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# **Organic–Inorganic Hybrids of Imidazole Complexes of** Zinc (II) for Catalysts in the Glycerolysis of Urea

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Bis(alkylimidazole) complexes of zinc, (RIm)<sub>2</sub>ZnX<sub>2</sub>, were prepared by a metal insertion reaction. The synthesized (RIm)<sub>2</sub>ZnX<sub>2</sub> exhibited good catalytic performance during synthesis of glycerol carbonate (GC) from glycerol and urea. (HEIm)<sub>2</sub>ZnCl<sub>2</sub> with a hydroxyl group exhibited the highest GC yield during glycerolysis of urea owing to incorporation of acid-base bifunctional active sites. (EIm)<sub>2</sub>ZnX<sub>2</sub> catalysts based on different halide anions showed increased reactivity as  $CI^- < Br^- < I^-$ , which is the order of nucleophilicity. The effects of reaction parameters such as temperature, reaction time, catalyst loading, and degree of vacuum on the reactivity were also investigated.

Keywords: Imidazole, Complex, Zinc, Glycerol Carbonate, Glycerol, Urea.

1. INTRODUCTION by Publishing Technology to: Floribeen prepared by the reaction of glycol with phosgene; Cyclic carbonates are useful solvents and chemical intermediates because they have low toxicity and biodegradability and a high boiling point. These compounds have many applications as processing agents for the production of polyacrylonitrile fibers, diluents for polyurethanes and epoxy resins, accelerants in dyeing and printing, additives in fuel, lubricants and hydraulic fluids, separation of carbon dioxide and hydrogen sulfide, and components of electrolytes used in lithium-ion rechargeable batteries, metal extractions, etc.1,2

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2one; GC) is a cyclic carbonate relatively new to the chemical industry that has been receiving increased interest owing to its large potential. Inexpensive glycerol carbonate could serve as a source of new polymeric materials such as glycidol, a high-value component in the production of a number of polymers.<sup>3,4</sup> Its high functionality, together with the versatile and well-investigated reactivity of its hydroxyl functions, is the basis for a variety of derivatives. Indeed, many polyglycerols have been commercialized for applications that range from cosmetics to controlled drug release.5

The main methods for the preparation of GC are based on the reaction of glycerol with (a) phosgene, a dialkyl carbonate, or an alkylene carbonate, (b) carbon monoxide and oxygen or carbon dioxide, or (c) urea. GC has traditionally however, because of the high toxicity and corrosive nature of phosgene, alternative methods for the preparation of GC such as the transesterification of dialkyl or alkylene carbonates with glycerol have been explored.<sup>6</sup> A method based on the reaction of glycerol with carbon monoxide and oxygen under high pressure in the presence of a catalyst is also known.7 However, a more cost-effective and simpler method involving the use of a highly safe material is desired. Aresta et al.<sup>8</sup> investigated the direct carboxylation of glycerol with carbon dioxide (5 MPa) at 177 °C using transition-metal alkoxides. However, the yield of GC by this method was found to be very low.

An alternative method is the carbonylation of urea, a reaction that was recently described in the literature.<sup>9–11</sup> The main advantage of this method is that the reactants, glycerol and urea, are inexpensive and easily available raw materials that are not explosive or poisonous. In addition, the ammonia that is usually generated when GC is synthesized from urea and glycerol can be easily converted to urea in the presence of carbon dioxide.

The reaction of urea with alkylene glycol was first reported by Su and Speranza;12 however, the decomposition of urea was severe. Doya et al.13 increased the yield of products by using zinc, magnesium and lead, or their compounds as catalysts under vacuum. Ball et al.<sup>14</sup> investigated the reaction of primary and secondary alcohols with urea to form carbonate and found that the reaction proceeded in two steps. Moreover, the combination of a weak Lewis

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acid with a Lewis base improved the carbonate formation. Corma et al.<sup>15</sup> reported that a balanced bifunctional acidbase catalyst in which the Lewis acid activates the carbonyl of the urea and the conjugated basic site activates the hydroxyl group of the glycerol were the most active and selective catalysts for the synthesis of GC from urea and glycerol.

