



Dual catalysis over ZnAl mixed oxides in the glycerolysis of urea: Homogeneous and heterogeneous reaction routes

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ABSTRACT

In this work, we prepared ZnO, ZnAl₂O₄, and ZnAl mixed oxides with different metal molar ratios and applied them for synthesizing glycerol carbonate (GC) from glycerol and urea. The reaction routes related to the Zn species over the ZnAl mixed oxides were investigated. The ZnAl mixed oxides were found to consist of two Zn crystalline phases: ZnO and ZnAl₂O₄. From the reaction results, the ZnAl mixed oxides showed much higher glycerol conversion and GC yield than the ZnO and ZnAl₂O₄. During the reaction, the dissolution of the Zn species from the ZnO phase over the ZnAl mixed oxides was observed while the ZnAl₂O₄ phase remained insoluble. The ZnO phase provided a homogeneous reaction route *via* the dissolved Zn species, resulting in the formation of a Zn complex containing the isocyanate (NCO) and zinc glycerolate. In contrast, the insoluble ZnAl₂O₄ phase was responsible for not only a heterogeneous reaction route, but also adsorption of the Zn NCO complex on the catalyst. We proposed that the adsorbed Zn NCO complex could play a role as an active site for an additional heterogeneous reaction route. Therefore, the ZnAl mixed oxides exhibited high GC yields through the dual catalysis routes: the homogeneous reaction route over the ZnO phase and the heterogeneous reaction route over the ZnAl₂O₄ phase.

1. Introduction

Nowadays, due to concern for the environment and the shortage of fossil fuels, biodiesel manufacturing has been developed as an alternative renewable energy resource. However, it is disadvantageous that a noticeable amount of glycerol is produced as a by-product in the process [1]. This type of glycerol has low commercial value, and there is an emerging concern about the environmental impact of this abundant crude glycerol and the sustainability of biodiesel [2,3]. Even though a traditional way to treat crude glycerol is to purify it, the market for pure glycerol is saturated and the price of crude glycerol has dropped [4]. To manufacture more value-added products and optimize the biodiesel process, glycerol can be converted into high-cost products using various chemical pathways, such as selective oxidation, selective hydrogenolysis, catalytic dehydration, pyrolysis and gasification, glycerol transesterification, and selective carboxylation [5].

A new research approach to utilize glycerol is to convert it into glycerol carbonate (GC) which has high economic value along with potential applications in cosmetics, batteries, polymers and pharmaceutical synthesis [6]. There are several methods to synthesize GC from glycerol using the transcarboxylation reaction with different carbonate sources: alkylene carbonate [7], dialkyl carbonate [8–10], CO₂

[11–13], and urea [14–23]. In particular, GC synthesis using urea has attracted attention for several reasons: i) urea is an inexpensive and readily available source, ii) the use of a solvent is unnecessary, and iii) the by-product NH₃ can be easily removed from a reactor by vacuuming or flowing nitrogen, which accelerates the forward reaction to GC.

The glycerolysis of urea can be accelerated by heterogeneous catalysts, which are mostly metallic oxides: γ -zirconium phosphate [16], calcined Zn hydroxalcite [21], La₂O₃ [22], and Co₃O₄/ZnO nanodispersions [23]. By investigating the catalytic performance of several metallic oxides and calcinated hydroxalcite, Climent et al. [21] proposed a heterogeneous reaction route through the interaction of reactants (glycerol and urea) with a pair of Lewis acid-base sites. In addition, the reaction of glycerol and urea can also be catalyzed by homogeneous catalysts like zinc salts [20]. The zinc isocyanate (NCO) complex formed in the liquid phase was suggested as a main active site for the homogeneous reaction route. The existence of the Zn NCO complex was also confirmed in the cases of Zn-containing solid catalysts [18], ZnO [10], and zinc glycerolate [19]. This is because the Zn species in the solid phases can leach into the liquid phase, providing evidence for the homogeneous reaction route in the heterogeneous Zn-based catalysts. However, there has not been a report describing dual catalysis that includes homogeneous and heterogeneous reaction routes at the

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Table 1
Physicochemical properties of the prepared catalysts.

