SELECTIVE CHLORINATION OF GLYCEROL TO 3-CHLORO-1,2-PROPANEDIOL CATALYZED BY BRØNSTED ACIDIC IONIC LIQUIDS

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Abstract - Brønsted acidic ionic liquids composed of 1-butyl-3-methylimidazolium, triethylbutylammonium, and 1-butylpyridinium cation counterparts and HSO_4^- and $H_2PO_4^-$ anion counterparts were used as the catalysts for the selective chlorination of glycerol with hydrogen chloride to 3-chloro-1,2-propandiol. From the perspective of the glycerol conversion and product yields, the catalytic activities of the ionic liquids containing HSO_4^- were higher than the ionic liquids containing $H_2PO_4^-$. As compared with the carboxylic acid catalysts, Brønsted acidic ionic liquids favored the catalytic chlorination of glycerol to 3-chloro-1,2-propandiol. When the glycerol chlorination was catalyzed by the Brønsted acidic ionic liquids at 110 ºC for 12 h with the catalyst loading of 0.75 mol·kg⁻¹ glycerol, the 3-chloro-1,2-propandiol yield was more than 81% at the complete conversion of glycerol.

Keywords: Glycerol, 3-Chloro-1,2-dipropanol, Brønsted acidic ionic liquids, Chlorination.

INTRODUCTION

Biodiesel is an environmentally friendly and renewable fuel. With the rapid growth of biodiesel production, glycerol is produced as the main byproduct, *ca.* 10% of biodiesel, causing the glycerol market to be oversupplied (Katryniok *et al.*, 2013; Tesser *et al.*, 2007; Yi *et al.*, 2014). Nowadays, researchers have paid great attention to the conversion of glycerol to high-valued chemicals, such as propanediol, propylene glycol, dichloropropanol, acrolein, and acrylic acid by hydrogenolysis (Dasari *et al.*, 2005; Ma *et al.*, 2008), catalytic chlorination (Santacesaria *et al.*, 2010), dehydration (Shen *et al.*, 2012), and oxydehydration

methods (Shen *et al.*, 2014; Zhou *et al.*, 2007). Monochloropropandiol is produced as an intermediate chemical for dichloropropanol production.

3-Chloro-1,2-propandiol (3-MCPD) is an important raw material for the production of glycerol carbonate and glycidol (Choi *et al.*, 2013; Gade *et al.*, 2012; Gómez-Jiménez-Aberasturi *et al.*, 2010; Ochoa-Gómez *et al.*, 2011; Pagliaro and Rossi 2010), which are used for the synthesis of polymers, pharmaceuticals, cosmetics, and photochemicals. Furthermore, chiral 3-MCPD is an important medical intermediate for the synthesis of *L*-carnitine (Li *et al.*, 2011;Yang *et al.*, 2011). 3-MCPD is conventionally produced by the hydrolysis of epoxy chloropropane, which

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is produced by using propylene as a starting material *via* chlorination, chlorohydrination, and subsequent saponification processes (Carrà *et al.*, 1979; Nadato *et al.*, 1987). However, the production process is very complicated. In the production of dichloropropanol *via* the chlorination of glycerol, 3-MCPD is produced first as an intermediate product, which can be rapidly chlorinated to dichloropropanol over carboxylic acid catalysts (de Araujo Filho *et al.*, 2016; de Araujo Filho *et al.*, 2016; Hou *et al.*, 2015). Over heteropolyacid catalysts, 3-MCPD with a maximum selectivity of 42.3% was obtained, accompanied by the formation of dichloropropanol and other byproducts (Song *et al.*, 2010). Selective chlorination of glycerol to 3-MCPD with a high selectivity is worthy of investigation.

Recently, reactions catalyzed by ionic liquids have attracted the interest of researchers in virtue of their negligible vapor pressure, high thermal stability, high ionic conductivity, and composition tunability (Chen *et al.*, 2010;Duan *et al.*, 2006; Olivier-Bourbigou and Magna, 2002; Wang *et al.*, 2012). Brønsted acidic ionic liquids bearing acid anions and organic cations, such as HSO_4^-, $H_2PO_4^-$, $[Bmim]^+$, $[BPy]^+$, and $[N_{2224}]^+$, have been used in many typical acid-catalyzed organic reactions (Srivastava, 2010; Wang *et al.*, 2008; Wang *et al.*, 2008). The acidity of Brønsted acidic ionic liquids can be changed by changing the components of the anion counterparts, which affect their catalytic activities for acid-catalyzed reactions. Brønsted acidic ionic liquids not only supply protons for catalyzing the chlorination of glycerol, their steric effect may also affect the selectivity of chlorinated product.

