

## Isolation and characterization of intermediate catalytic species in the Zn-catalyzed glycerolysis of urea

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### ABSTRACT

Homogeneous zinc-catalyzed synthesis of glycerol carbonate from the reaction of glycerol with urea was investigated. Among the zinc-based catalysts tested, ZnCl<sub>2</sub> showed the highest catalytic activity. Spectroscopic and elemental analyses of the zinc species, isolated from the reaction conducted in the presence of ZnCl<sub>2</sub>, revealed that Zn(NH<sub>3</sub>)Cl<sub>2</sub> was generated first as an intermediate species, which in turn reacted with glycerol to produce zinc glycerolate, Zn(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) and NH<sub>4</sub>Cl. The activity of Zn(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) was considerably lower than that of ZnCl<sub>2</sub>, but the activity was greatly enhanced by the combined use of NH<sub>4</sub>Cl, implying that both Zn(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) and NH<sub>4</sub>Cl were functioning as essential ingredients for the carbonylation of glycerol by urea. The formation of Zn(C<sub>3</sub>H<sub>6</sub>O<sub>3</sub>) was also observed when ZnBr<sub>2</sub>, ZnI<sub>2</sub>, ZnF<sub>2</sub>, Zn(NO<sub>3</sub>)<sub>2</sub>, Zn(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, or ZnO was used as the catalyst.

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### 1. Introduction

The use of biodiesels as a renewable energy source is increasing exponentially due to the rising prices of fossil fuels and also to the worldwide environmental concern about global warming. Currently, most of the biodiesels are being produced by the transesterification of vegetable oils, but the co-production of large quantities of glycerol is a major obstacle in the expansion of biodiesel industry. Therefore, it is extremely important to cut the cost of biodiesel production through the development of effective ways to convert low-grade glycerol into value added chemicals, including 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, polyesters, and fuel additives [1–3].

Transformation of glycerol into glycerol carbonate (GLC) has also received recent interest because GLC has many potential applications as a gas-separation membrane material, a high boiling polar solvent, a surfactant, and an intermediate of fine chemicals and polycarbonates, due to its low toxicity, biodegradability, and high

polarity [4–6]. A number of processes have been reported for the synthesis of GLC from glycerol using a variety of carbonyl sources, including COCl<sub>2</sub>, CO/O<sub>2</sub>, CO<sub>2</sub>, dialkylcarbonates, and urea [7–12]. Of these, the use of urea as the carbonyl source can be considered the most economical way to synthesize GLC in terms of the cost of the starting material (Scheme 1).

Much effort has been devoted to searching for the effective catalysts and catalytic systems for the synthesis of GLC from glycerol and urea, and as a result, various heterogeneous catalytic systems have been developed based on metal oxides, sulfates, and phosphates [13–17].

It has also been reported that the carbonylation of glycerol with urea proceeds in a homogeneous way, especially in the presence of a zinc-based catalyst [13,16]. Although the improvement of catalytic activity has been significant, characterization of the active species, especially in homogeneous catalytic systems, has rarely been attempted.

We now report in detail on the homogeneous synthesis of GLC from glycerol and urea using various zinc-based catalysts as well as the isolation and characterization of intermediate catalytic species.

### 2. Experimental

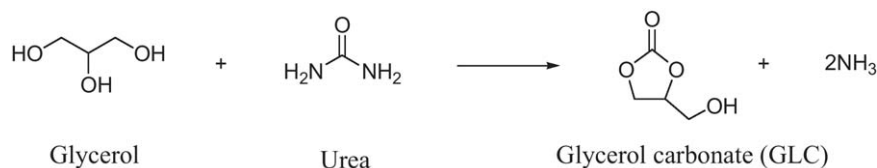
All reagents including glycerol, urea, and zinc compounds were purchased from Aldrich Chemical Co. and used as received without further purification. GLC was purchased from TCI (Japan).

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**Scheme 1.** Synthesis of glycerol carbonate (GLC) from glycerol and urea.

