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Consecutive carbonylation and decarboxylation of glycerol with urea for the synthesis of glycidol via glycerol carbonate

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ABSTRACT

$Zn(OAc)_2$-catalyzed carbonylation and decarboxylation of glycerol and urea for the synthesis of glycidol were conducted at 150 °C, 2.7 kPa for 2 h and 170 °C, 2.0 kPa for 1.5 h, respectively. When the reaction conducted in a one-pot consecutive way, the yield of glycidol was 20%. However, when the formed zinc glycerolate ($Zn(C_3H_6O_3)$) was filtered out after the carbonylation, the yield increased to 50% with respect to the amount of glycerol, whereas the yields of glycidol were very low when other zinc salts such as $ZnCl_2$, $ZnSO_4$ and $Zn(NO_3)_2$, were used as catalysts. The high catalytic activity of $Zn(OAc)_2$ for this carbonylation and decarboxylation of glycerol and urea could be ascribed to the formation of $Zn(NH_3)_x(OAc)_2$, which was determined from IR and TOF-SIMS studies.

1. Introduction

Due to the surplus production of glycerol associated with biodiesel synthesis, glycerol conversion to more attractive chemicals, including 1,3-propanediol, epichlorohydrin, acrolein, glyceric acid, dihydroxy acetone, etc., is a focus of interest these days [1–3]. Glycerol carbonate is one of the chemicals that can be synthesized from the glycerol. Although glycerol carbonate itself has many application areas, such as solvents, electrolytes, plastics, and pharmaceuticals, we are particularly interested in it as a starting material for glycidol, 3-hydroxyproplyene oxide, which is being used as a stabilizer for oils and polymers, demulsifiers, surface coating agents, gelation agents and pharmaceuticals, etc. [4,5].

Currently, glycidol is being synthesized by H_2O_2-mediated epoxidation of allyl alcohol using tungsten-based catalyst [6]. In terms of green chemistry, this method is quite valuable from the point of view of using a heterogeneous catalyst and no by-product formation except water. However, use of an expensive oxidant and degradation of the catalyst are challenging problems for economical glycidol production. Another method for synthesizing glycidol is by chlorination of glycerol with Cl_2 and epoxidation of the product by treating with an equimolar amount of a base [7]. Although this process also uses glycerol as a starting material, drawbacks such as the formation of chloride salt and production of large amounts of waste water limit the efficiency of this method.

Synthesis of glycidol from glycerol via glycerol carbonate is composed of a two-step reaction. The first step is synthesis of glycerol carbonate from glycerol and the next step is decarboxylation of glycerol carbonate to glycidol and CO_2 (Scheme 1). Of the various glycerol carbonate synthesis methods, the reaction of glycerol with urea is the most attractive route in that urea is a comparatively inexpensive carbonylation agent and it can also be directly re-synthesized from the byproducts ammonia and CO_2, which are produced from the first and second reaction steps, respectively.

For the glycerol carbonate synthesis reaction from glycerol and urea, various kinds of heterogeneous and homogeneous catalysts have been reported. As a catalyst, although titanium, tin, magnesium, zirconium, tungsten, lanthanum, and gold in the form of metal oxides or impregnation in supporting material have been reported [8–14], zinc-based catalyst system is the most extensively studied due to its high catalytic activity [15–22].

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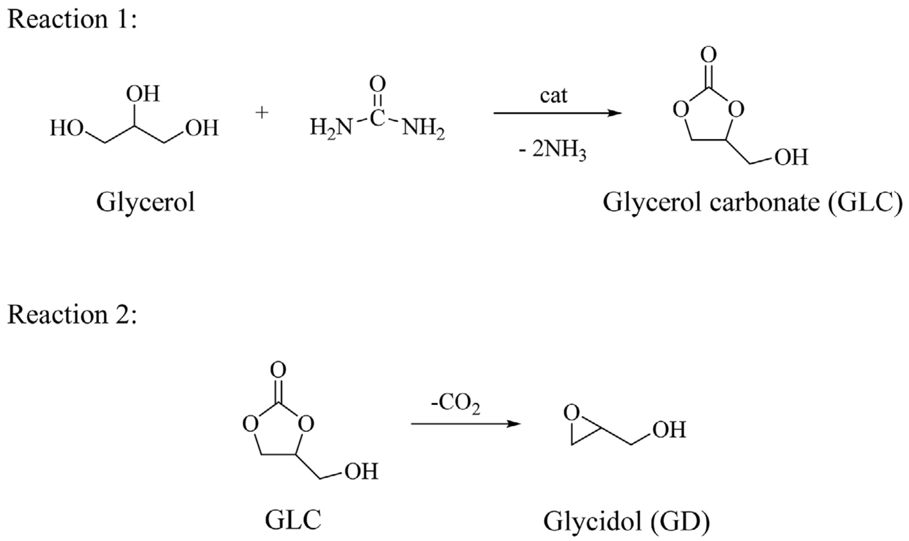

