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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(C₃H₆O₃)) 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 ZnCl₂, ZnSO₄ and Zn(NO₃)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(NH₃)_x(OAc)₂, which was determined from IR and TOF-SIMS studies.

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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-hydroxypropylene 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 H₂O₂-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 Cl₂ 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 CO₂ (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 CO₂, which are produced from the first and second reaction steps, respectively.

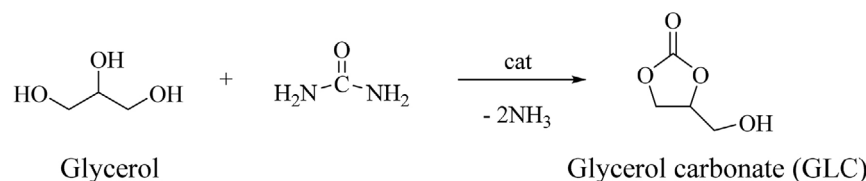
For the glycerol carbonate synthesis reaction from glycerol and urea, various kinds of heterogeneous and homogeneous catalysts have been reported. As a catalyst, although titanium, tin, magnesium, zirconium, tungsten, lanthanum, and gold in the form of metal oxides or impregnation in supporting material 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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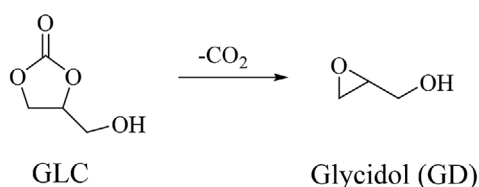
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Reaction 1:



Reaction 2:

**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 ($\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$) and ammonium chloride during the reaction [15]. Turney et al. used $\text{Zn}(\text{C}_3\text{H}_6\text{O}_3)$ 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 ($-\text{N}=\text{C}=\text{O}$) [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, $\text{Zn}(\text{OAc})_2$ had the highest yield of glycidol while other zinc cata-

lysts, such as ZnCl_2 , $\text{Zn}(\text{NO}_3)_2$, and ZnSO_4 , had a negligible glycidol yield. The real catalytic species for the $\text{Zn}(\text{OAc})_2$ -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 $\text{Zn}(\text{NH}_3)_2\text{Cl}_2$ 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 $\text{Zn}(\text{OAc})_2$ (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 \times 0.32 mm \times 0.25 μm) and a flame-ionization detector. For the quantitative analysis, an external standard method was used.

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