### 2.1. Glycerol carbonate synthesis

Glycerol (23.0 g, 250 mmol), urea (15.0 g, 250 mmol), and  $\text{ZnCl}_2$  (0.68 g, 5 mmol) were loaded into a 100 mL round-bottomed flask equipped with a condenser and an electric heater. The top of the condenser was connected to an aspirator, and the pressure inside the flask was controlled using a vacuum release valve and a vacuum gauge. The flask was then heated to a specified reaction temperature, and the vacuum inside was maintained at 2.67 kPa. After the reaction was completed, the flask was cooled to room temperature and the solid materials were isolated through filtration. The remaining solution was analyzed using a HPLC after the addition of water and *t*-butanol as an external reference.

### 2.2. Isolation and characterization of intermediate catalytic species

#### 2.2.1. $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$

Glycerol (23.0 g, 250 mmol), urea (15.0 g, 250 mmol), and  $\text{ZnCl}_2$  (7.1 g, 52.0 mmol) were loaded into a 100 mL round-bottomed flask and heated to 130 °C at 2.67 kPa. When the reaction mixture became transparent after approximately 30 min at 130 °C, the flask was cooled to room temperature and 100 mL of MeOH was added to precipitate the solid material, which was identified as  $\text{ZnCl}_2(\text{NH}_3)_2$  by XRD, FT-IR, and elemental analyses. Isolated yield: 77.5%. Anal. Calcd for  $\text{ZnCl}_2(\text{NH}_3)_2$ : Zn, 39.3%; N, 16.8%; H, 1.2%. Found: Zn, 38.0%; N, 16.2%; H, 1.2%.

#### 2.2.2. $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$

Glycerol (23.0 g, 250 mmol), urea (15.0 g, 250 mmol), and  $\text{ZnCl}_2$  (0.71 g, 5.2 mmol) were added to a 100 mL round-bottomed flask and heated to 150 °C at 2.67 kPa. After 2 h of the reaction, the solution was cooled to room temperature and 100 mL of MeOH was added to precipitate the dissolved zinc complex,  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ . Isolated yield: 38.2%. Anal. Calcd for  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ : Zn, 42.1%; C, 23.2%; H, 3.9%. Found: Zn, 42.1%; C, 24.5%; H, 3.9%.

### 2.3. Instrumentation

Quantification of the reaction products was made on a Waters HPLC equipped with an Aminex HPX-87H column (Biorad) and a RI detector (Waters 410). The mobile phase used was a 5 mM  $\text{H}_2\text{SO}_4$  aqueous solution and the flow rate was set at 0.6 mL/min. For the quantitative analysis, an external standard method was used. FT-IR

spectra of catalyst samples were recorded on a Nicolet FT-IR spectrometer (iS10, USA) equipped with a SMART MIRACLE accessory over a range of 400–4000  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$ . X-ray diffraction (XRD) was measured using a Shimadzu XRD-6000 with a Cu K $\alpha$  radiation source (40 kV and 30 mA).