Scheme 1. Synthetic routes of glycidol from glycerol and urea via glycerol carbonate.

Park et al. used zinc chloride as a catalyst for the reaction of glycerol and urea and found that over 70% of glycerol carbonate was obtained at 150 °C and 2.7 kPa. In this reaction, the zinc chloride converted to zinc glycerolate ($Zn(C_3H_6O_3)$) and ammonium chloride during the reaction [15]. Turney et al. used $Zn(C_3H_6O_3)$ as a catalyst for the glycerol carbonate synthesis reaction and suggested that zinc complex containing an isocyanate ligand formed as a reaction intermediate [17]. Similarly, Fujita et al. conducted the same reaction using solid catalyst containing zinc and concluded that the active catalytic species was a homogeneous complex of zinc atoms having an isocyanate group (—N=C=O) [16]. In these papers, the high activity of the zinc species was ascribed to the Lewis acid property of zinc, in which zinc ions activate urea and thereby facilitate a nucleophilic attack of glycerol to the reaction center.

Previously, we investigated the decarboxylation of glycerol carbonate to glycidol and found that hydrogen-bond basicity of anions in an alkali metal salt or imidazolium salt was a decisive factor in the synthesis of glycidol with a high yield [23]. Furthermore, we also found that the presence of a Lewis acid, such as $ZnCl_2$, seriously deteriorated the catalytic activity. This result indicated that when glycerol carbonate was synthesized from the Lewis acid-catalyzed reaction, the catalyst needed be separated before the decarboxylation to obtain a high yield of glycidol. In fact, Sasa et al. suggested that to prevent deactivation of the next decarboxylation catalyst, glycerol carbonate synthesized using zinc sulfate should be distilled using an energy intensive high vacuum thin film apparatus or be treated using ion exchange resin for the removal of the catalyst [22].

Another way to prevent catalyst poisoning during the glycidol synthesis reaction by the catalyst used in glycerol carbonate synthesis is to use a heterogeneous catalyst at the glycerol carbonate synthesis step. For this method, zinc-incorporated heteropoly acid [19], zinc hydroxystannate [24], zinc loaded MCM-41[25], zinc ion-exchanged zeolite [21], and zinc supported on polymeric ionic liquids [18] have been developed. However, although they show a quite high glycerol carbonate yield and recyclability of the catalyst, a complicated preparation step and leaching of the catalytic species is a challenging factor for the real application of these catalysts to glycidol synthesis.

In this research, we tried a one-pot consecutive glycidol synthesis reaction from glycerol and urea through glycerol carbonate using a homogeneous zinc catalyst. Of the various zinc catalysts, $Zn(OAc)_2$ had the highest yield of glyciol while other zinc catalysts, such as $ZnCl_2$, $Zn(NO_3)_2$, and $ZnSO_4$, had a negligible glycidol yield. The real catalytic species for the Zn(OAc)-catalyzed glycidol synthesis reaction was estimated by using IR and TOF-SIMS.

2. Experimentals

2.1. General

Glycerol, urea, zinc and ammonium compounds were purchased from Aldrich Chemical Co. (USA), and glycerol carbonate (GLC) was obtained from TCI (Japan). Zinc glycerolate and $Zn(NH_3)_2Cl_2$ compounds were prepared according to the literature procedure [15]. All reagents were used as received without further purification.