In the present work, the catalytic performances of the Brønsted acidic ionic liquids composed of 1-butyl-3--methylimidazolium ($[Bmim]^+$), triethylbutylammonium ($[N_{2224}]^+$), and 1-butylpyridinium ($[BPy]^+$) cation counterparts and HSO_4^- and $H_2PO_4^-$ anion counterparts were investigated for the chlorination reaction of glycerol with HCl. The acidities of the Brønsted acidic ionic liquids were evaluated by UV-vis spectroscopy. Brønsted acid sites of the Brønsted acidic ionic liquids were determined by a FT-IR technique with the use of pyridine as a probe molecule. The effect of reaction parameters, reaction temperature and catalyst loading, on the chlorination reaction was investigated. The reaction routes were also briefly discussed.

MATERIALS AND METHODS

Chemicals

Hydrogen chloride was of industrial grade and was purchased from Shandong Wangdali Co. Ltd.

2-Chloro-1,3-propanediol (2-MCPD), 3-MCPD, 1,3-dichloro-1-propanol (1,3-DCP), and 2,3-dichloro-1-propanol (2,3-DCP) were purchased from Xiya Chemical Reagents Co. Ltd. 1-Methylimidazole, triethylamine, pyridine, *n*-butyl bromide, phosphoric acid, sulfuric acid, glycerol, and *n*-butanol were of reagent grade and were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were used as received without further purification.

Synthesis of Brønsted acidic ionic liquids

Synthesis of 1-butyl-3-methylimidazolium bromide ([Bmim]Br). According to the reported method (Ramenskaya *et al.*, 2008), [Bmim]Br was synthesized as follows. *N*-Methylimidazole (0.5 mol) and *n*-butyl bromide (0.55 mol) were added into a 250 mL three-necked flask equipped with a reflux condenser under stirring and a nitrogen atmosphere. The reaction was carried out under reflux for 10 h. The resultant mixture was cooled to room temperature and the as-synthesized [Bmim]Br was washed with ethyl acetate thrice. The remaining ethyl acetate was removed with a rotary evaporator at 70 ºC and [Bmim]Br was dried in a vacuum oven at 70 ºC for 24 h.

Synthesis of 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄) and l-butyl-3-methylimidazolium dihydrogen phosphate ([Bmim]H₂PO₄) (Dubreuil *et al.*, 2002; Wang *et al.*, 2008). Given amount of [Bmim]Br was added in a three-necked flask in an ice-water bath and then concentrated sulfuric acid (98%) or phosphoric acid (85%) in the same mole amount as that of [Bmim]Br was added dropwise into it under vigorous stirring. The mixture was slowly heated up to 60 ºC and stirred for 18 h. The as-synthesized [Bmim]HSO₄ and [Bmim]H₂PO₄ samples were evaporated with a rotary evaporator and dried in a vacuum at 70 ºC for 24 h.

Synthesis of 1-butylpyridinium bromide ([BPy]Br) (Xiong and Yang, 2014). Under nitrogen atmosphere, 20 mL of ethanol as solvent and 0.5 mol of pyridine were added to a 250 mL three-necked flask with a reflux condenser. Then 0.55 mol of *n*-butyl bromide was added under reflux and stirring for 4 h. The solvent and unreacted chemicals were separated from the reaction solution by reduced pressure distillation technique. The as-prepared [BPy]Br was cooled to room temperature, washed with ethyl acetate (3×20 mL), and recrystallized in dichloromethane. The [BPy]Br sample was dried in a vacuum oven at 50 ºC for 24 h.

Synthesis of 1-butylpyridinium hydrogen sulfate ([BPy]HSO₄) and 1-butylpyridinium dihydrogen

phosphate ([BPy]H$_2$PO$_4$) (Du *et al.*, 2006). The synthesis procedures for [BPy]HSO$_4$ and [BPy]H$_2$PO$_4$ were the same as those mentioned for the synthesis of [Bmim]HSO$_4$ and [Bmim]H$_2$PO$_4$.

Synthesis of triethylbutylammonium bromide ([N$_{2224}$]Br) (Yu *et al.*, 2009). Under a nitrogen atmosphere, 0.5 mol of triethylamine and 0.5 mol of *n*-butyl bromide were added into a 250 mL three-necked flask containing 50 mL ethanol and reacted under reflux for 24 h. The resultant mixture was washed with ethyl acetate thrice. The remaining ethyl acetate was removed with a rotary evaporator and white solid [N$_{2224}$]Br was dried in a vacuum oven at 60 ºC for 24 h.