## 3. Results and discussion

### 3.1. Catalyst screening

The catalytic activities of various zinc compounds were evaluated for the reaction of glycerol with urea to produce GLC at 150 °C for 2 h with a urea/glycerol molar ratio of 1. To shift the equilibrium toward the formation of GLC,  $\text{NH}_3$  was removed as soon as it formed using an aspirator (2.67 kPa). As listed in Table 1, the reaction proceeded even in the absence of a catalyst, but the yield and selectivity of GLC were only 29.5 and 56.2%, respectively (entry 1).  $^{13}\text{C}$  NMR and liquid chromatographic analyses of the product mixture showed that glycerol carbamate, an intermediate of GLC, was produced in large quantities along with trace amounts of diglycerol. The GLC yield and selectivity, however, were greatly enhanced by the use of a zinc compound as the catalyst. For instance, the use of 2 mol%  $\text{ZnCl}_2$  with respect to glycerol produced GLC in yield of 80.2% with a selectivity of 99.7%. Similar results were also obtained with  $\text{ZnBr}_2$  and  $\text{ZnI}_2$ , whereas  $\text{ZnF}_2$  resulted in a much lower GLC yield and selectivity, possibly due to the low solubility of  $\text{ZnF}_2$  in glycerol. For comparison, the activities of other zinc compounds including  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , and  $\text{ZnO}$  were also evaluated. As shown in Table 1,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  exhibited the highest conversion of glycerol (85.3%) although the GLC selectivity (93.2%) was slightly lower than that of  $\text{ZnCl}_2$  (99.7%). By contrast,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{ZnO}$  exhibited much reduced activities compared with other zinc compounds tested, producing GLC in yields of 44.3 and 47.9%, respectively. The origin of the different catalytic activity of  $\text{ZnX}_2$  ( $\text{X} = \text{halide}, \text{NO}_3, \text{OAc}$ ) with the variation of  $\text{X}$  is not clear at the moment, but the Lewis acidity of  $\text{ZnX}_2$  and ease of  $\text{Zn}-\text{X}$  dissociation are likely to be responsible for the activity difference.

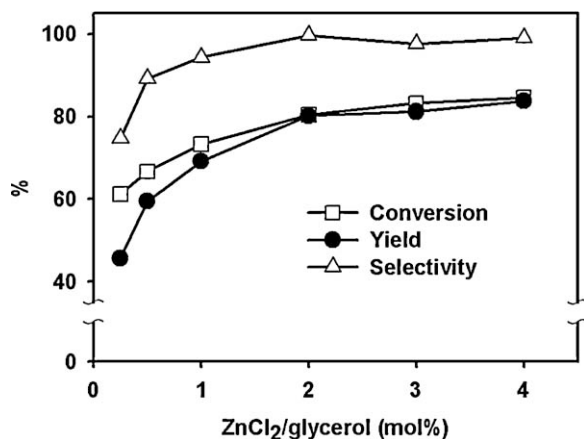
### 3.2. Effect of catalyst loading

The effect of catalyst loading on the yield of GLC was investigated using  $\text{ZnCl}_2$  as the catalyst at 150 °C for 2 h with a reduced pressure of 2.67 kPa. As shown in Fig. 1, the GLC yield and glycerol conversion increased continuously with an increasing  $\text{ZnCl}_2$ /glycerol ratio up

**Table 1**  
Activities of various zinc catalysts for the glycerolysis of urea.<sup>a</sup>

Entry	Catalyst	Conversion (%)	GLC yield (%)	GLC selectivity (%)
1	–	52.5	29.5	56.2
2	$\text{ZnF}_2$	76.4	64.3	84.1
3	$\text{ZnCl}_2$	80.4	80.2	99.7
4	$\text{ZnBr}_2$	81.4	79.2	97.2
5	$\text{ZnI}_2$	80.9	76.9	94.9
6	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	85.3	79.6	93.2
7	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$	67.2	44.3	66.0
8	$\text{ZnO}$	69.9	47.9	68.5

<sup>a</sup> Reaction condition: glycerol = 250 mmol, urea = 250 mmol, catalyst/glycerol = 2 mol%,  $P = 2.67$  kPa,  $T = 150$  °C,  $t = 2$  h.



**Fig. 1.** Effect of catalyst loading on the glycerolysis of urea. Reaction condition: glycerol = 250 mmol, urea = 250 mmol,  $T = 150^\circ\text{C}$ ,  $t = 2\text{ h}$ ,  $P = 2.67\text{ kPa}$ .

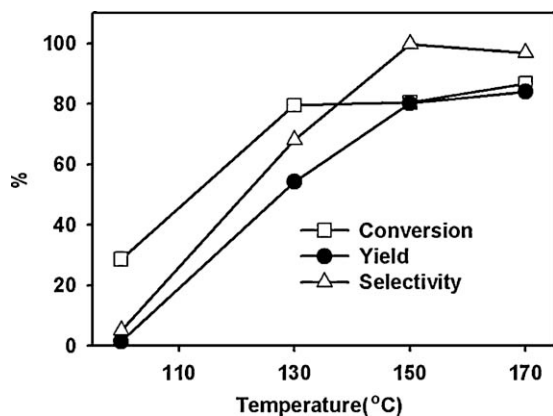
to 2 mol%, but remained almost unchanged on further increase of the molar ratio. This could be attributed to the limited solubility of the active species.