Ionic liquids are well known as environmentally benign media for catalytic processes or chemical extraction because of their outstanding properties, which include negligible vapor pressure, excellent thermal stability, and special characteristics as opposed to conventional organic and inorganic solvents.<sup>16-24</sup> The ionic liquids have recently been successfully applied as immobilizing reagents for transition metal catalysts, combining the advantages of both homogeneous and heterogeneous catalysis and leading to improved process performance.25-27 With the purpose of turning the acidic character, ionic liquids containing metals are recently receiving greater attention.<sup>28-30</sup> Beyond their application as mere reaction media, the metal containing ionic liquid possessing a weak base as anion have been successfully used as catalysts themselves, e.g., in Friedel-Crafts alkylation.31,32

In this study, imidazolium based zinc containing ionic liquid  $((RIm)_2ZnX_2)$ , which is a bifunctional acid-base catalyst in which the zinc ions serve as the acid center and the anion as the base, was prepared by metal insertion reaction and the catalytic performance of  $(RIm)_2ZnX_2$  for the synthesis of glycerol carbonate from glycerol and urea by carbonylation under solvent free conditions was investigated. The effects of reaction time, reaction temperature, degree of vacuum and amount of catalyst were discussed to increase our understanding of the reaction mechanism along with the morphological effects of  $(RIm)_2ZnX_2$ .

# 2. MATERIALS AND METHODS 2.1. Materials

1-alkylimidazoles (*N*-imidazole, 1-methyl, 1-ethyl, 1-butyl and 1-(2-hydroxyerthyl) imidazole) and metal halides (zinc chloride, zinc bromide, zinc iodide, magnesium chloride and copper chloride) were purchased from Sigma-Aldrich with high purity (>99%). Glycerol (>99%), urea (> 99%), glycerol carbonate (>99%), and methanol (>99%) were obtained from Sigma-Aldrich. All materials were used without further purification.

## 2.2. Synthesis of (RIm)<sub>2</sub>ZnX<sub>2</sub> Catalyst

The zinc containing ionic liquid catalyst based on 1-alkylimidazole,  $(RIm)_2ZnX_2$ , was prepared by a metal insertion reaction as follows.<sup>27</sup> For the synthesis of  $(RIm)_2ZnX_2$ , an ethanol solution (100 mL) containing 1-alkylimidazole (40 mmol) was added to an ethanol solution containing zinc halide (20 mmol). This mixture was stirred for 2 h at 50 °C, after which the mixture was filtered. A crystal solid was obtained after drying at

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Scheme 1. Synthesis of glycerol carbonate.

100 °C for 24 h under vacuum. The products were named  $(Im)_2ZnCl_2$  (ZnCl<sub>2</sub>, *N*-imidazole),  $(MIm)_2ZnCl_2$  (ZnCl<sub>2</sub>, 1-methylimidazole),  $(EIm)_2ZnCl_2$  (ZnCl<sub>2</sub>, 1-ethylimidazole),  $(BIm)_2ZnCl_2$  (ZnCl<sub>2</sub>, 1-butylimidazole),  $(HEIm)_2ZnCl_2$  (ZnCl<sub>2</sub>, 1-(2-hydroxyethyl)imidazole),  $(EIm)_2ZnBr_2$  (ZnBr<sub>2</sub>, 1-ethylimidazole) and  $(EIm)_2ZnI_2$  (ZnI<sub>2</sub>, 1-ethylimidazole).

## 2.3. Characterization of (RIm)<sub>2</sub>ZnX<sub>2</sub> Catalyst

The <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained on a Varian 500 MHz. Fourier transform infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) of the catalysts was conducted with the Theta Probe AR-XPS System X-ray source using monochromated Al K $\alpha$  radiation (hv = 1486.6 eV).