Synthesis of triethylbutylammonium hydrogen sulfate ([N$_{2224}$]HSO$_4$) and triethylbutylammonium dihydrogen phosphate ([N$_{2224}$]H$_2$PO$_4$) ([Attri] *et al.*, [2011]). The synthesis procedures for [N$_{2224}$]HSO$_4$ and [N$_{2224}$]H$_2$PO$_4$ were the same as those mentioned for the synthesis of [Bmim]HSO$_4$ and [Bmim]H$_2$PO$_4$.

Characterization of Brønsted acidic ionic liquids

Determination of acid sites of Brønsted acidic ionic liquids

Brønsted acid sites of the ionic liquids were determined using pyridine as a probe molecule by monitoring the band range of 1300-1600 cm^{-1} (Qureshi *et al.*, 2009; Yang and Kou, 2004). All samples were prepared by mixing pyridine and ionic liquid with a mole ratio of 3:1. The spectra were recorded on a FT-IR spectrophotometer (Nicolet Nexus 470) at room temperature.

UV-vis acidity evaluation

The Hammett function is used to evaluate the Brønsted acidity of a Brønsted acidic ionic liquid in a solution with a basic indicator to trap the dissociative proton. The Hammett acidity function was detected using UV-vis spectroscopy (Gu *et al.*, 2005; Thomazeau *et al.*, 2003). This method consists of evaluating the protonation extent of the uncharged indicator base (named I) in a solution, in terms of the measurable ratio [I]/[IH$^+$]. The Hammett function (H_0) is defined as follows:

$$H_0 = pk(I)_{aq} + \log([I]/[IH^+]) \qquad (1)$$

To evaluate the acidities of those above-mentioned Brønsted acidic ionic liquids, *4*-nitroaniline was chosen as the indicator (the concentration

was 10 mmol/L, the Hammett content is 0.99 in dichloromethane). After adding a molar equivalent of Brønsted acidic ionic liquids into the dichloromethane solution of *4*-nitroanline, the UV-vis absorbance of the unprotonated *4*-nitroanline was recorded with an Analytik Jena S600 spectrophotometer at 350 nm.

Chlorination reaction

Fifty grams of glycerol and a given amount of Brønsted acidic ionic liquids with the ratios of ionic liquid to glycerol of 0.25-1.0 mol kg^{-1} were added into a 100 mL four-necked round bottom flask equipped with a hydrogen chloride inlet tube, a thermometer, a condenser, and a magnetic stirrer under stirring at 100 rpm. Nitrogen stream was introduced into the reactor to replace the air inside the reactor before the chlorination reaction. When the reaction solution was heated to a prescribed temperature (70-130 ºC), hydrogen chloride was introduced into the reactor at a flow rate of 80 mL min^{-1}. The exhaust gas was absorbed with an aqueous alkali solution.

The reaction mixture was analyzed on a gas chromatograph, equipped with a flame ionization detector (FID) and a PEG capillary column (0.25 mm × 30 m). *n*-Butanol was used as an internal standard sample. The conversion of glycerol and the yields of 2-MCPD, 3-MCPD, 1,3-DCP, and 2,3-DCP were calculated according to the following equations.

$$Glycerol\ Conversion = \frac{Glycerol_{in} - Glycerol_{out}}{Glycerol_{in}} \times 100\% \quad (1)$$

$$Product\ Yield = \frac{Product_{out}}{Glycerol_{in}} \times 100\% \qquad (2)$$

RESULTS AND DISCUSSION

Acid sites of Brønsted acidic ionic liquids

Although the pyridine adsorption method can not be used to quantitatively detect the amount of Brønsted acid in ionic liquids, it is widely used to determine the presence of Brønsted acid sites (Bui *et al.* 2012; Yang and Kou, 2004). The presence of a peak near 1540 cm^{-1} is an indication of the formation of pyridinium ions resulting from the presence of Brønsted acid sites.

As shown in Fig. 1, pure pyridine shows a well resolved band at 1438 cm^{-1}. When pyridine was mixed with nine Brønsted acidic ionic liquids, the adsorption peaks appearing at 1540 cm^{-1} were observed, indicating the presence of Brønsted acid sites in all the samples.
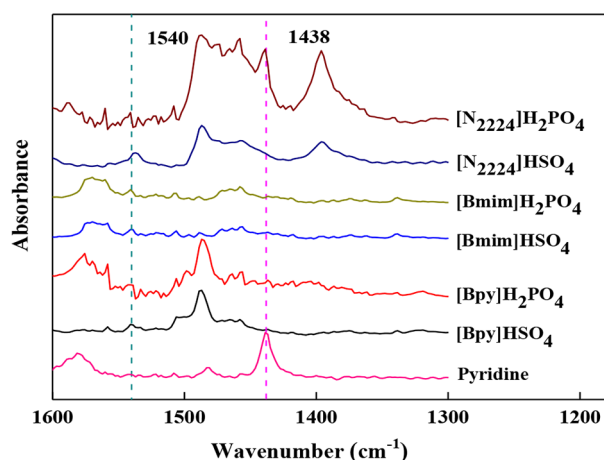
Figure 1. FT-IR spectra of pyridine with Brønsted acidic ionic liquids. The mole ratio of pyridine to ionic liquid is 3:1.