2.2. One-pot glycidol synthesis reaction

Reaction 1: Glycerol (23.0 g, 250 mmol), urea (15.0 g, 250 mmol), and $Zn(OAc)_2$ (0.459 g, 2.5 mmol) were added to the 100 mL round-bottomed flask equipped with a magnetic stirrer and condenser. The pressure inside the flask was controlled using a vacuum release valve and a vacuum gauge. When the pressure was reduced to 2.7 kPa by a vacuum pump, the reaction mixture was heated in an oil bath to a 150 °C and conducted the reaction for 2.0 h. For the analysis, the flask was cooled to room temperature and solid materials were isolated through filtration. The liquid phase was analyzed using a high performance liquid chromatography (HPLC).

Reaction 2: After the reaction 1, the temperature was increased to 175 °C and the pressure was reduced to 2.0 kPa. Volatiles produced during the decarboxylation reaction were collected in a cold receiver immersed in a dry ice-acetonitrile bath. The product mixture was analyzed using a HPLC and the volatiles collected in the cold receiver were analyzed by a gas chromatography (GC).

2.3. Instruments

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 H_2SO_4 aqueous solution and the flow rate was set at 0.6 mL/min. The volatiles collected in the cold receiver was quantified through Agilent GC (7890A) equipped with a HP-INNOWAX capillary column (30 m × 0.32 mm × 0.25 μm) and a flame-ionization detector. For the quantitative analysis, an external standard method was used.

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Table 1
One-pot consecutive reaction of glycerol and urea to glycidol[a].

Entry	Cat.	Reaction 1		Reaction 2	
		Glycerol Conv. (%)	GLC Yield (%)	GD/GLC Yield (%)[a]	GD/GLC Sel. (%)
1	$ZnCl_2$	85.8	72.1	8.0/65.0	9.4/75.8
2	$ZnSO_4$	86.5	73.9	9.2/58.5	10.6/67.6
3	$Zn(NO_3)_2$	79.8	74.1	8.1/69.2	10.2/86.6
4	$Zn(OAc)_2$	80.6	72.5	19.9/51.6	24.8/64.0
5	$ZnO + NH_4OAc$ (1/4)	87.8	71.6	58.2/5.4	50.0/5.4
6	$Zn(C_3H_6O_3)$	85.6	74.3	9.7/26.0	10.8/29.1

Reaction 1: cat./glycerol = 0.01, glycerol/urea = 1, 150 °C, 2.7 kPa, 2.0 h.
Reaction 2: 175 °C, 2.0 kPa, 1.5 h.

[a] The yields are based on the used glycerol at the reaction 1.

Table 2
Consecutive reaction of glycerol with urea to glycidol after filtration of $Zn(C_3H_6O_3)$[a].

Entry	Cat.	Reaction 1		Reaction 2	
		Glycerol Conv. (%)	GLC Yield (%)	GD/GLC Yield (%)	GDYield[b] (%)
1	$ZnCl_2$	86.4	73.6	1.9/71.7	2.6
2	$ZnSO_4$	86.6	72.3	6.3/61.5	8.7
3	$Zn(NO_3)_2$	79.8	74.0	8.7/68.6	11.7
4	$Zn(OAc)_2$	80.5	75.3	50.6/20.9	67.1

Reaction 1: cat./G = 0.01, G/U = 1, 150 °C, 2.7 kPa, 2.0 h.
Reaction 2: 175 °C, 2.0 kPa, 1.5 h.

[a] The yields are based on the used glycerol at the reaction 1.

[b] The yield are based on GLC synthesized at the reaction 1.

Fourier transform infrared spectroscopy (FT-IR) spectra of catalyst samples were recorded on a Nicolet FT-IR spectrometer (iS10) equipped with a SMART MIRACLE accessory over a range of 400–4000 cm^{-1} at a resolution of 2 cm^{-1}. X-ray diffraction (XRD) was measured using a Shimadzu XRD-6000 with a Cu Kα radiation source (40 kV and 30 mA). Thermogravimetric analysis (TGA) was performed on a thermal analyzer (TGA Q50) heated from 30 °C to 500 °C at 10 °C/min under a flow of nitrogen.

The zinc contents were measured using an inductively coupled plasma (ICP) emission spectroscopy (iCAP 6500 DUO, Thermo Fisher Scientific Inc.). Anion concentrations were determined using a Dionex IC 25 ion chromatograph (IC) equipped with an Ion Pac AS 19 column (4 × 250 mm).