## 2.4. Synthesis of Glycerol Carbonate from Glycerol and Urea

The synthesis of GC from the reaction of glycerol with urea was carried out in a 50 mL glass reactor equipped with a magnetic stirrer and condenser (Scheme 1). For each typical reaction, (RIm)<sub>2</sub>ZnX<sub>2</sub> catalyst, glycerol (50 mmol), and urea (50 mmol) were charged into the reactor. When the desired temperature was attained, the reaction was initiated by stirring under vacuum or under nitrogen purging to remove ammonia as a by-product. Analysis of the products and reactants was performed using a gas chromatograph (HP 6890N) equipped with an FID and a capillary column (HP-INNOWAX, polyethylene glycol). Tetraethylene glycol (TEG) was used as an internal standard. The conversion and selectivity were calculated based on the assumption that glycerol was a limited reactant.

## 3. RESULTS AND DISCUSSION

## 3.1. Characterization of Catalysts

The NMR data of the  $(RIm)_2ZnX_2$  samples are as follows: **Bis(N-imidazolium)zinc** chloride  $((Im)_2ZnCl_2)$ . <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 7.25$  (*s*, CH, 1 H), 8.14 (*s*, CH, 1 H), 13.45 (*s*, NH, 1 H). **Bis(1-methylimidazolium)zinc** chloride  $((MIm)_2ZnCl_2)$ . <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 3.74$  (*t*, NCH<sub>3</sub>, 3 H), 7.03 (*s*, CH, 1 H), 7.37 (*s*, CH, 1 H), 8.06 (*s*, CH, 1 H). **Bis(1-ethylimidazolium)zinc** chloride  $((EIm)_2ZnCl_2)$ . <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ):  $\delta v = 1.36$  (*t*, CH<sub>3</sub>, 3 H), Organic-Inorganic Hybrids of Imidazole Complexes of Zinc (II) for Catalysts in the Glycerolysis of Urea

4.10 (t, NCH<sub>3</sub>, 3 H), 7.06 (s, CH, 1 H), 7.48 (s, CH, 1 H), 8.14 (s, CH, 1 H). Bis(1-bytulimidazolium)zinc chloride ((BIm)<sub>2</sub>ZnCl<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO $d_6$ ):  $\delta = 0.87$  (t, CH<sub>3</sub>, 3 H), 1.23 (m, CH<sub>2</sub>, 2 H), 1.72 (m, CH<sub>2</sub>, 2 H), 4.08 (t, NCH<sub>3</sub>, 3 H), 7.06 (s, CH, 1 H), 7.46 (s, CH, 1 H), 8.14 (s, CH, 1 H). Bis[1-(2-hydroxyethyl)imidazolium zinc chloride ((HEIm)<sub>2</sub> **ZnCl**<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 3.68$ (t, CH<sub>3</sub>, 3 H), 4.12 (t, NCH<sub>3</sub>, 3 H), 5.03 (s, OH, 1 H), 7.05 (s, CH, 1 H), 7.42 (s, CH, 1 H), 8.08 (s, CH, 1 H). Bis(1-ethylimidazolium)zinc bromide ((EIm)<sub>2</sub>ZnBr<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO- $d_6$ ):  $\delta = 1.36$  (t, CH<sub>3</sub>, 3 H), 4.12 (t, NCH<sub>3</sub>, 3 H), 7.07 (s, CH, 1 H), 7.51 (s, CH, 1 H), 8.18 (s, CH, 1 H). Bis(1-ehtylimidazolium)zinc iodide  $((EIm)_{2}ZnI_{2})$ . <sup>1</sup>H-NMR (400 MHz, DMSO- $d_{6}$ ):  $\delta = 1.38$ (t, CH<sub>3</sub>, 3 H), 4.15 (t, NCH<sub>3</sub>, 3 H), 7.15 (s, CH, 1 H), 7.58 (s, CH, 1 H), 8.26 (s, CH, 1 H).