### 3.3. Effect of temperature

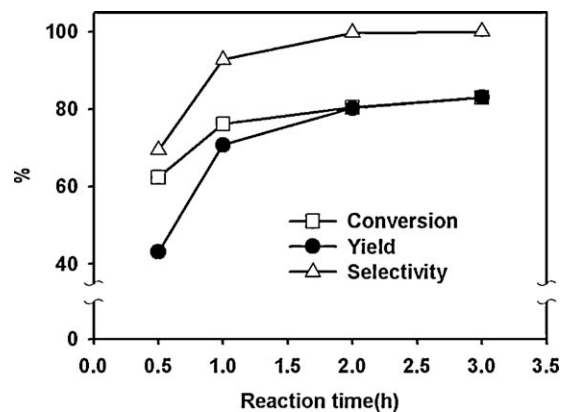
The carbonylation of glycerol by urea was affected by the reaction temperature. As shown in Fig. 2, the conversion of glycerol reached a maximum at temperature of  $130^\circ\text{C}$ , whereas the highest GLC yield and selectivity were attained at  $150^\circ\text{C}$ . This is a typical pattern for a two-step reaction of a diol with urea [11,18]. It is obvious that 2,3-dihydroxypropyl carbamate (HPC) which structure is shown in Eq. (2) in Scheme 2, formed first and then transformed into GLC through the intramolecular interaction between the hydroxyl group and the carbonyl group. However, the loss of  $\text{NH}_3$  from HPC would be much more difficult than that from urea due to the reduced nucleophilicity of hydroxyl group in HPC compared with that of glycerol, thereby requiring higher temperature. However, the conversion of glycerol remained almost constant on further increase of the reaction temperature above  $150^\circ\text{C}$ . Such a phenomenon can be most possibly ascribed to the decomposition of urea at temperatures over  $150^\circ\text{C}$  [19].

### 3.4. Effect of reaction time

Fig. 3 shows the effect of reaction time on the synthesis of GLC conducted at  $150^\circ\text{C}$  and at a glycerol/ $\text{ZnCl}_2$  molar ratio of 50. As



**Fig. 2.** Effect of reaction temperature on the glycerolysis of urea. Reaction condition: glycerol = 250 mmol, urea = 250 mmol, catalyst/glycerol = 2 mol%,  $T = 2\text{ h}$ ,  $P = 2.67\text{ kPa}$ .



**Fig. 3.** Effect of reaction time on the glycerolysis of urea. Reaction condition: glycerol = 250 mmol, urea = 250 mmol, catalyst/glycerol = 2 mol%,  $T = 2\text{ h}$ ,  $P = 2.67\text{ kPa}$ .

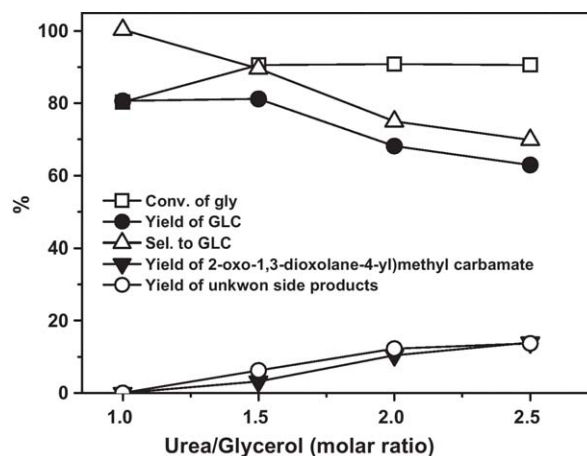
revealed in Fig. 3, at the early stage of the reaction at 0.5 h, the GLC selectivity was less than 70%, implying that substantial amounts of HPC remained in the reaction mixture. The selectivity to GLC, however, reached to >99% after 2 h of the reaction, indicating that all the remaining HPC was converted to GLC. No increase in the glycerol conversion and GLC yield was observed on further extension of the reaction time to 3 h.

