded into the liquid film between KBr windows. All the IR spectra were recorded on a Bruker Vector 22 spectrometer with an MCT detector at a resolution of 1 cm^{-1} and 32 scans.

2.3.2. NMR

Liquid-state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Varian DRX-400 spectrometer. The resonance frequency employed in ^{13}C NMR was 100.6 MHz. The sample was added with 10% DMSO-d_6 in the sample tube, and the chemical shifts were referenced to tetramethylsilane (TMS). In the standard sample measurements, 4% of glucose or cellulose was dissolved in the [Bmim]Cl. The samples were heated at 90 °C to reduce the viscosities of the mixture. In contrast, the *in situ* NMR experiment was carried out in a home-made glass NMR sample tube, with the temperature accurately controlled. The sample tube was loaded into NMR machine and heated quickly to 80 °C and reacted at that temperature for 24 h. *In situ* ^{13}C NMR spectra were recorded during the reaction with the accumulation of 800 scans.

3. Results and discussion

The cellulose hydrolysis reaction results (100 °C, 1 h) over the various acidic IL catalysts are exhibited in Fig. 2. For the blank experiment without the presence of acidic IL, i.e., the reaction in the solvent of [Bmim]Cl, the yield of TRS is negligible. Indeed, little activity is observed even when the reaction is prolonged to 100 h, confirming that [Bmim]Cl is not active for the production of reducing sugars. In contrast, the presence of weakly acidic ILs of [C_1COOHmim]Cl and [Bmim]HSO_4 catalyze the hydrolysis of cellulose, and TRS of 3% and 5% are achieved after 1 h reaction. We note further reaction time at 24 h enhance the release of reducing sugars to 17% and 28% over [C_1COOHmim]Cl and [Bmim]HSO_4, respectively. It is remarkable that the presence of the sulfonic acid group in the ILs, i.e., [C_4SO_3Hmim]Cl and [C_4SO_3Hmim]HSO_4, greatly increase the reaction rates of the cellulose hydrolysis, and the hydrolysis are nearly complete in 1 h. TRS of 95% and 85% are observed on [C_4SO_3Hmim]Cl and [C_4SO_3Hmim]HSO_4, respectively. The major products of the cellulose transformation, as revealed by chromato analysis, are glucose and HMF, further careful inspection discloses a variety of organic substances (containing carbon,

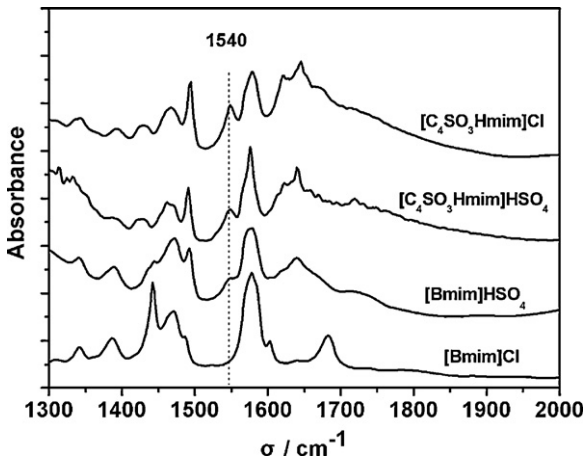

Fig. 3. FT-IR spectra of ionic liquids with pyridine as probe molecule. From bottom to top: [Bmim]Cl, [Bmim]HSO_4, [C_4SO_3Hmim]HSO_4, and [C_4SO_3Hmim]Cl.

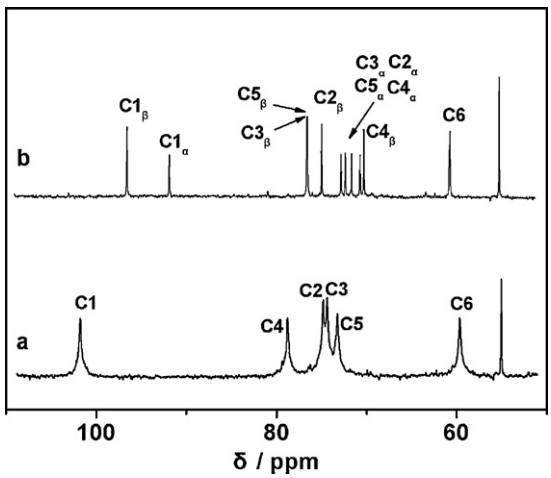

Fig. 4. ^{13}C NMR of (a) cellulose and (b) glucose in the solvent [Bmim]Cl.

hydrogen, and/or oxygen) are present as by-products. However, the amounts of the by-products are minor and the nature of those molecules is very difficult to identify. We suggest that the hydrolysis discrepancy between the same volume of [C_4SO_3Hmim]Cl and [C_4SO_3Hmim]HSO_4 does not indicate the acid strength of [C_4SO_3Hmim]Cl is stronger than [C_4SO_3Hmim]HSO_4. On the contrary, it might implicate that [C_4SO_3Hmim]HSO_4 has less amount of the active acid sites.

