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

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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

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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,  $ZnCl_2$  showed the highest catalytic activity. Spectroscopic and elemental analyses of the zinc species, isolated from the reaction conducted in the presence of  $ZnCl_2$ , revealed that  $Zn(NH_3)Cl_2$  was generated first as an intermediate species, which in turn reacted with glycerol to produce zinc glycerolate,  $Zn(C_3H_6O_3)$  and  $NH_4Cl$ . The activity of  $Zn(C_3H_6O_3)$  was considerably lower than that of  $ZnCl_2$ , but the activity was greatly enhanced by the combined use of  $NH_4Cl$ , implying that both  $Zn(C_3H_6O_3)$  and  $NH_4Cl$  were functioning as essential ingredients for the carbonylation of glycerol by urea. The formation of  $Zn(C_3H_6O_3)$  was also observed when  $ZnBr_2$ ,  $ZnI_2$ ,  $ZnF_2$ ,  $Zn(NO_3)_2$ ,  $Zn(CH_3CO_2)_2$ , or ZnO was used as the catalyst.

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polarity [4–6]. A number of processes have been reported for the synthesis of GLC from glycerol using a variety of carbonyl sources, including  $COCl_2$ ,  $CO/O_2$ ,  $CO_2$ , 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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