### 3.5. Effect of urea/glycerol molar ratio

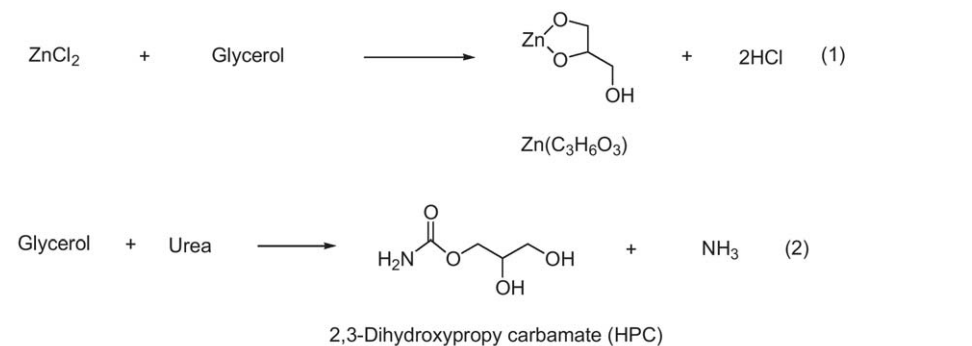
The effect of the molar ratio of urea/glycerol was investigated in the range of 1–2.5. As depicted in Fig. 4, the conversion of glycerol increased with an increasing molar ratio of urea/glycerol up to 1.5, and then remained constant at 90.4% on further increase of the molar ratio to 2.5. On the other hand, the GLC yield and selectivity decreased with the increase of the molar ratio because of the formation of various side products including (2-oxo-1,3-dioxolane-4-yl)methyl carbamate, which is an overreaction product of GLC with urea [14].

### 3.6. Isolation and characterization of intermediate catalytic species

To have a clue on the nature of active species for the synthesis of GLC from the glycerolysis of urea, a solid zinc species was recovered from the reaction and characterized by FT-IR, XRD, and elemental analyses.



**Fig. 4.** Effect of molar ratio of urea/glycerol on the glycerolysis of urea. Reaction condition: glycerol = 250 mmol, catalyst/glycerol = 2 mol%,  $T = 2\text{ h}$ ,  $P = 2.67\text{ kPa}$ .



**Scheme 2.** Reaction pathways for the formation of zinc glycerolate ( $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ ).

**Table 2**  
Activities of various catalytic species isolated from the reactions of glycerol with urea.<sup>a</sup>

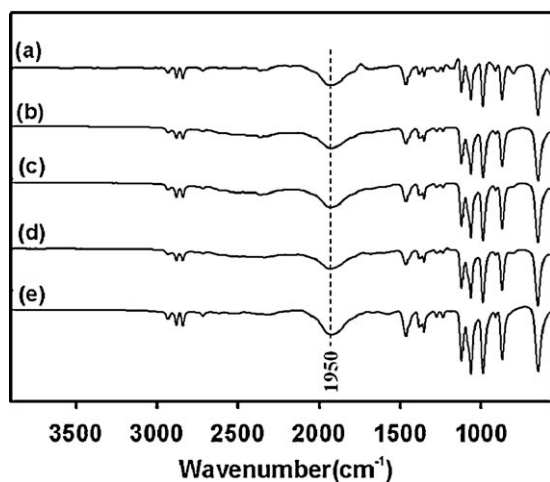
Entry	Catalyst	Conversion (%)	GLC yield (%)	GLC selectivity (%)
1	$\text{Zn}(\text{NH}_3)_2\text{Cl}_2$	83.1	82.6	99.4
2	$\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$	61.9	42.3	65.1
3	$\text{NH}_4\text{Cl}$	48.0	25.1	52.2
4	$\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)/\text{NH}_4\text{Cl}$ (1/1)	81.3	79.8	98.1
5	$\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)/\text{NH}_4\text{NO}_3$ (1/1)	85.5	78.2	91.5
6	$\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)/\text{NH}_4\text{OAc}$ (1/1)	73.8	50.5	68.5

<sup>a</sup> Reaction condition: glycerol = 250 mmol, urea = 250 mmol, catalyst/glycerol = 2 mol%,  $P = 2.67$  kPa,  $T = 150$  °C,  $t = 2$  h.