Acidities of Brønsted acidic ionic liquids

The absorption spectra of *4*-nitroaniline for various Brønsted acidic ionic liquids in dichloromethane are shown in Fig. 2. The values of [I], [I]/[IH$^+$], and H_0 are listed in Table 1. The H_0 values were in the order [N$_{2224}$]H$_2$PO$_4$ > [Bmim]H$_2$PO$_4$ > [BPy]H$_2$PO$_4$ > [N$_{2224}$]HSO$_4$ > [Bmim]HSO$_4$ > [BPy]HSO$_4$. The results revealed that the Brønsted acidic ionic liquids containing HSO$_4^-$ anion possessed higher acidity than those containing H$_2$PO$_4^-$ anion. Furthermore, the acidity of the Brønsted acidic ionic liquid was also influenced by the cation type. The effect of the cations on the acidity was in the order of [BPy]$^+$ > [Bmim]$^+$ > [N$_{2224}$]$^+$.
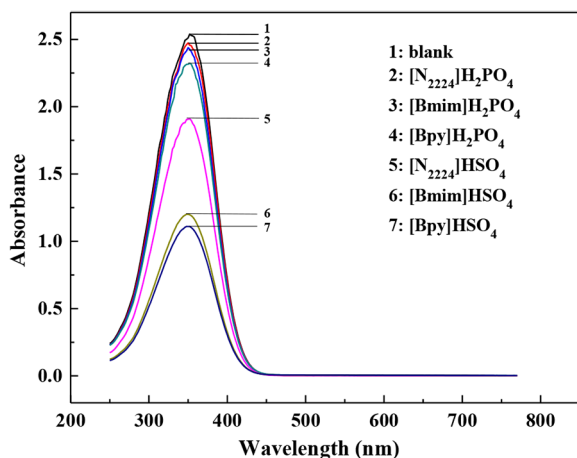
Figure 2. Absorption spectra of 4-nitroaniline for various Brønsted acidic ionic liquids in dichloromethane.

Chlorination reaction catalyzed by Brønsted acidic ionic liquids

Conversion of glycerol

Fig. 3 shows the conversions of glycerol in the glycerol chlorination reaction with gaseous HCl catalyzed by the Brønsted acidic ionic liquids with the catalyst loading of 0.75 mol kg^{-1} glycerol at 110 ºC.

When the chlorination reaction was carried out without catalyst, prolonging the reaction time from 3 h to 12 h, the conversions of glycerol gradually increased from 27.6% to 68.72%. When [Bmim]H$_2$PO$_4$ and [Bmim]HSO$_4$ were used as the catalysts for glycerol chlorination at 110 ºC for 3 h, the conversions of glycerol were 58.73% and 66.29%, respectively. After reacting for 12 h, the conversions reached 100%. When [BPy]H$_2$PO$_4$ and [BPy]HSO$_4$ were used as the catalysts at 110 ºC for 3 h, the conversions of glycerol were 56.57% and 65.04%, respectively. After reacting for 12 h, the conversions reached 99.1% and 100%. When [N$_{2224}$]H$_2$PO$_4$ and [N$_{2224}$]HSO$_4$ were used as the catalysts at 110 ºC for 3 h, the conversions of glycerol were 50.25% and 63.92%, respectively. Prolonging the reaction time to 12 h, the conversions reached 94.4% and 99.2%.

The results revealed that the Brønsted acidic ionic liquids exhibited good catalytic activity for the chlorination of glycerol. The chlorination rates for all the ionic liquids in first 3 h were in the order [Bmim]HSO$_4$ (66.29%) > [BPy]HSO$_4$ (65.04%) > [N$_{2224}$]HSO$_4$ (63.92%) > [Bmim]H$_2$PO$_4$ (58.73%) > [BPy]H$_2$PO$_4$ (56.57%) > [N$_{2224}$]H$_2$PO$_4$ (50.25%) >> without the use of catalyst (27.59%).

