



## Feature Article

# High-efficiency and low-cost Li/ZnO catalysts for synthesis of glycerol carbonate from glycerol transesterification: The role of Li and ZnO interaction



Xianghai Song, Yuanfeng Wu, Fufeng Cai, Donghui Pan, Guomin Xiao\*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China

## ARTICLE INFO

## Article history:

Received 29 August 2016

Received in revised form

12 December 2016

Accepted 22 December 2016

Available online 23 December 2016

## Keywords:

Li/ZnO

[Li<sup>+</sup> O<sup>-</sup>] species

Transesterification

Glycerol carbonate

## ABSTRACT

A series of efficient and low-cost Li/ZnO catalysts were prepared by a simple impregnation method and investigated for the synthesis of glycerol carbonate (GC) from the transesterification of glycerol with dimethyl carbonate (DMC). The Li/ZnO catalysts were characterized using XRD, SEM, FT-IR, TG-DSC, TPD and XPS. It was found that the basicity of the catalysts highly depended on the Li loading and calcination temperature. The weak and moderate basic sites on the catalyst surfaces originated from the ZnO and Li<sup>+</sup> interaction. The strong basic sites were attributed to the substitution of Zn<sup>2+</sup> by Li<sup>+</sup> in the ZnO lattice, which led to straining of Zn-O bonds and the formation of [Li<sup>+</sup> O<sup>-</sup>] species. It was the strong basic sites rather than the weak and moderate basic sites that catalyzed the transesterification of glycerol with DMC. The highest catalytic activity was observed over the ZnO loaded with 1 wt.% LiNO<sub>3</sub> and calcined at 500 °C. Glycerol conversion of 97.40% and GC yield of 95.84% were obtained over this catalyst at 95 °C in 4 h.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Biodiesel has received growing attention in recent years as a promising alternative to fossil fuel [1]. However, rapid development in the biodiesel industry has led to the accumulation of abundant glycerol (a byproduct accounting for about 10 wt.% of the total biodiesel product), which results in the dramatic decrease of glycerol price and jeopardizes the biodiesel production economy [2]. Thus, it is urgent to find new applications of glycerol. Recent research emphasis has been focused on converting glycerol to other valuable chemicals [3–5]. Among various glycerol derivatives, glycerol carbonate (GC) is found to be a useful product of great importance [6]. GC, due to its low flammability, low toxicity, high boiling point and biodegradability, is an important cosmetic ingredient and used for the manufacture of coating, biolubricant, glycidol (GD), polycarbonates, polyesters and polyurethanes [7–10].

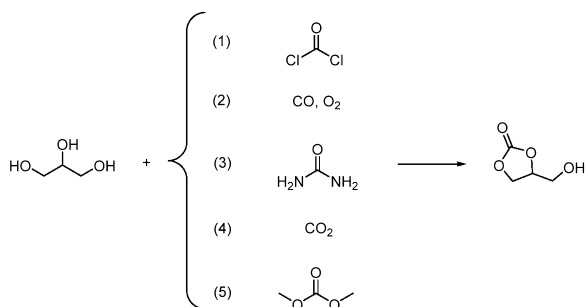
Various approaches have been employed to synthesize GC from glycerol (Scheme 1). The carbonylation of glycerol with phosgene or carbon monoxide is a traditional method in the GC synthesis [11,12], but it has been abandoned due to the high toxicity of reactants. Another method is the glycerolysis of urea in the pres-

ence of Lewis acid catalysts [13,14]. However, the byproduct NH<sub>3</sub> needs to be removed continuously during the reaction, so as to improve the GC yield. Production of GC from glycerol and CO<sub>2</sub> under super-critical conditions is an ideal pathway, because of the low costs of raw materials, high atom utilization efficiency, and no other byproducts except H<sub>2</sub>O [15,16]. However, the utilization of this method is limited by thermodynamic disadvantages, poor CO<sub>2</sub> activity and low product yield. The transesterification of glycerol with dimethyl carbonate (DMC) over basic catalysts is an important and preferred method. Typically, the reaction proceeds under mild conditions with high GC yield, and hardly any side reaction.