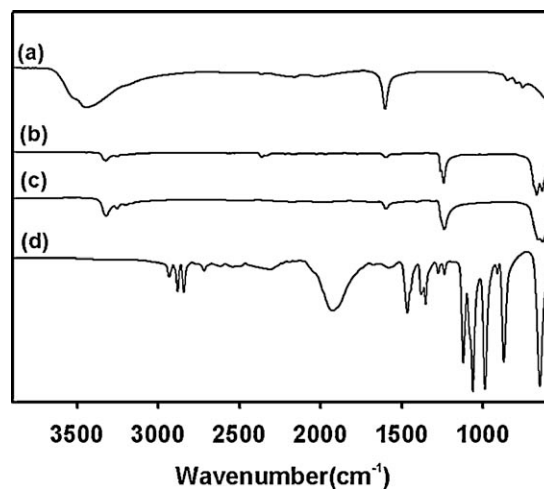
Fig. 5 shows the FT-IR spectra of the solids isolated from the reactions of glycerol with urea in the presence of zinc halide ( $\text{ZnX}_2$ ,  $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ). Interestingly, irrespective of the halide type, all the solids isolated showed exactly the same FT-IR spectrum as that of zinc glycerolate,  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ . From the FT-IR result, it is evident that glycerol reacts with  $\text{ZnX}_2$ , generating  $2\text{HX}$  and  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  (see Eq. (1) in Scheme 2). A similar phenomenon was also observed for the reaction of glycerol with urea in the presence of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , or  $\text{ZnO}$  (see Supporting information, Fig. S2). Zinc glycerolate is known to possess a polymeric structure by X-ray crystallographic analysis [20,21] (see Supporting information, Fig. S3). In the unit cell, each alkoxy oxygen atom of the glycerolate ligand bridges to two Zn atoms, and the hydroxyl group bonded to a single zinc atom while interacting strongly with an alkoxy oxygen atom

through a hydrogen bond formation. Due to such a bridging and hydrogen bonding property of the hydroxyl group of glycerolate ligand, the O–H stretching frequency was not observed in the FT-IR spectrum of zinc glycerolate. The characteristic absorption band centered at  $1950\text{ cm}^{-1}$  can be associated with the O–H...O bending mode.

Serendipitously, we have isolated another type of intermediate species,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  from the reaction of glycerol with urea in the presence of  $\text{ZnCl}_2$ . A turbid solution containing  $\text{ZnCl}_2$ , glycerol, and urea was heated to  $130$  °C for 30 min until the solution became transparent. The resulting solution was cooled down to room temperature and treated with acetone to obtain white solid precipitates. The solid product was characterized as  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  by FT-IR, XRD, and elemental analyses (Figs. 6 and S4 in Supporting



**Fig. 5.** FT-IR spectra of Zn species isolated from the reaction of glycerol with urea in the presence of zinc halide: (a)  $\text{ZnF}_2$ , (b)  $\text{ZnCl}_2$ , (c)  $\text{ZnBr}_2$ , (d)  $\text{ZnI}_2$  and (e)  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  synthesized [16].



**Fig. 6.** FT-IR spectra of (a)  $\text{ZnCl}_2 \cdot x\text{H}_2\text{O}$ , (b)  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  isolated from the reaction of glycerol with urea at  $130$  °C, (c)  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  synthesized according to the literature [18] and (d)  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ .



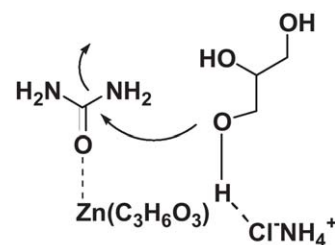
information). It is worth noting that  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  was the only solid isolated when the reaction was conducted for 2 h at the same temperature of  $130^\circ\text{C}$ . This is a strong indication that  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  is a precursor of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ . Since the reaction of glycerol with urea produces GLC along with the evolution of  $\text{NH}_3$  even in the absence of a catalyst, the formation of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  from the interaction of acidic  $\text{ZnCl}_2$  with basic  $\text{NH}_3$  can easily be conceivable. From these results, it is more reasonable to assume that  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  is produced from the interaction of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  with glycerol, not from the direct reaction of  $\text{ZnCl}_2$  with glycerol.

The facile transformation of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  into  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  can be ascribed to the elongated Zn–Cl bond distance of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  (Zn–Cl: 227 ppm) [22] compared with that of  $\text{ZnCl}_2$  (Zn–Cl: 205 ppm) [23]. With such a Zn–Cl bond lengthening, the hydrogen bond interactions between the hydroxyl groups and the Cl ligand get stronger, thereby facilitating the generation of HCl. Taken together, we concluded that, in the  $\text{ZnCl}_2$ -catalyzed synthesis of glycerol carbonate from glycerol and urea,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  is generated first and then transforms into  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  through the interaction with glycerol along with the formation of two equivalent of  $\text{NH}_4\text{Cl}$ . The mechanistic pathway to the formation of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  is depicted in Eqs. (2) and (3) of Scheme 2. Although we failed to isolate  $\text{NH}_4\text{Cl}$  due to its high solubility in the reaction mixture, the presence of  $\text{NH}_4\text{Cl}$  was identified by liquid chromatography (see Supporting information, Fig. S5).

To have a better understanding of the active species, the catalytic activities of  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ ,  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ , and a 1:1 mixture of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$  were evaluated. As listed in Table 2,  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$  exhibited comparable activity to that of  $\text{ZnCl}_2$  which is shown in Table 1, but  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  alone showed considerably lower activity than  $\text{ZnCl}_2$ . Considering the negligible activity of  $\text{NH}_4\text{Cl}$  (entry 3), it is worth to note the enhancement of the activity of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  by the presence of  $\text{NH}_4\text{Cl}$ , suggesting the participation of  $\text{NH}_4\text{Cl}$  in the  $\text{ZnCl}_2$ -catalyzed synthesis of glycerol carbonate. Similar phenomenon was also observed for the catalysis in the presence of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . As listed in Table 2, the yield of GLC increased drastically from 42.3 to 78.2% when  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  was used along with  $\text{NH}_4\text{NO}_3$ , which is also generated during the reaction in the presence of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . By contrast, the addition of synergy effect exerted by the addition of  $\text{NH}_4\text{OAc}$  was not pronounced (entry 6). The reason is not clear at the moment, but the reduced synergy effect of  $\text{NH}_4\text{OAc}$  can be attributed to its thermal instability under the experimental condition. In fact, thermogravimetric analysis (TGA) shows that  $\text{NH}_4\text{OAc}$  decomposes completely at the temperature below  $130^\circ\text{C}$ , most possibly into  $\text{NH}_3$  and  $\text{CH}_3\text{CO}_2\text{H}$ . This is a striking difference from  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ , which are stable up to  $200^\circ\text{C}$  (Supporting information, Fig. S6).

Previous studies suggested that the catalysts should possess both Lewis acidity and basicity to be active for the reaction between glycerol and urea, and there is a subtle balance between the acidity and basicity: Lewis acid for the activation of the carbonyl group of urea and Lewis base for the activation of the hydroxyl groups of glycerol [11,17,18]. In this regard, for the reaction of glycerol and urea in the presence of the catalytic system of  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)/\text{NH}_4\text{Cl}$ ,  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$  could be considered as a Lewis acid and a Lewis base, respectively as shown in Scheme 3.