The FT-IR spectral analyses of the  $(RIm)_2ZnCl_2$ samples,  $(Im)_2ZnCl_2$ ,  $(EIm)_2ZnCl_2$  and  $(HEIm)_2ZnCl_2$ (Fig. 1), confirm that different alkyl groups were attached to the ring nitrogen of the  $(RIm)_2ZnCl_2$ . Clearly, the -C—H stretching frequency near 3110 cm<sup>-1</sup> and many of the bands observed from 1600 to 600 cm<sup>-1</sup> are associated with various vibrational modes of the ring.<sup>33</sup> Differences among the alkyl groups of the  $(RIm)_2ZnCl_2$  are noted in the region from 2885–2980, 3320 and 3425 cm<sup>-1</sup>, corresponding to the -C—H stretching of the ethyl groupof  $(EIm)_2ZnCl_2$ , -N—H stretching of the  $(Im)_2ZnCl_2$  and -OH stretching of the  $(HEIm)_2ZnCl_2$ , respectively.

The XPS measurement of  $(RIm)_2ZnCl_2$  allows to confirm the structure of the catalysts. The N 1s spectra of  $(RIm)_2ZnCl_2$  are depicted in Figure 2. The  $(RIm)_2ZnCl_2$ catalysts contain two nitrogen species that originate from the two imidazolium nitrogens near 399.5 and 401.0 eV. The characteristic peak of nitrogen species from the amine portion appearing around 399.5 eV could be attributed to the imidazolium nitrogen attached to the alkyl group and



Figure 1. FT-IR spectra of  $(RIm)_2ZnCl_2$ : (a)  $(Im)_2ZnCl_2$ , (b)  $(EIm)_2ZnCl_2$ , (c)  $(HEIm)_2ZnCl_2$ .



Figure 2. XPS N 1s spectra of  $(RIm)_2 ZnCl_2$ .

the other peak can be regarded as a signal from the positively charged nitrogen atom of the quaternary ammonium moiety.<sup>34–37</sup> Moreover, the Cl 2p spectra of  $(RIm)_2ZnCl_2$ were measured to identify the bonding aspect of the halogen associated with the zinc species (Fig. 3). Niedermaier et al.<sup>37</sup> reported that the Cl 2p peak at 200.2 eV is of covalently bound chlorine (Cl<sub>cov</sub>), while 197.2 eV corresponds to ionic chlorine (Cl<sub>ion</sub>). The XPS data showed only one peak near 197.5 eV in (RIm)<sub>2</sub>ZnCl<sub>2</sub>, confirming that the bonds between chlorine and zinc are not covalent, but ionic in nature. The aforementioned results confirm the structure of (RIm)<sub>2</sub>ZnX<sub>2</sub> catalysts as shown in Scheme 2.



Figure 3. XPS Cl 2p spectra of (RIm)<sub>2</sub>ZnCl<sub>2</sub>.

$${}_{2}^{\mathsf{R}} \stackrel{\mathsf{N}}{\longrightarrow} \mathsf{N} + \mathsf{Zn}\mathsf{X}_{2} \xrightarrow{\mathrm{EtOH}} {}_{50\,^{\circ}\mathrm{C},\,2\,\mathrm{h}} \stackrel{\mathsf{R}}{\longrightarrow} {}_{\mathsf{N}} \xrightarrow{\mathsf{X}} {}_{\mathsf{N}} \xrightarrow{\mathsf{X}} {}_{\mathsf{N}} \xrightarrow{\mathsf{N}} {}_{\mathsf{N}} \xrightarrow{\mathsf{X}} \xrightarrow{\mathsf{X}} \xrightarrow{\mathsf{X}} {}_{\mathsf{N}} \xrightarrow{\mathsf{X}} \xrightarrow{\mathsf{X}}$$

-R: methyl, ethyl, butyl, 2-hydroxyethyl-X: Cl, Br, I

Scheme 2. Preparation of (RIm)<sub>2</sub>ZnX<sub>2</sub>.

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1.5

Table I. The reactivity of the metal containing ionic liquids (RIm)<sub>2</sub>ZnX<sub>2</sub> in the glycerolysis of urea.