Without the use of catalyst, glycerol was chlorinated with HCl. It can be explained as the results of the acidic protons (H$^+$) formed by the hydrolysis of HCl catalyzing glycerol chlorination. However, HCl is more volatile and is the reason why a lower glycerol conversion was obtained. Although the Brønsted acidic ionic liquids with the same loading of 0.75 mol kg^{-1} were used for the chlorination of glycerol and the Brønsted acidic ionic liquids with H$_2$PO$_4^-$ anions could supply more protons than those with HSO$_4^-$ anions for the chlorination reaction, the latter gave higher catalytic activities than the former. The results revealed that the Brønsted acidic ionic liquid with high

Table 1. H$_0$ values of various Brønsted acidic ionic liquids in dichloromethane.[a]

BAILs	Absorbance [AU]	[I] [%]	[HI$^+$] [%]	H_0
Blank	2.5386	100	0	-
[N$_{2224}$]H$_2$PO$_4$	2.4737	97.4	2.6	2.56
[Bmim]H$_2$PO$_4$	2.4382	96.0	4.0	2.37
[BPy]H$_2$PO$_4$	2.3220	91.5	8.5	2.02
[N$_{2224}$]HSO$_4$	1.9103	75.3	24.7	1.47
[Bmim]HSO$_4$	1.2003	47.3	52.7	0.94
[BPy]HSO$_4$	1.1103	43.7	56.3	0.88

[a]Concentration: 10 mmol/L; indicator: *4*-nitroanline.
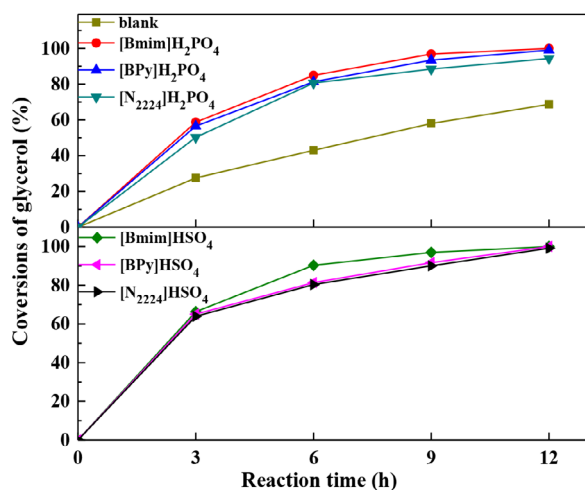
Figure 3. The conversions of glycerol in chlorination reactions with gaseous HCl catalyzed by Brønsted acidic ionic liquids with the catalyst loading of 0.75 mol kg^{-1} glycerol at 110 ºC.

Brønsted acidity exhibited high catalytic activity for the chlorination of glycerol. Furthermore, the types of organic cations in the Brønsted acidic ionic liquids probably also affected their catalytic activities.

YIELD OF PRODUCT

The product yields in the chlorination of glycerol catalyzed by the as-prepared Brønsted acidic ionic liquids are shown in Fig. 4.

When the chlorination reaction was carried out without the use of catalyst, after reacting for 12 h, the yields of 3-MCPD, 2-MCPD, 1,3-DCP, and 2,3-DCP were 59.83%, 3.75%, 4.78%, and 0.35%, respectively.

When the chlorination of glycerol was catalyzed by the [Bmim]H$_2$PO$_4$ and [Bmim]HSO$_4$ Brønsted acidic ionic liquids at 110 ºC, prolonging the reaction time from 3 to 12 h, the yields of 3-MCPD increased from 53.15% to 81.86% and from 58.50% to 81.62%, respectively. The yields of 1,3-DCP increased from 3.08% to 13.16% and from 3.88% to 13.58%. The maximum yields of 2-MCPD of 4.70% and 4.46% were obtained after reacting for 9 h and 12 h, respectively. After 12 h, the yields of 2,3-DCP were less than 0.32% and 0.34%, respectively.
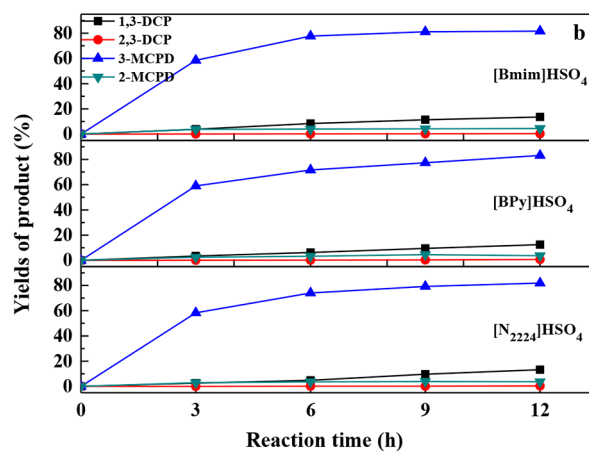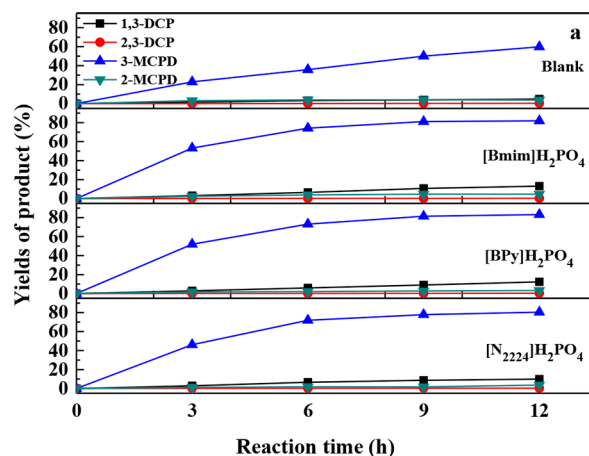
Figure 4. Yields of products in the chlorination of glycerol catalyzed by Brønsted acidic ionic liquids with the catalyst loading of 0.75 mol/kg glycerol at 110 ºC.