It is reported by Yang and Kou that the application of pyridine on the ionic liquids provides an easy approach for studying the acidities of ionic liquids, and the appearance of a band near 1540 cm^{-1} is the characteristic band for the formation of pyridinium ions, resulted from the presence of Brønsted acidity [13]. Fig. 3 shows the IR spectra of the employed ionic liquids with pyridine as the probe molecule. Since [C_1COOHmim] is a solid under room temperature, it is not included in the figure for the comparison. No signal at 1540 cm^{-1} can be detected over the mixture of [Bmim]Cl and pyridine, implicating that the Brønsted acidity is nearly negligible on the solvent of [Bmim]Cl. Nevertheless, a small but distinct band is clearly observed after [Bmim]HSO_4 is added with pyridine, confirming the presence of Brønsted acidity on [Bmim]HSO_4. Moreover, such a band is more pronounced over [C_4SO_3Hmim]HSO_4 and [C_4SO_3Hmim]Cl. Despite the difficulty in the quantitative analysis under the present experimental conditions, we suggest that the increase of the intensity of the band at 1540 cm^{-1}, i.e., [C_4SO_3Hmim]Cl > [C_4SO_3Hmim]HSO_4 > [Bmim]HSO_4 > [Bmim]Cl, might be related with their Brønsted acid amounts, and such increase is consistent with their increasing reaction yields of TRS in Fig. 2.

^{13}C NMR spectroscopy is employed as a characterization tool to identify the products of the cellulose products and to study the reaction process, this is based on the observation that the solvent of [Bmim]Cl does not display the ^{13}C resonance signal in the studied region between 55 and 120 ppm [14]. Since glucose is the building unit for the cellulose, [15] their ^{13}C NMR spectra in the solvent of [Bmim]Cl are displayed in Fig. 4. The glucose possess two diastereomers of α-glucopyranose and β-glucopyranose in the solution, this is reflected by the characteristic bands at 91.9 ppm and 96.6 ppm, which are assigned to the C1 atom in α and β isomers, respectively [16]. The peaks between 60 and 80 ppm are attributed to various carbon atoms (C2–C6) in the glucose structure. In contrast to the spectrum of glucose, the chemical shift of C1 and C4 atoms in the cellulose shift to 101.8 and 78.8 ppm, respectively, because of the formation of β-1,4 glycosidic bonds among glucose to form the cellulose, which are similar to that reported in the literature [14]. Moreover, the absence of resonance signal between 90 and 100 ppm indicates that cellulose is not transformed into the glucose in the presence of only solvent, supporting the conclusion that the hydrolysis of cellulose to reducing sugars is nearly negligible without the acidic catalyst. Therefore, cellulose and glucose undoubtedly exhibit characteristic bands in the ^{13}C NMR spectroscopy and they do not interfere. We take this as a strong proof to use ^{13}C NMR spectroscopy to monitor the cellulose hydrolysis process. For the sake of simplicity, we take characteristic bands at 101.8 ppm for the presence of cellulose, 96.6 and 91.9 ppm for the presence of glucose, respectively.

The *in situ* ^{13}C NMR investigation of the cellulose hydrolysis upon the acidic catalyst of [C_4SO_3Hmim]Cl at 80 °C is presented in Fig. 5. The ^{13}C NMR spectra are plotted against the reaction time to show the evolution of the reaction products as the reaction proceeds. For the first 0.5 h, only the resonance attributed to cellulose is observed, implicating that the cellulose hydrolysis is insignificant or the product formation is not high enough for the ^{13}C NMR detection. However, after the reaction proceeds for 1 h, two slight but distinct resonances are clearly observed