Samples	BET Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)	Intensity Ratio of ZnO/ZnAl ₂ O ₄ in XRD ^a	Acidic Sites (mmol/g)	Basic Sites (mmol/g)	Acidic Sites/Basic Sites
ZnAl ₂ O ₄	17	0.137	32.6	0	0.112	0.089	1.258
Zn ₆ Al ₄	52	0.189	13.3	0.86	0.342	0.274	1.248
Zn ₇ Al ₃	77	0.301	17.0	1.29	0.375	0.383	0.979
Zn ₈ Al ₂	86	0.353	13.6	2.34	0.364	0.293	1.242
co-Zn ₇ Al ₃	46	0.164	11.6	8.78	0.305	0.365	0.844
ZnO	7	0.017	10.3	∞	0.015	0.025	0.600

^a Intensity ratios of the ZnO/ZnAl₂O₄ phases were obtained from the deconvolution in XRD patterns using the XPOWder software.

same time over ZnAl mixed oxide catalysts.

In this work, we prepare ZnAl mixed oxide catalysts via a co-precipitation method using a polystyrene (PS) template, and we apply the catalysts for the glycerolysis of urea in order to investigate the catalytic behavior of the homogeneous and heterogeneous reaction routes. The XRD patterns of the prepared ZnAl mixed oxide catalysts show the existence of two Zn phases: ZnO and ZnAl₂O₄. The ZnO phase follows the homogeneous reaction route through the dissolution of Zn species into the reaction liquid and the subsequent formation of the Zn NCO complex. In addition, the Zn NCO complex adsorbs on the ZnAl₂O₄ phase and we propose that it can create a heterogeneous reaction route. The reaction routes taking place over the Zn NCO complex in the liquid and solid phases enhances the catalytic performance of the ZnAl mixed oxide catalysts along with the conventional heterogeneous reaction route over the ZnAl₂O₄ phase.

2. Experimental

2.1. Catalyst preparation

In this study, the ZnAl mixed oxide catalysts were prepared by a co-precipitation method using PS templates in a PS-water suspension environment [24]. Emulsion polymerization was used to synthesize nano-sized PS particles, and the detailed procedure is described elsewhere [25]. PS powder was used as a hard template to prepare the ZnAl mixed oxide catalysts in various ratios of Zn and Al precursors. Typically, certain amounts of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were dissolved in a 1:1 water:ethanol solution. Another solution of (NH₄)₂CO₃ in a 1:1 water:ethanol solution was prepared as the precipitation agent. These solutions were dropped into a suspension of PS powder in a 1:1 water:ethanol solution under vigorous stirring at 60 °C while the pH was maintained at 6. The mixture was aged for 18 h at constant pH and with continuous stirring. Then, the precipitate was filtered and washed by deionized water. The resultant solid was dried overnight at 70 °C and calcined at 600 °C for 6 h with a ramping rate of 1 °C/min to ensure the complete combustion of the polystyrene template. The prepared catalysts were designated as Zn_aAl_b, where a:b is the molar ratio of the Zn:Al precursors.

Conventional ZnAl mixed oxide with a molar ratio of Zn:Al = 7:3 (designated as co-Zn₇Al₃), ZnO and the ZnAl₂O₄ catalysts were prepared by the co-precipitation method. In the case of ZnO, an aqueous solution of Zn(NO₃)₂·6H₂O was precipitated by a basic solution of NaOH and NaNO₃ under a constant pH of 6 and vigorous stirring. The mixed solution was then filtered and washed by deionized water. The resultant solid was dried at 100 °C and finally calcined at 450 °C for 6 h. In this study, the calcination temperatures for the catalyst were chosen following the references [21,26]. The ZnAl₂O₄ catalyst was prepared by the same method except using Al(NO₃)₃·9H₂O as an Al precursor and ammonia solution as a basic solution. The solution pH was adjusted to 7.5. The co-Zn₇Al₃ catalyst was also prepared using the aqueous solution of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O (the molar ratio of Zn:Al = 7:3) for comparison.

2.2. Reaction test

The reaction tests were carried out in a 100 ml round-bottom three-neck flask, where one neck was connected to a vacuum line through a water condenser. Typically, 0.2 mol of glycerol was added to the flask at 80 °C, and the solution was mixed by a magnetic stirrer to reduce the viscosity. After 10 min, 0.2 mol of urea was added and mixed. When all of the urea was completely dissolved in glycerol, a certain amount of the catalysts (5 wt.% to the initial glycerol) was added to the flask. The reaction was performed for 3 h under vacuum pressure (3 kPa) at 140 °C with constant stirring.

The products were dissolved in ethanol and separated from the solid catalysts by filtering. The liquid product was quantitatively analyzed

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