When the chlorination of glycerol was catalyzed by the [BPy]H$_2$PO$_4$ and [BPy]HSO$_4$ Brønsted acidic ionic liquids at 110 ºC, prolonging the reaction time from 3 to 12 h, the yields of 3-MCPD increased from 51.93% to 83.21% and from 58.97% to 83.12%, respectively. The yields of 1,3-DCP increased from 2.82% to 12.34% and from 3.46% to 12.46%. The maximum yields of 2-MCPD of 3.16% and 4.54% were obtained after

reacting for 12 and 9 h, respectively. After 12 h, the yields of 2,3-DCP were less than 0.34% and 0.70%.

When the chlorination of glycerol was catalyzed by $[N_{2224}]H_2PO_4$ and $[N_{2224}]HSO_4$ Brønsted acidic ionic liquids at 110 ºC, with the increase of reaction time from 3 h to 12 h, the yields of 3-MCPD increased from 46.15% to 80.43% and from 58.29% to 81.82%. The yields of 1,3-DCP increased from 2.83% to 9.9% and from 2.60% to 13.27%. The maximum yields of 2-MCPD of 3.63% and 3.89% were obtained after reacting for 12 and 9 h, respectively. After 12 h, the yields of 2,3-DCP were less than 0.38% and 0.34%.

Over the Brønsted acidic ionic liquid catalysts, the 3-MCPD yield stayed at a high level of *ca.* 80% for a long reaction time. The 1,3-DCP yield was less than 14% and a small amount of 2-MCPD and 2,3-DCP were formed. Furthermore, as compared with the case using carboxylic acid as the catalyst (Hou *et al.*, 2015), the 3-MCPD yield increased by 10% over the Brønsted acidic ionic liquid catalysts, indicating that the Brønsted acidic ionic liquids favored the chlorination of glycerol to 3-MCPD, probably due to the steric hindrance effect of large molecules.
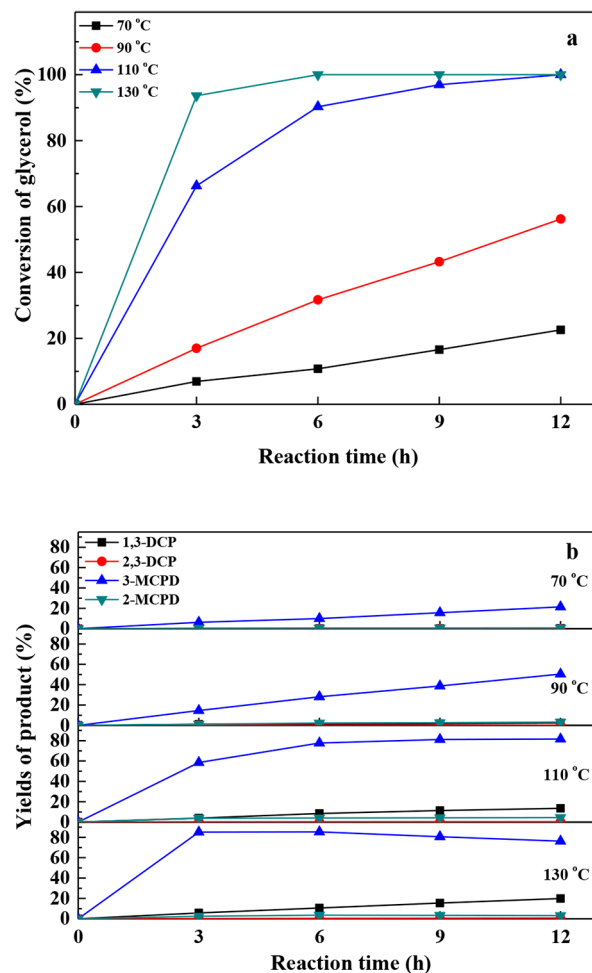
Effect of reaction temperature