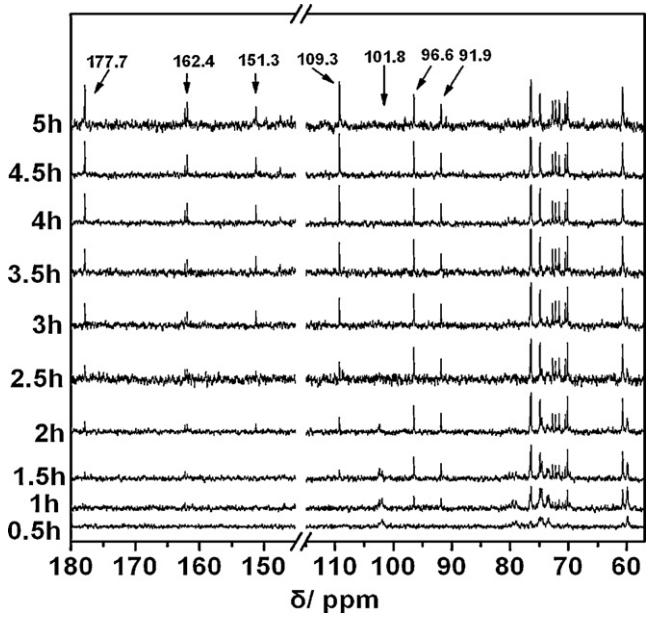

Fig. 5. *In situ* ^{13}C NMR study of the cellulose hydrolysis over [C_4SO_3Hmim]Cl. The reaction was conducted at 80 °C under atmosphere pressure in a home-made sample tube in NMR machine.

at 96.6 and 91.9 ppm, which are related to the presence of glucose. In other words, the cellulose undergoes hydrolysis to form glucose. Although it is reported that various products are plausible such as cellobiose, cellotriose, in the cellulose hydrolysis [17], we tentatively draw the conclusion that the majority of the cellulose hydrolysis products in our system is glucose because no other product can be identified by ^{13}C NMR. This suggestion is further underpinned by the observation of the decrease of cellulose signal (101.8 ppm) and the simultaneous increase of the glucose signal (96.6 and 91.9 ppm) at the reaction time of 1.5 h. Moreover, a slight resonance at 109.3 ppm at 1.5 h is distinguishable. Longer reaction time (2–2.5 h) leads to further increase of the characteristic peaks assigned to glucose and the decrease of the resonance related with cellulose. When the reaction is prolonged to 3 h, the cellulose nearly disappears, indicating that it is completely transformed. In contrast, four characteristic bands at 177.7, 162.4, 151.3 and 109.3 are clearly observed, and those characteristic bands are assigned to the formation of 5-hydroxymethylfurfural (HMF) [18]. Clearly, the degradation of glucose to HMF takes place on the acidic environment employed in this research. As the reaction further proceeds from 3.5 h to 5 h, we observe pronounced increase of the characteristic resonance signal associated with HMF, accompanied by the decrease of the peak intensities related with glucose. The ^{13}C NMR measurements suggest that the cellulose hydrolysis can be simplified as two consecutive steps: (1) cellulose is hydrolyzed in the presence of acidic catalyst to the glucose, a kind of reaction intermediate; (2) the produced glucose is further converted into HMF, also catalyzed by the catalyst of $[C_4SO_3Hmim]Cl$. The detailed isomerization mechanisms from glucose to HMF in the presence of IL have been discussed by Zhao et al. [19].

The hydrolysis of cellulose upon the acidic catalysts is an extremely complex process in which a variety of reactions can take place together and many products are formed. Based on our observation that the products detected are only glucose and HMF, we tentatively simplify the cellulose reaction process in our system as

$$\text{Cellulose} \xrightarrow{K_1} \text{glucose} \xrightarrow{K_2} \text{HMF}$$

in which K_1 and K_2 are reaction rate constants for the hydrolysis and further degradation steps, respectively. As proposed by a number of reports, [5,20] such a simplified model can provide a reasonable estimation for the study of kinetic parameters. Li et al. concluded that the kinetics above follow a consecutive first order sequence [5]. Assume the initial concentration of cellulose is α at the beginning of the reaction, the concentrations of cellulose, glucose and HMF in a given reaction time t can be written as

$$\frac{dx}{dt} = -K_1 x \quad (1)$$

$$\frac{dy}{dt} = K_1 x - K_2 y \quad (2)$$

$$\frac{dz}{dt} = K_2 y \quad (3)$$

where x, y and z are the concentration of cellulose, glucose and HMF, respectively. After further integration, we can obtain

$$x = ae^{-Kt} \quad (4)$$

More importantly, the glucose concentration y can be expressed as

$$y = \frac{K_1 a}{K_2 - K_1}(e^{-K_1 t} - e^{-K_2 t}) \quad (5)$$

Therefore, for a given reaction at a certain temperature, the reaction rate constants K_1 and K_2 can be simulated by plotting the glucose concentration (determined by experiments) and the reaction time [5].