Positive SIMS mass spectra were acquired for each sample using a time of flight secondary ion mass spectrometry (TOF-SIMS) (ION-TOF GmbH, Münster, Germany) equipped with a reflectron analyzer, a bismuth ion gun (25 keV, 10 kHz) and a pulsed electron flood source for charge neutralization. The pulsed primary $Bi_3{}^+$ ion beam of 25 kV at an ion current of 0.3 pA was bombarded onto the samples at 45° incidence angle. The positively charged secondary ions were guided to a reflectron-type time-of-flight (TOF) mass spectrometer by impressing acceleration voltage of 2 kV and reaccelerated to 10 kV before being detected by a micro-channel plate (MCP) detector. The samples were measured in the high-current bunched mode ($m/\triangle m = 11{,}000$; 5 μm beam diameter), by which high mass resolution was achieved to temporarily compress the pulse width of the primary ions. The primary ion beams were scanned randomly over a field of view of 20 × 20 μm^2 at a resolution of 128 × 128 pixels with a cycle time of 150 μs.

3. Results and discussions

3.1. Consecutive carbonylation and decarboxylation

As shown in Scheme 1, synthesis of glycidol (GD) from glycerol and urea involve a two-step reaction. The first step (Reaction 1) is carbonylation of glycerol with urea to make glycerol carbonate (GLC) and the second step (Reaction 2) is decarboxylation of GLC to GD. Reaction 1 was conducted at 150 °C for 2.0 h under 2.7 kPa, which was followed by reaction 2 conducted at 175 °C for 1.5 h under 2.0 kPa. These are the optimized reaction conditions based on our previous research [15,23]. Because of their similar reaction conditions, the flask was heated to 175 °C with a vacuum condition of 2.0 kPa to conduct decarboxylation after carbonylation.

Four kinds of zinc salts, i.e. $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$ and $Zn(OAc)_2$, were used with a 1 mol% concentration with respect to the amount of glycerol for the consecutive GD synthesis reaction. Table 1 shows that, after reaction 1, all the zinc catalysts gave similar GLC yields of above 70%, which agrees with the previous results [15]. However, after reaction 2 which was conducted right after reaction 1, all tested zinc catalysts, except $Zn(OAc)_2$, had a very low GD yield of less than 10% based on the glycerol used. In the case of $Zn(OAc)_2$, the GD yield reached 19.9%, which was twice that of the other zinc compounds. Nevertheless, it seems clear that the zinc catalyst, a Lewis acid, is inactive to decarboxylation of GLC, which indicates that direct consecutive carbonylation and decarboxylation of glycerol and urea for GD synthesis is not an effective method.

3.2. Decarboxylation after filtration of $Zn(C_3H_6O_3)$

Previously, we observed that $ZnCl_2$ changed to zinc glycerolate ($Zn(C_3H_6O_3)$) and ammonium chloride via $Zn(NH_3)_2Cl_2$ during reaction 1 as depicted in Scheme S1 in Supplementary data [15]. Fortunately, the solubility of $Zn(C_3H_6O_3)$ in the reaction 1 product was quite low at room temperature; after reaction 1, white solids were formed in all the zinc catalysts. XRD and IR analyses of the white solids, i.e. $Zn(C_3H_6O_3)$, revealed that they were present not only in the $ZnCl_2$-catalyzed reaction but also in other reactions with zinc compounds as well (Figs. S1 and S2 in Supplementary data).

The transformation of the soluble zinc salt to a less soluble $Zn(C_3H_6O_3)$ after reaction 1 enabled the separation of the Lewis acid component before reaction 2, which was catalyzed by anions, a kind of Lewis base. Furthermore, due the presence of ammonium salts of chloride, sulfate, nitrate and acetate, which are known to catalyze decarboxylation of GLC [22,23], we expected that the yield

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Table 3
Concentration of zinc and anion in the solid and liquid after the reaction 1.