Considering that the $[Bmim]HSO_4$ catalyst exhibited a higher reaction rate than the other Brønsted acidic ionic liquid catalysts, it was taken as the model catalyst to investigate the effect of other experimental parameters on the glycerol chlorination reaction.

Fig. 5 shows the conversion of glycerol and yields of products in the chlorination of glycerol with HCl catalyzed by the $[Bmim]HSO_4$ ionic liquid with the catalyst loading of 0.75 mol·kg^{-1} glycerol at different reaction temperatures.

When the reaction temperatures were 70 and 90 ºC, the conversions of glycerol were 22.57% and 56.23% after reacting for 12 h (Fig. 5a). Glycerol was completely converted after reacting at 100 and 130 ºC for 12 and 6 h, respectively. High reaction temperature favored glycerol conversion.

After reacting for 12 h, increasing the reaction temperatures from 70 to 110 ºC, the yields of 3-MCPD increased from 21.43% to 81.62%%, the yields of 2-MCPD increased from 0.80% to 4.46%, the yields of 1,3-DCP increased from 0.31% to 13.58%, and the yields of 2,3-DCP increased from 0.04% to 0.34%. However, when the reaction temperature was increased to 130 ºC, the maximum yield of 3-MCPD of 85.39% was obtained after reacting for 6 h, indicating that the high reaction temperature favored the chlorination of glycerol to 3-MCPD in a short reaction time period.
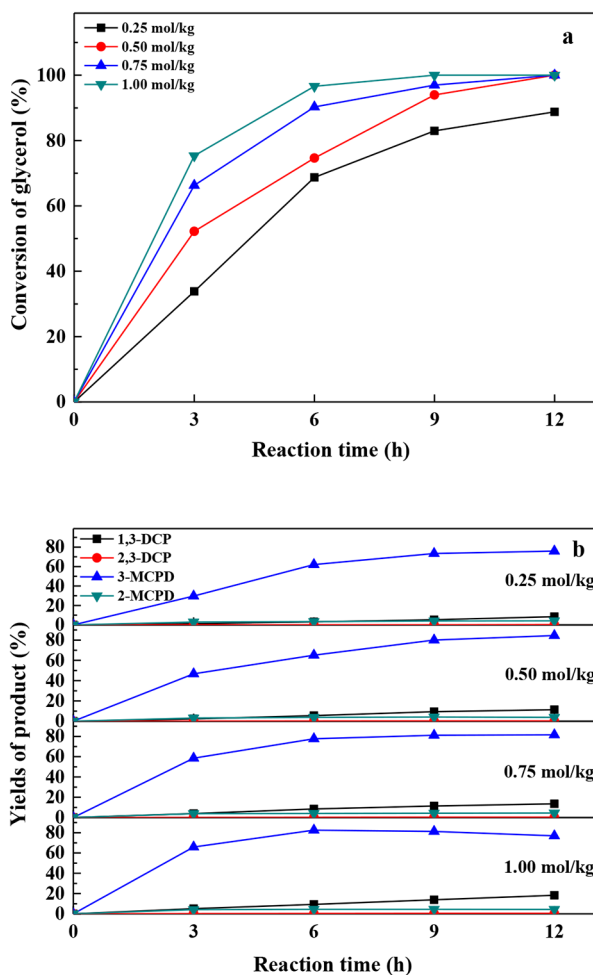

Figure 5. The conversions of glycerol and yields of products in the chlorination of glycerol with HCl catalyzed by $[Bmim]HSO_4$ ionic liquid with the catalyst loading of 0.75 mol/kg glycerol at different reaction temperatures.

Effect of catalyst loading

Fig. 6 shows the conversions of glycerol and yields of products in the chlorination of glycerol with HCl catalyzed by the $[Bmim]HSO_4$ ionic liquid with different catalyst loadings at 110 ºC.

The conversions of glycerol slightly increased with increasing catalyst loading. When the catalyst loading was increased to 0.5 mol/kg glycerol, after reacting for 12 h, glycerol was completely converted (Fig. 6a).