Among the methods mentioned above, the transesterification of glycerol is a promising one, and has received much research attention in recent years. A number of catalysts, including homogeneous and heterogeneous catalysts, have been studied for the glycerol and DMC transesterification to produce GC. Compared with heterogeneous catalysts, homogeneous catalysts are generally more reactive and have a much higher TOF. Homogeneous catalysts such as K<sub>2</sub>CO<sub>3</sub> [7], NaOH [17] and CH<sub>3</sub>OK [18] have been reported to catalyze this reaction. However, a serious drawback accompanied with homogeneous catalysts is their hard separation from the product. In any case, if the quantity of catalyst is minute, scarce problems are to be expected if left in the product mixture. On the other side, heterogeneous catalysis is very interesting and of great importance. Various heterogeneous catalysts, such as CaO [19], CaO-La<sub>2</sub>O<sub>3</sub> [20], KF-hydroxyapatite [21], K<sub>2</sub>CO<sub>3</sub>-MgO [22], ZnO/La<sub>2</sub>O<sub>3</sub> [23], Mg-Al

\* Corresponding author at: Southeast University, Road No. 2, Jiangning District, Nanjing 211189, China.

E-mail address: [Xiaogm@seu.edu.cn](mailto:Xiaogm@seu.edu.cn) (G. Xiao).



**Scheme 1.** Methods of preparing glycerol carbonate from glycerol.

hydrothermalite [24] and ionic liquids [25] have been used to synthesize GC from glycerol and DMC. However, there are still some problems need to be addressed for heterogeneous catalysts, such as poor reusability, high reaction temperature, requirement of additional solvent, long reaction time, and requirement of high glycerol to DMC molar ratio. A new strategy needs to be fostered, with the aim of getting higher activities and stabilities at moderate operating conditions. And new catalysts still need to be explored.

It was reported that, doping with lithium could improve the basicity of solid base catalysts, therefore enhancing the catalytic activity in base-catalyzed reactions [26,27]. Recently, synthesis of GC from glycerol and dimethyl carbonate over  $\text{LiNO}_3/\text{Mg}_4\text{AlO}_{5.5}$  was reported by Liu et al. [28]. Full glycerol conversion and 96.28% GC yield were achieved in this reaction, which was far superior to that of  $\text{Mg}_4\text{AlO}_{5.5}$  with only 52.09% glycerol conversion. Lithium incorporation onto MgO was reported to create the strongest basic sites compared with other alkali or alkaline earth metal ions, because of the higher Li molar concentration and the ion size effect [29,30].

Li-doped ZnO has found its application in many fields, such as conductive coating, electrodes for dye-sensitized solar cells, and field emission materials. But only few authors have studied it as a catalyst for various reactions [31]. As far as we know, Li-doped ZnO catalyst has not been studied in GC synthesis from glycerol transesterification. Thus, in this work, Li-modified ZnO as solid base catalysts were prepared by impregnating ZnO in  $\text{LiNO}_3$  solution, and their catalytic activities were investigated. The properties of the Li/ZnO catalysts were characterized by X-ray diffractometry (XRD), thermogravimetric-differential scanning calorimetry (TG-DSC), Fourier transform infrared spectrometry (FT-IR), scanning electron microscopy (SEM),  $\text{CO}_2$ -temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Besides, the structure and activity correlations of Li/ZnO catalysts for the GC synthesis were also discussed.

## 2. Experimental section

### 2.1. Materials

ZnO (AR), was purchased from Xilong Chemical Co., Ltd.  $\text{LiNO}_3$  (99.9 wt%),  $\gamma\text{-Al}_2\text{O}_3$  (99.9 wt.%), anhydrous KF (99.5 wt%), CsF (99.0 wt%) were obtained from Aladdin Industrial Corporation, Shanghai, China.  $\text{ZrO}_2$  (AR), dimethyl carbonate (DMC) (99.0 wt%), glycerol (99.0 wt.%), were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

### 2.2. Catalyst preparation

Li-doped ZnO catalysts used in this work were prepared by a simple wet impregnation method. In a typical preparation, 5 g of ZnO was impregnated using 50 mL of  $\text{LiNO}_3$  aqueous solution of appropriate concentration. The result mixture was then stirred at

ambient temperature for 12 h. After removing the water on a rotary evaporator, the obtained white solid was dried at  $100^\circ\text{C}$  for 10 h and then calcined at an appropriate temperature for 5 h to get the corresponding catalyst. The obtained catalyst was named as nLi/ZnO-T, where n and T represented  $\text{LiNO}_3$  loading and calcination temperature, respectively. For example, 5 wt.%  $\text{LiNO}_3$  supported on ZnO calcined at  $300^\circ\text{C}$  was denoted as 0.05Li/ZnO-300.