Catalyst	$X_G$ (%)	$S_{\rm GC}~(\%)$	$Y_{\rm GC}~(\%)$
(Im) <sub>2</sub> ZnCl <sub>2</sub>	90.1	89.6	80.7
$(MIm)_2ZnCl_2$	87.3	89.7	78.3
$(EIm)_2ZnCl_2$	83.6	85.5	71.4
$(BIm)_2ZnCl_2$	74.2	80.4	59.7
(HEIm) <sub>2</sub> ZnCl <sub>2</sub>	92.7	93.4	86.6
(EIm) <sub>2</sub> ZnCl <sub>2</sub>	83.6	85.5	71.4
(EIm) <sub>2</sub> ZnBr <sub>2</sub>	87.1	85.1	74.1
(EIm) <sub>2</sub> ZnI <sub>2</sub>	90.3	92.7	83.8

*Notes*: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, cat./glycerol = 1 mol%, Temp. = 140 °C, Degree of vacuum = 14.7 kPa, Reaction time = 6 h.

#### **3.2.** Evaluation of Reactivity of (RIm)<sub>2</sub>ZnX<sub>2</sub> Catalysts

Table I shows the conversion of glycerol, and the selectivity and yield of GC using  $(RIm)_2ZnX_2$  catalysts having various functional groups and counteranions under a vacuum pressure of 14.7 kPa after 6 h of reaction at 140 °C. A glycerol conversion of 90.1% was achieved using  $(Im)_2ZnCl_2$ . When compared to  $(Im)_2ZnCl_2$  that does not possess a functional group in the free N of the imidazole, all of the  $(RIm)_2ZnCl_2$  catalysts having an alkyl group exhibited lower catalytic activity for the glycerolysis of urea. Changing the alkyl group of  $(RIm)_2ZnCl_2$  from methyl ( $(MIm)_2ZnCl_2$ ) to butyl ( $(BIm)_2ZnCl_2$ ) resulted in a decrease in the conversion of glycerol, probably because of the steric hindrance of the bulky butyl group, which might inhibit the approach of the glycerol and urea to the active center.

However,  $(\text{HEIm})_2 \text{ZnCl}_2$  with a hydroxyl functional group showed the highest glycerol conversion (92.7%) and GC yield (86.6%). To the best of our knowledge this is the highest GC yield ever reported for the glycerolysis of urea. Some recent reports are summarized in Table II. The OH group in  $(\text{HEIm})_2 \text{ZnCl}_2$  may activate urea since the hydroxyl oxygen atom is an acceptor of a weak N—H···O hydrogen bond of urea.<sup>38</sup> The high

Table II. Reactivity of different catalysts in the glycerolysis of urea.

Table III. The effect of catalyst loading in the glycerolysis of urea									
Amount of catalyst (mmol)	$X_G$ (%)	$S_{\rm GC}~(\%)$	$Y_{\rm GC}$ (%)						
0.1	67.2	61.2	41.1						
0.2	64.1	73.6	47.1						
0.3	80.9	74.2	60.1						
0.5	83.6	85.5	71.4						
1.0	87.2	88.7	77.3						

*Notes*: Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, cat. = x mmol (EIm)<sub>2</sub>ZnCl<sub>2</sub>, Temp. = 140 °C, Degree of vacuum = 14.7 kPa, Reaction time = 6 h.

87.9

89.3

78.5

hydrophilic character of (HEIm)<sub>2</sub>ZnCl<sub>2</sub> may also assist the adsorption of the hydrophilic glycerol to the catalyst.<sup>39</sup>

The effect of the anion of  $(EIm)_2 ZnX_2$  on reactivity is also shown in Table I. Comparison of the catalytic activities of the  $(EIm)_2 ZnX_2$  catalysts based on different counter anions revealed that the conversion of glycerol and yield of GC increased as  $Cl^- < Br^- < I^-$ . The effect of the counteranion on the reactivity is attributed to the nucleophilicity of the anion, and the order of the nucleophilicity also increases as  $Cl^- < Br^- < I^-$ .<sup>40,41</sup>

The effect of catalyst loading on the yield of GC was investigated using  $(EIm)_2ZnCl_2$  as the catalyst at 140 °C for 6 h with a reduced pressure of 14.7 kPa. As shown in Table III, the yield of GC and glycerol conversion increased continuously as the amount of catalyst increased up to 2 mol%. However, the yield remained constant as the amount of catalyst increased further.