After reacting at 110 ºC for 12 h, increasing the catalyst loadings from 0.25 to 1.0 mol/kg glycerol, the yields of 1,3-DCP slightly increased from 8.43% to 18.33%, the yields of 2-MCPD and 2,3-DCP were less than 4.50% and 0.44%, respectively (Fig. 6b). The maximum 3-MCPD yield of 81.62% was obtained at the catalyst loading of 0.75 mol·kg^{-1} glycerol, indicating that 3-MCPD could be chlorinated to DCP at a high catalyst loading level.

Figure 6. The conversion of glycerol and yields of products in the chlorination of glycerol with HCl catalyzed by [Bmim]HSO$_4$ ionic liquid with different catalyst loadings at 110 ºC.

Reaction routes

When the Brønsted acidic ionic liquids were used as the catalysts in the chlorination of glycerol, 3-MCPD was produced as the main product. Small amounts of 2-MCPD, 1,3-DCP, and 2,3-DCP were detected. The reaction mechanism in the glycerol chlorination catalyzed by Brønsted acidic ionic liquid was suggested as that in Scheme 1.
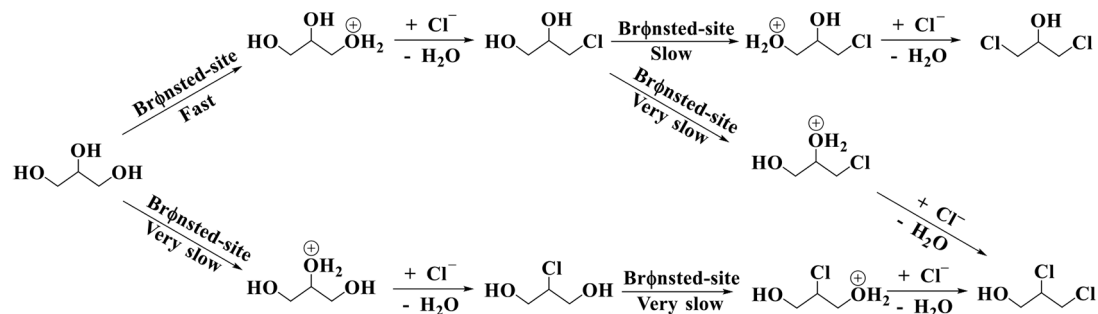
For the chlorination of glycerol to 3-MCPD catalyzed by Brønsted acidic ionic liquids, it is suggested that the glycerol molecule is first protonated at the terminal hydroxyl group by a proton from the Brønsted acidic ionic liquid and then the resultant protonated glycerol is attacked by a chloride anion to form 3-MCPD, accompanied by the formation of H$_2$O. The resultant 3-MCPD could be protonated at the terminal hydroxyl group by ionic liquid catalyst and then chlorinated by chloride anion to form 1,3-DCP.

2-MCPD can be produced via the protonation at the middle hydroxyl group of glycerol. The steric hindrance effect of the large ionic liquid molecule favored the formation of 3-MCPD rather than 2-MCPD. With the reaction going on, 2-MCPD can be further chlorinated to form 2,3-DCP. The spent Brønsted acid sites can be re-protonated by the protons abundant in the solution.

The experimental results showed that the yields of products changed upon prolonging the reaction time, indicating that all the chlorination reactions were under kinetic control rather than thermodynamic control. Furthermore, the formation rate of 3-MCPD was much higher than those of other products, revealing that the Brønsted acidic ionic liquids favored the chlorination of glycerol to 3-MCPD.

CONCLUSIONS

Catalytic chlorination of glycerol with HCl to 3-MCPD over Brønsted acidic ionic liquid catalysts with 1-butyl-3-methylimidazolium, triethylbutylammonium, and 1-butylpyridinium as the cation counterparts and HSO$_4^-$ and H$_2$PO$_4^-$ as the anion counterparts was investigated. The acidities of the Brønsted acidic ionic liquids were in the order of ionic liquids containing HSO$_4^-$ anion > ionic liquids containing H$_2$PO$_4^-$ anion. The ionic liquids with high acidity gave high catalytic activity for glycerol chlorination. The Brønsted acidic ionic liquids exhibited high catalytic activities for the selective chlorination of glycerol to 3-MCPD. When the chlorination of glycerol was catalyzed by

Scheme 1. The reaction routes in the chlorination of glycerol with gaseous HCl over Brønsted acidic ionic liquid catalysts.

[Bmim]HSO$_4$ Brønsted acidic ionic liquid with the catalyst loading of 0.75 mol/kg glycerol, the maximum yield of 3-MCPD of 85.39% was obtained at 130 ºC for 6 h.

ACKNOWLEDGEMENTS

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