Cat. (2.5 mmol)	Zn^{2+}(mmol)			Anion (mmol)	GD Yield (%)
	In liq.	In solid	Total	In liq.	
$ZnCl_2$	0.70	1.70	2.40	4.24	1.9
$ZnSO_4$	0.82	1.62	2.44	2.27	6.3
$Zn(NO_3)_2$	0.40	1.98	2.38	4.46	8.7
$Zn(OAc)_2$	1.20	1.19	2.39	0.13	50.6

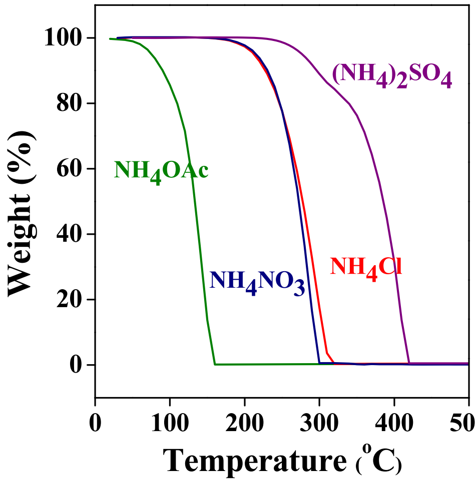

Fig. 1. Thermal stabilities of the various ammonium salts.

of GD would increase significantly if $Zn(C_3H_6O_3)$ was filtered out from the reaction 1 product solution.

As Table 2 shows, the yield of GD in the $Zn(OAc)_2$ catalyzed system increased from 19.9% to 50.6% by the filtering out of the zinc species after the reaction 1. This yield of GD corresponded to 67.1% based on the GLC formed, which was similar to the highest yield of GD using the [BMIm]NO_3 catalyzed decarboxylation (68.7%) [23]. However, no filtration effect was observed in $ZnCl_2$, $ZnSO_4$, and $Zn(NO_3)_2$ catalyzed systems (Table 2, Entries 1–3).

This experimental result may indicate that, in the case of $Zn(OAc)_2$, Lewis acidic zinc species are removed by the filtration, while other zinc compounds, such as $ZnCl_2$, $ZnSO_4$ and $Zn(NO_3)_2$, still remain in the product solution. However, the analyses of zinc and anion concentrations using ICP and IC in the filtered solid and product solution after reaction 1 gave the completely opposite result.

Table 3 shows, after reaction 1, the major amount of zinc species were filtered out in the form of $Zn(C_3H_6O_3)$ during the $ZnCl_2$, $ZnSO_4$ and $Zn(NO_3)_2$ catalyzed reactions, while about half amount of the zinc component remained in the product solution at the $Zn(OAc)_2$ catalyzed reaction. Furthermore, the concentrations of acetate anion was very little at $Zn(OAc)_2$ catalyzed reaction, which is a great contrast to the rest of the zinc catalyst systems.

This low acetate ion concentration in the reaction 1 product could be explained from the low thermal stability of NH_4OAc (Fig. 1). As mentioned earlier, when zinc salt was used in reaction 1, it changed to $Zn(C_3H_6O_3)$ and ammonium salt. Therefore, in the case of $Zn(OAc)_2$ system, NH_4OAc will form. At the reaction 1 conditions of 150 °C and 2.7 kPa, NH_4OAc decomposed to NH_3 and HOAc and was removed from the reaction solution, while other ammonium salts remains in the solution due to the high thermal stability.

To understand the high catalytic activity of the $Zn(OAc)_2$ system for consecutive GD synthesis reactions, independent decarboxylation of GLC using reagent GLC was conducted with the same conditions as reaction 2. The concentration of the catalyst was set to 1 mol%. Fig. 2 shows that no decarboxylation occurred at the $ZnCl_2$, $ZnSO_4$, $Zn(NO_3)_2$, $Zn(C_3H_6O_3)$ catalyzed reactions, while $Zn(OAc)_2$ gave a 10.4% yield of GD. This result confirms that the Lewis acid does not play any role in this reaction. The ammonium salts of Cl^-, SO_4^{2-}, NO_3^-, and OAc^- –catalyzed decarboxylation of GLC were conducted also and only NH_4OAc produced GD with a yield of 24.4% (Fig. 3). In this regard, when the remaining concentration of acetate ions during the $Zn(OAc)_2$-catalyzed reaction 1 was considered, the high GD yield of $Zn(OAc)_2$ could not be attributed to the presence of NH_4OAc.