The role of  $\text{NH}_4\text{Cl}$  as a Lewis base in the activation of glycerol was demonstrated by FT-IR and  $^1\text{H}$  NMR spectroscopy. Fig. 7 shows that, upon interaction with  $\text{NH}_4\text{Cl}$ , the peak corresponding to O–H stretching frequency of glycerol centered at  $3310\text{ cm}^{-1}$  moved to a lower frequency at  $3264\text{ cm}^{-1}$ , indicating that there are strong hydrogen bonding interactions between the hydroxyl groups and the chloride anion. The degree of peak shift increases with increasing amounts of  $\text{NH}_4\text{Cl}$ . The interaction of  $\text{NH}_4\text{Cl}$  with glycerol is also supported by  $^1\text{H}$  NMR spectroscopy (see Supporting information, Fig. S7). Upon interaction with  $\text{NH}_4\text{Cl}$ , the hydroxyl protons of



Scheme 3. Activation of urea and glycerol by  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$ .

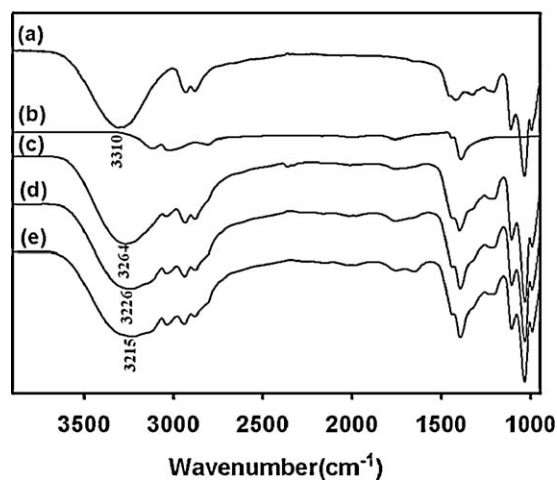


Fig. 7. FT-IR spectra: (a) glycerol, (b)  $\text{NH}_4\text{Cl}$ , (c) glycerol +  $\text{NH}_4\text{Cl}$  (1:1), (d) glycerol +  $\text{NH}_4\text{Cl}$  (1:2) and (e) glycerol +  $\text{NH}_4\text{Cl}$  (1:3).

glycerol appeared at 4.52 (t,  $\text{CH}_2\text{OH}$ ) and 4.42 (d,  $\text{CHOH}$ ) shifted downfield and coalesced into a broad peak centered at 4.65 ppm, implying that there exist hydrogen bond interactions between the hydroxyl hydrogen atoms and the chloride anion of  $\text{NH}_4\text{Cl}$ . By contrast, the N–H peak of  $\text{NH}_4\text{Cl}$  shifted slightly upfield from 7.40 to 7.32 ppm.

#### 4. Conclusion

The reaction of glycerol and urea produced GLC in medium to excellent yields in the presence of a zinc compound selected from  $\text{ZnCl}_2$ ,  $\text{ZnBr}_2$ ,  $\text{ZnI}_2$ ,  $\text{ZnF}_2$ ,  $\text{ZnO}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ . Of the zinc compounds tested,  $\text{ZnCl}_2$  exhibited the best catalytic performance, producing GLC in yield of 80.2% with a selectivity of 99.7% when the reaction was conducted at  $150^\circ\text{C}$  for 2 h at the urea/glycerol and  $\text{ZnCl}_2$ /glycerol molar ratios 1 and 0.02, respectively. Characterization of the zinc species recovered from the reaction of glycerol with urea in the presence of  $\text{ZnCl}_2$  demonstrates that  $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ , generated first from the reaction of  $\text{ZnCl}_2$  with  $\text{NH}_3$ , is transformed into  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  along with the formation of  $\text{NH}_4\text{Cl}$ . The comparison of the catalytic activities of various zinc species shows that  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  and  $\text{NH}_4\text{Cl}$  are the active combination for the glycerolysis of urea, where  $\text{NH}_4\text{Cl}$  plays a role in activating glycerol and  $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$  functions to activate urea.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2012.04.031>.

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