<sup>SCI</sup> The following kinetic studies of the effects of reaction time, temperature, and degree of vacuum were carried out using 1 mol% of (EIm)<sub>2</sub>ZnCl<sub>2</sub> and (HEIm)<sub>2</sub>ZnCl<sub>2</sub> to understand the effect of hydroxyl groups in this catalyst.

The effect of reaction time on the synthesis of GC was studied at 140 °C under a reduced pressure of 14.7 kPa. As shown in Figure 4, the conversion of glycerol increased as the reaction progressed. After the reaction had proceeded for 1 h, the GC selectivity was < 55%, implying that substantial amounts of the reaction intermediate,

Catalyst	Cat. amount	Temp. (°C)	Reduced pressure	$X_G$ (%)	$S_{\rm GC}~(\%)$	Ref.	Year
Hydrotalcite (Zn)	5 wt%	145	4 kPa	82.0	72.0	[15]	2010
MgO	5 wt%	145	4 kPa	73.0	39.0	[15]	2010
ZnO	5 wt%	145	4 kPa	80.0	60.0	[15]	2010
Au/MgO	1.8 wt%	150	$N_2$ purge	81.0	55.1	[35]	2011
ZnSO <sub>4</sub>	1.8 wt%	150	$N_2$ purge	83.0	48.1	[35]	2011
MPR[pmim][Cl]	5 wt%	140	14.7 kPa	45.6	40.0	[36]	2011
MPR[pmim][Br]	5 wt%	140	14.7 kPa	44.8	43.0	[36]	2011
ZnCl <sub>2</sub>	2 mol%	150	2.67 kPa	80.4	80.2	[37]	2012
$Zn(C_3H_6O_3)/NH_4Cl$	2 mol%	150	2.67 kPa	81.3	79.8	[37]	2012
ZnO	5.4 wt%	130	3 kPa	61.0	42.1	[38]	2013
Smectite (Zn)	5.4 wt%	130	3 kPa	65.0	48.8	[38]	2013
Hydrotalcite (Zn/Al)	5.4 wt%	130	3 kPa	82.0	65.6	[38]	2013
ZnCl <sub>2</sub>	5.4 wt%	130	3 kPa	84.0	81.5	[38]	2013
ZnBr <sub>2</sub>	5.4 wt%	130	3 kPa	82.0	78.7	[38]	2013
(HEIm) <sub>2</sub> ZnCl <sub>2</sub>	1 mol%	140	14.7 kPa	92.7	86.6	This work	

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**Figure 4.** Effect of reaction time on the reactivity of  $(EIm)_2 ZnCl_2$ and  $(HEIm)_2 ZnCl_2$  (Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, cat./glycerol = 1 mol%, Temp. = 140 °C, Degree of vacuum = 14.7 kPa).

HPC (2,3-dihydroxypropyl carbamate) (3), remained in the reaction mixture. As the reaction progressed, HPC was further converted to GC and the selectivity toward GC production continuously increased to 93%. As shown in Scheme 3, the main by-products (other than HPC) were (2-oxo-1,3-dioxolan-4-yl) methyl carbamate (ODMC) (6) and 4-(hydroxymethyl)oxazolidium-2-one (5).