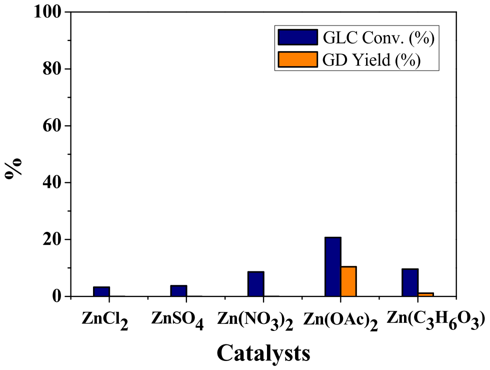

Fig. 2. Decarboxylation of glycerol carbonate to glycidol using zinc compounds. Reaction condition: Zinc salt/GLC = 1%, 175 °C, 2.0 kPa, 1.5 h.

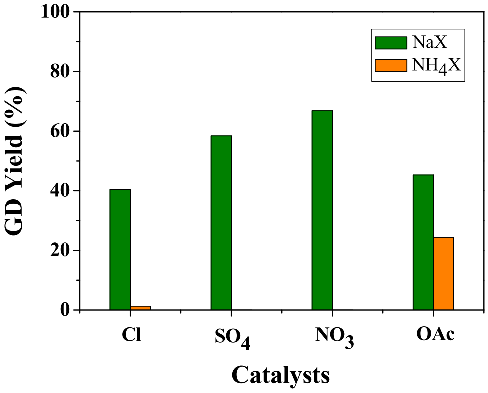

Fig. 3. Decarboxylation of glycerol carbonate to glycidol. Reaction condition: Zinc salt/GLC = 0.01, 175 °C, 2.0 kPa, 1.5 h.

Previously, by comparing the GD yields of LiCl, NaCl, KCl, and [Bmim]Cl-catalyzed reactions, we concluded that decarboxylation of GLC highly depends on the anion basicity, while the cation effect is of little significance [23]. However, the result of the ammonium salt indicated that the cation also played a decisive role at the decarboxylation of glycerol carbonate. When the cation is changed to a sodium salt, the yield of GD increased substantially as shown in Fig. 3.

3.3. *Estimation of catalyst species*

Although significantly high concentration zinc species were detected in the solution phase after the $Zn(OAc)_2$ catalyzed reaction 1, the exact zinc structure in the solution is still ambiguous, which would be a real catalytic species for the decarboxylation of GLC, reaction 2. One possible structure is an zinc complex having ammonia ligands, such as $Zn(NH_3)_x(OAc)_2$. In fact, in the case of the $ZnCl_2$-catalyzed reaction 1, $Zn(NH_3)_2Cl_2$ was isolated during the early stage of reaction 1 [15]. Yamaguchi et al. confirmed the crystalline structure of $Zn(NH_3)_2Cl_2$ and $Zn(NH_3)_4I_2$ [26,27]. These zinc-ammonia complexes are known to be synthesized from the

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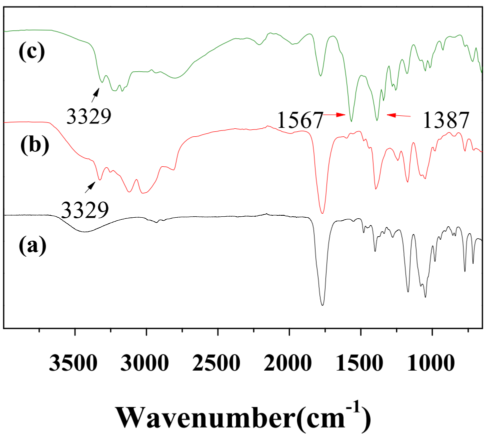


Fig. 4. IR spectra of (a) GLC, reaction products of (b) ZnO/NH_4Cl (1/2), and (c) ZnO/NH_4OAc(1/2) at 100 °C for 30 min in the presence of GLC.

$ZnCl_2$–NH_4OH or ZnO–NH_4Cl. In the $Zn(OAc)_2$ system, although we failed to isolate any form of $Zn(NH_3)_x(OAc)_y$ compound and also failed to find any literature related to that species, we detected the peak associated with Zn-NH_3 and Zn-OAc from the IR and TOF-SIMS studies.