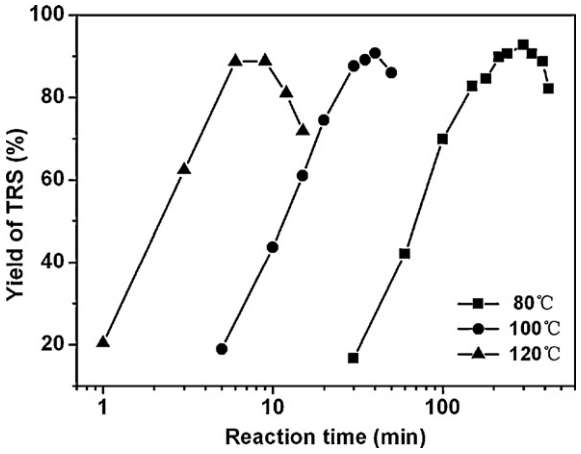

Fig. 6. Cellulose hydrolysis over $[C_4SO_3Hmim]Cl$ at different temperatures: (■) 80 °C, (●) 100 °C, and (▲) 120 °C.

Table 1
Reaction rate constants at different temperatures.

	Temperature (°C)		
	80	100	120
K_1 (min^{-1})	7.9×10^{-3}	6.6×10^{-2}	4.1×10^{-1}
K_2 (min^{-1})	1.6×10^{-3}	8.5×10^{-3}	4.1×10^{-2}

A series of cellulose hydrolysis upon the acidic catalyst of $[C_4SO_3Hmim]Cl$ have been carried out at 80 °C, 100 °C and 120 °C, respectively. The relations between the TRS (glucose) yield and the reaction time are displayed in Fig. 6. They seem to follow the same pattern, i.e., the increase of the glucose concentration at the beginning is owing to the hydrolysis of cellulose to glucose, and further decrease of the TRS yield is due to the degradation of glucose to the HMF. The results are in accordance with the conclusions from the ^{13}C NMR observations in Fig. 5. Clearly, short reaction time favors the production of glucose and longer reaction time facilitates formation of HMF in a given temperature. Moreover, the hydrolysis is remarkably dependent on the reaction temperature. Hydrolysis of cellulose seems to be faster at higher temperature as well as the degradation of the glucose to HMF. Thus, the cellulose hydrolysis in the acidic ILs is both dependent on the reaction time and the reaction temperature. Undoubtedly, the kinetic parameters are crucial to optimize the reaction process to obtain desired reaction products. The simulated reaction rate constants are listed in Table 1.

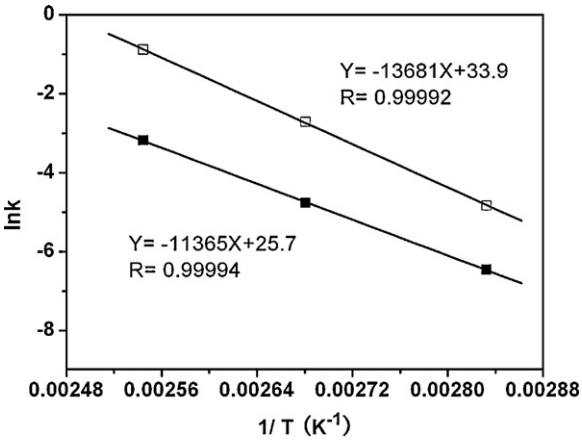

Fig. 7. Arrhenius plot of different reaction steps in the cellulose hydrolysis over $[C_4SO_3Hmim]Cl$. (□) cellulose hydrolysis to glucose, (■) glucose degradation to HMF.

The reaction rates of both reaction steps increase at elevated temperature, implying relatively high temperature might be necessary for the practical application. In addition, Arrhenius plots for the cellulose hydrolysis and glucose degradation are shown in Fig. 7. We estimate that the apparent activation energies for the cellulose hydrolysis to glucose and glucose degradation to HMF are 114 and 95 kJ mol^{-1}, respectively.

4. Conclusion

The acidic ionic liquids readily catalyze the cellulose hydrolysis in the solvent of [Bmim]Cl in the range of 80–120 °C, resulting in the dominant productions of glucose and 5-hydroxymethylfurfural (HMF). The Brønsted acidity, particularly the acid strength, in the catalysts are crucial to break the β-1,4 glycosidic bonds in the cellulose to form glucose, and further convert glucose to HMF. The hydrolysis process and the product formation are both dependent on the reaction time and the reaction temperature. *In situ* ^{13}C NMR spectroscopy is proven to be an efficient characterization method to study the cellulose hydrolysis in the ionic liquids.

Acknowledgements

This work received financial support from the Ministry of Science and Technology of China (2010CB732202), and the Natural Science Foundation of China. D.M. thanks the CAS for support through the Bairen project.

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