Figure 5 shows the effects of reaction temperature on the synthesis of GC in the presence of  $(EIm)_2ZnCl_2$ 



**Figure 5.** Effect of reaction temperature on the reactivity of  $(EIm)_2ZnCl_2$  and  $(HEIm)_2ZnCl_2$  (Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, cat/glycerol = 1 mol%, Degree of vacuum = 14.7 kPa, Reaction time = 6 h).

and  $(\text{HEIm})_2\text{ZnCl}_2$ . The conversion of glycerol continuously increased as the temperature increased from 100 °C to 160 °C. The selectivity toward GC production increased with temperature, reaching a maximum of 93.4% for  $(\text{HEIm})_2\text{ZnCl}_2$  at 140 °C; however, the selectivity decreased as the temperature increased above 150 °C, probably because of the transformation of GC to ODMC (6) or the polymerization of GC and/or glycerol. At 160 °C, the selectivity of GC was very small (close



4-(hydroxymethyl)oxazolidin-2-one (5) (2-oxo-1,3-dioxolan-4-yl)methyl carbamate (6)

Scheme 3. Possible reaction pathways for the glycerolysis of urea.

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**Figure 6.** Effect of degree of vacuum on the reactivity of  $(EIm)_2 ZnCl_2$ and  $(HEIm)_2 ZnCl_2$  (Reaction conditions: Urea = 50 mmol, Glycerol = 50 mmol, cat./glycerol = 1 mol%, Temp. = 140 °C, Reaction time = 6 h).

to 4%). The formation of polymers from GC or glycerol has been reported to be one of the main factors responsible for the low selectivity toward GC.<sup>15</sup>

Figure 6 shows the effects of the degree of vacuum on the reactivity of the  $(EIm)_2ZnCl_2$  and  $(HEIm)_2ZnCl_2$  catalysts. The conversion of glycerol increased as the degree of vacuum increased from 101.3 to 1.1 kPa. Application of a high degree of vacuum could enhance the removal of the generated ammonia gas, thereby accelerating the forward reaction of glycerol and urea. The selectivity towards GC also appeared to have followed a similar trend with increase in the applied vacuum from 101.3 to 1.1 kPa, because a high degree of vacuum might have increased the conversion of HPC to GC. Interestingly, removal of ammonia by nitrogen purging at a flow rate of 150 mL/min was also effective for the glycerolysis of urea, showing 82.6% of glycerol conversion and 73.3% GC yield for (EIm)<sub>2</sub>ZnCl<sub>2</sub> under the same reaction conditions.

The results of previous studies<sup>42, 43</sup> in conjunction with the above findings suggest that the catalysts should possess both Lewis acidity and basicity to be active for the reaction between glycerol and urea, and that there is a subtle balance between the acidity and basicity. Specifically, the Lewis acid group is required for activation of the carbonyl group of urea and the Lewis base activates the hydroxyl groups of glycerol.<sup>9, 14, 15</sup> In this regard, for the reaction of glycerol and urea in the presence of the catalytic system, (RIm)<sub>2</sub>ZnX<sub>2</sub>, Zn and the halide anion could be considered as a Lewis acid and a Lewis base. In addition, the basicity of the OH group at the alkyl substituent of the catalyst can also activate the glycerol.

The role of the quaternized functional group as a Lewis base in the activation of glycerol was substantiated by

Park et al.<sup>43</sup> who used FT-IR and <sup>1</sup>H NMR analysis to demonstrate that there were strong hydrogen bonding interactions between the hydroxyl group of glycerol and the chloride anion of  $NH_4Cl$ .

## 4. CONCLUSIONS

Glycerolysis of urea using  $(RIm)_2ZnX_2$  catalysts was evaluated herein, illustrating the importance of the structure and functionality of the  $(RIm)_2ZnX_2$  catalysts on their reactivity. The incorporation of zinc halide into the bis(imidazolium) salt structure is advantageous for the glycerolysis of urea owing to the introduction of acid-base bifunctional active sites.  $(RIm)_2ZnX_2$  exhibited good catalytic activity even in the absence of a solvent.  $(RIm)_2ZnX_2$  with a hydroxyl group and more nucleophilic counteranions exhibited better reactivity for the synthesis of GC. High temperature, long reaction time, and a high degree of vacuum were favorable for the high conversion of glycerol.

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