To prepare the sample for IR study, ZnO was mixed with 2 equivalents of NH_4Cl and NH_4OAc, respectively, in the GLC solvent and stirred at 100 °C for 30 min. When the samples were cooled to room temperature, the ZnO/NH_4Cl/GLC mixture showed a white precipitate, $Zn(NH_3)_2Cl_2$, as noted in a previous study [26], while the ZnO/NH_4OAc/GLC mixture was a transparent viscous solution. IR spectra shown in Fig. 4 revealed asymmetric N—H stretching resulting from metal-NH_3 at 3329 cm^{-1} at both of the samples [28]. Furthermore, in the ZnO/NH_4OAc/GLC mixture, bidentate Zn-O in $Zn(OAc)_2$ were detected at 1567 and 1387 cm^{-1} [29]. We also analyzed the samples using TOF-SIMS spectroscopy and found $Zn(NH_3)_3^+$ $Zn(NH_3)_5^+$, and $Zn(NH_3)_4(OAc)$ ions in the ZnO/NH_4OAc/GLC mixture, while $Zn(NH_3)Cl^+$, $Zn(NH_3)_2Cl^+$, and $Zn(NH_3)_2Cl_3^+$ ions were detected in the ZnO/NH_4Cl/GLC mixture (Figs. S3 and S4 Supplementary data).

Using a ZnO-ammonium salt mixture, consecutive carbonylation and decarboxylation were conducted and the result is shown in Fig. 5. Interestingly, only the ZnO and NH_4OAc mixture had a high glycidol yield of 48.5%, which is quite similar to the result obtained from $Zn(OAc)_2$-catalyzed consecutive reaction of 50.6% after filtration of $Zn(C_3H_6O_3)$ (Table 2, entry 4). In contrast, ZnO combined with NH_4Cl, $(NH_4)_2SO_4$, and NH_4NO_3 revealed poor activity to the GD yield just as $ZnCl_2$, $ZnSO_4$ and $Zn(NO_3)_2$ showed no activity to the decarboxylation of GLC.

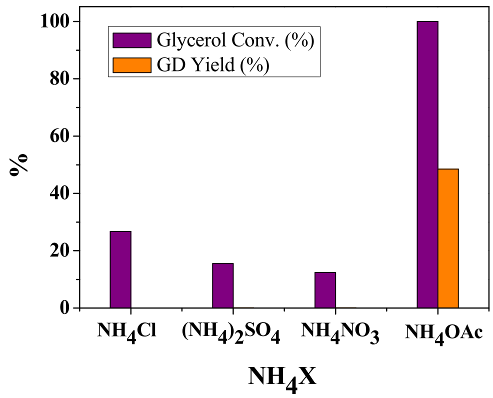


Fig. 5. Effect of ZnO-NH_4X on the consecutive carbonylation and decarboxylation of glycerol.

Reaction condition: ZnO/glycerol = 0.01, ZnO/NH_4X = 1/3, G/U = 1, 150 °C, 2.7 kPa, 2.0 h.

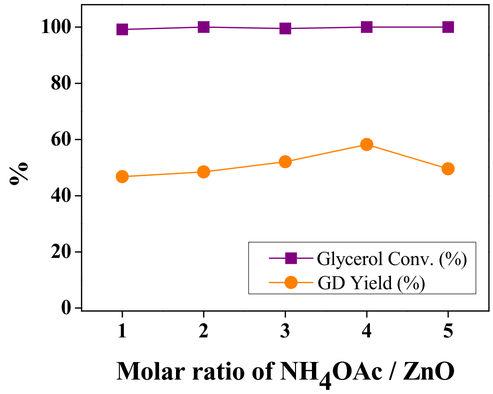
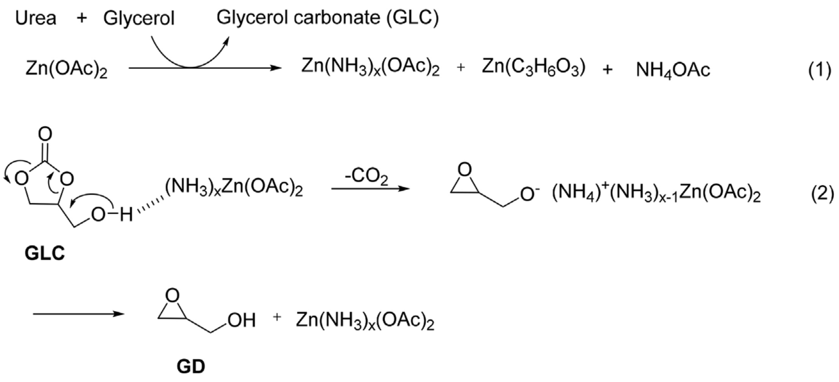


Fig. 6. Effect of NH_4OAc/ZnO ratio on the consecutive carbonylation and decarboxylation of glycerol.

