

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, ZnCl₂ showed the highest catalytic activity. Spectroscopic and elemental analyses of the zinc species, isolated from the reaction conducted in the presence of ZnCl₂, revealed that Zn(NH₃)Cl₂ was generated first as an intermediate species, which in turn reacted with glycerol to produce zinc glycerolate, Zn(C₃H₆O₃) and NH₄Cl. The activity of Zn(C₃H₆O₃) was considerably lower than that of ZnCl₂, but the activity was greatly enhanced by the combined use of NH₄Cl, implying that both Zn(C₃H₆O₃) and NH₄Cl were functioning as essential ingredients for the carbonylation of glycerol by urea. The formation of Zn(C₃H₆O₃) was also observed when ZnBr₂, ZnI₂, ZnF₂, Zn(NO₃)₂, Zn(CH₃CO₂)₂, 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 COCl₂, CO/O₂, CO₂, 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

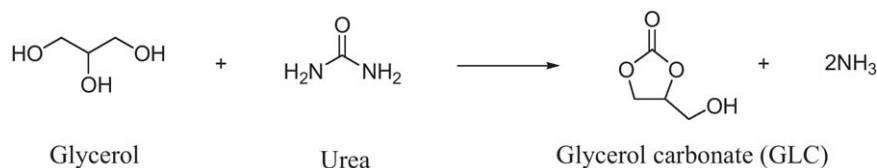
All reagents including glycerol, urea, and zinc compounds were purchased from Aldrich Chemical Co. and used as received without further purification. GLC was purchased from TCI (Japan).

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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 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 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 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 H_2SO_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 cm^{-1} at a resolution of 2 cm^{-1} . X-ray diffraction (XRD) was measured using a Shimadzu XRD-6000 with a Cu $\text{K}\alpha$ 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, 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}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% 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 ZnBr_2 and ZnI_2 , whereas ZnF_2 resulted in a much lower GLC yield and selectivity, possibly due to the low solubility of 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 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 ZnCl_2 (99.7%). By contrast, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and 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 ZnX_2 ($\text{X} = \text{halide}, \text{NO}_3, \text{OAc}$) with the variation of X is not clear at the moment, but the Lewis acidity of 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 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 ZnCl_2 /glycerol ratio up

Table 1
Activities of various zinc catalysts for the glycerolysis of urea.^a

Entry	Catalyst	Conversion (%)	GLC yield (%)	GLC selectivity (%)
1	–	52.5	29.5	56.2
2	ZnF_2	76.4	64.3	84.1
3	ZnCl_2	80.4	80.2	99.7
4	ZnBr_2	81.4	79.2	97.2
5	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	ZnO	69.9	47.9	68.5

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

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