Other catalysts, such as Li/ $\text{ZrO}_2$ , Li/ $\gamma\text{-Al}_2\text{O}_3$ , K/ZnO and Cs/ZnO, were prepared by loading 10 wt.% alkaline metal salts on the support in the same way as Li/ZnO and calcined at  $500^\circ\text{C}$  for 5 h.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded on an Ultima IV X-ray diffractometer using  $\text{Cu K}\alpha$  radiation (40 kV and 40 mA) as the X-ray source. The scanning range ( $2\theta$ ) was from  $20$  to  $75^\circ$ , with a scanning rate of  $20^\circ\text{min}^{-1}$  and a step function of  $0.02$ .

The morphologies of the synthesized catalysts were studied by scanning electron microscopy (SEM) images using a Philips XL-30 ESEM operating at a voltage of 10 kV.

The surface functional groups of the catalysts were determined by fourier transform infrared spectrometer (FT-IR) using a Nicolet 5700 spectrometer. FT-IR spectra were recorded in the wavenumber range of  $400\text{--}4000\text{ cm}^{-1}$  with KBr pellets as a reference for the measurements.

Thermogravimetric and differential scanning calorimeter (TG-DSC) were conducted with a SDT 2960 DSC instrument. The catalysts (about 5 mg) were placed into an aluminum pan, and the experiment was performed under air atmosphere ranging from  $50$  to  $800^\circ\text{C}$  at a heating rate of  $20^\circ\text{C}$  per minute.

The basicity of the catalysts was measured by  $\text{CO}_2$  temperature programmed desorption ( $\text{CO}_2$ -TPD). In a typical experiment, the catalyst (100 mg) was pretreated in a flow of He ( $30\text{ mL min}^{-1}$ ) at  $200^\circ\text{C}$  for 1 h to remove moisture and other adsorbed gases. After cooling to  $100^\circ\text{C}$ , the catalyst was exposed to pure  $\text{CO}_2$  for 0.5 h and then purged with He flow ( $30\text{ mL min}^{-1}$ ) for 1 h to exclude physically adsorbed  $\text{CO}_2$ . Subsequently, the sample was heated to  $800^\circ\text{C}$  at a rate of  $10^\circ\text{C min}^{-1}$  and the desorbed  $\text{CO}_2$  was detected using a thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher Scientific ESCALAB 250Xi X-ray photoelectron spectrometer. Mg  $\text{K}\alpha$  radiation ( $1253.6\text{ eV}$ ) was used as the X-ray source at an ultrahigh pressure of  $3.0 \times 10^{-7}$  mbar. The collected elements binding energy (BE) were calibrated by referencing the C 1s peak at  $284.6\text{ eV}$ . The precision of BE was within  $\pm 0.1\text{ eV}$ .

### 2.4. Catalytic activity test

The transesterification of Glycerol with DMC was performed in a 50 mL round bottomed flask equipped with a condenser at atmospheric pressure. In a typical experiment, 50 mmol (4.6 g) of glycerol and 100 mmol (9.0 g) of DMC were placed into the flask, followed by 0.23 g (5 wt.%) of catalyst. Subsequently, the reaction system was heated to the desired temperature for a designed time. After the reaction, the catalyst was separated from the reaction system by centrifugation. The product was analyzed using a gas chromatograph (GC-6890, China), equipped with a flame ionization detector and a capillary column (SE-30,  $30\text{ m} \times 0.25\text{ mm}$ ). Ethylene glycol monobutyl ether was added to the product as an internal standard substance for the quantification analysis.

Download English Version:

<https://daneshyari.com/en/article/4755787>

Download Persian Version:

<https://daneshyari.com/article/4755787>

[Daneshyari.com](https://daneshyari.com)