Reaction 1: Cat./G = 0.01, G/U = 1, 150 °C, 2.7 kPa, 2.0 h. Reaction 2: 175 °C, 2.0 kPa, 1.5 h.

The variation in the molar ratio of NH_4OAc/ZnO revealed that the maximum amount of GD yield 58.2% was obtained when the ratio was 4 (Fig. 6), which is slightly higher than the result obtained from $Zn(OAc)_2$ catalyzed consecutive reaction of 50.6% obtained after filtration of $Zn(C_3H_6O_3)$ (Table 2, entry 4), which are presumably due to the higher catalyst concentration of $Zn(NH_3)_x(OAc)$ at the ZnO-NH_4OAc-catalyzed system.

Based on these experiments, we concluded that the $Zn(OAc)_2$ based consecutive carbonylation and decarboxylation from glycerol and urea proceeds as Scheme 2.



Scheme 2. Reaction scheme for the synthesis of $Zn(NH_3)_x(OAc)_2$ (1) and plausible reaction mechanism for the decarboxylation of glycerol carbonate to glycidol (2).

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During reaction 1, $Zn(OAc)_2$ changed to $Zn(NH_3)_x(OAc)_2$, $Zn(C_3H_6O_3)$, and NH_4OAc. At this stage, two zinc species, $Zn(NH_3)_x(OAc)_2$ and $Zn(C_3H_6O_3)$, seemed to play almost the same role as a catalyst, which can be presumed from results shown in Table 1, entries 5 and 6. However, in reaction 2, $Zn(C_3H_6O_3)$, a Lewis acid, didn't catalyze the reaction as shown in Fig. 2, while $Zn(NH_3)_x(OAc)_2$ acted as a decarboxylation catalyst. Therefore, $Zn(C_3H_6O_3)$ should be filtered out before reaction 2 to get a high yield of GD from the synthesized GLC at the $Zn(OAc)_2$ – catalyzed reaction. The activity of $Zn(NH_3)_x(OAc)_2$ toward the decarboxylation could be ascribed to the acetate anion and/or ammonia those are loosely coordinated to zinc ion, thereby activate the hydroxyl group of glycerol carbonate to make glycidol as shown in Scheme 2, step (2).

4. Conclusion

Carbonylation of glycerol with urea to glycerol carbonate and decarboxylation of glycerol carbonate to glycidol were conducted consecutively in the presence of zinc catalyst. By the carbonylation using $Zn(OAc)_2$, $ZnCl_2$, $ZnSO_4$, and $Zn(NO_3)_2$, glycerol carbonate was synthesized with a yield over 70% at the all used zinc catalysts. But the consecutive decarboxylation resulted poor yield of glycidol irrespective of used zinc catalyst. The poor glycidol yields could be ascribed to the existence of Lewis acidic zinc glycerolate, $Zn(C_3H_6O_3)$, which was produced by the zinc salt during the carbonylation. By the filtration of $Zn(C_3H_6O_3)$ after the carbonylation, yield of glycidol was increased to 50% based on the glycerol used at the $Zn(OAc)_2$ catalyst system. However, other zinc salts showed no increase in the glycidol yield. ICP, IR and TOF-SIMS studies showed that $Zn(OAc)_2$ partially changed to $Zn(NH_3)_x(OAc)_2$, for which the Lewis acidity might be negligible due to the NH_3 binding to Zn. While, the presence of acetate anions and ammonia which might be loosely bonded to the zinc species in $Zn(NH_3)_x(OAc)_2$, seemed to catalyze the decarboxylation of glycerol carbonate to glycidol.

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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.cattod.2016.12.039.

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