



# Preparation of highly stable Ca-Zn-Al oxide catalyst and its catalytic performance for one-pot synthesis of dimethyl carbonate

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## ABSTRACT

Ca-Zn-Al oxide was prepared by co-precipitation method and the effect of preparation conditions on its catalytic performance was investigated. The Ca-Zn-Al oxide exhibited an excellent catalytic activity and stability for one-pot synthesis of dimethyl carbonate (DMC) from urea, 1,2-propylene glycol (PG), and methanol. XRD characterization and activity evaluation results indicated that new crystalline phases  $\text{Ca}_3\text{Al}_4\text{ZnO}_{10}$  and  $\text{ZnAl}_2\text{O}_4$  could create a synergistic effect with CaO and ZnO, being responsible for the excellent catalytic performance of Ca-Zn-Al oxide. Response surface methodology (RSM) was used to investigate the effect of operating variables and to optimize conditions for the first-step reaction of PG and urea to propylene carbonate. Then the effect of reaction conditions for the transesterification of propylene carbonate with methanol to DMC was also investigated. As a result, a DMC yield of 84.7% was obtained under the appropriate reaction conditions. The Ca-Zn-Al oxide could be reused for four times without a significant change in its catalytic activity.

## 1. Introduction

Dimethyl carbonate (DMC) is considered as a green chemical and is widely used in a variety of fields owing to its versatile chemical reactivity and unique physical properties, especially as a safe substitute for phosgene, dimethyl sulfate or methyl halide [1–3]. In addition, it is a potential additive to gasoline because of its high oxygen content, low toxicity, and good biodegradability [4].

The methods for the synthesis of DMC include phosgenation process [5], transesterification of cyclic carbonates with methanol [6], alcoholysis of urea [7], reaction of methanol with  $\text{CO}_2$  [8], and oxidative carbonylation of methanol [9]. Among these routes, transesterification of propylene carbonate (PC) with methanol is an attractive route due to its several distinct advantages such as high DMC yield, mild reaction conditions and no corrosion to equipments. However, PC is derived from depleting petroleum and a great deal of 1,2-propylene glycol (PG) is co-produced as a byproduct in the production process, leading to a low utilization of the feed. To solve the problems mentioned above, we proposed an idea to transform the by-product PG back into PC by the reaction of PG with urea in 2004 [10]. According to this idea, an integrated reaction process can be described as the synthesis of DMC from urea and methanol using PG as a recycle agent (see Scheme 1). In this way, not only can the problem of PG utilization be solved, but also the reliance of PC supply on the petrochemical industry can be decreased.

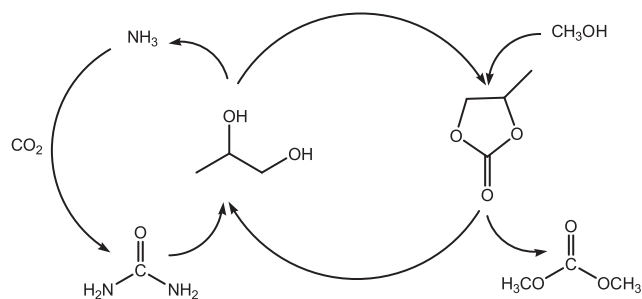
In addition, the released ammonia can be recycled to produce urea by the reaction with  $\text{CO}_2$ . So this process meets the principles of green chemistry. However, both the above patent and other studies only related to one or two separate reactions for DMC synthesis [11–17]. Wang et al. [18] used zinc-yttrium oxide to catalyze the synthesis of DMC by a two-step process starting from urea, ethylene glycol, and methanol, and focused on the catalytic performance of zinc-yttrium oxide for the two individual steps. In the first step, ethylene carbonate with a yield of 94% was synthesized from urea and ethylene glycol. In the second step, the transesterification of ethylene carbonate with methanol to DMC was performed, and the yield of DMC was 71%. The integration of multi-step reactions is a matter of great importance for solving the problems separation and purification operation [19]. For this reason, we prepared Ca-Zn-Al oxide catalyst by introducing calcium hydroxide into Zn-Al hydroxide, and successfully performed one-pot reaction of urea, PG and methanol to DMC in 2015. The effect of reaction conditions was investigated by single factor experiment which cannot show the interactions among the factors. Furthermore, the stability of that Ca-Zn-Al oxide catalyst was poor; the yield of DMC decreased from 83.9% to 69.9% at the second run of catalyst [20]. Previous studies on the transesterification route and one-pot synthesis of DMC were performed using traditional one-factor-at-a-time approaches to optimize the operating parameters. Such experimental methods cannot consider interactions among the process variables. Response surface methodology

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Scheme 1. Route for DMC synthesis using PG as a recycle agent.

(RSM) is a mixture of mathematical and statistical techniques and can be used to evaluate the effects of process variables and their interactions on response variables [21,22]. Hence, RSM has been extensively applied with good results on chemistry and chemical engineering, biochemical engineering, food engineering, and so on [21–24].

Consequently, we prepared a Ca-Zn-Al oxide catalyst by co-precipitation method and used it to catalyze the one-pot synthesis of DMC from urea, PG and methanol in the present study. The catalyst preparation conditions and reaction conditions were optimized to improve DMC yield and Ca-Zn-Al oxide stability.

## 2. Experimental

### 2.1. Materials and reagents

All of the chemical reagents used in this paper, namely, urea (AR, Tianjin Chemical Reagent Factory, China), 1,2-propylene glycol (AR, Tianjin Chemical Reagent Co. Ltd., China), anhydrous methanol (AR, Rionlon Tianjin Chemical Co. Ltd., China), calcium nitrate (AR, Sinopharm Chemical Reagent Co., Ltd, China), zinc nitrate, aluminium nitrate, sodium carbonate and sodium hydroxide (AR, Tianjin Fengchuan Chemical Reagent Technology Co. Ltd., China), were used as received without further purification.

### 2.2. Catalyst preparation

Ca-Zn-Al oxide catalysts were prepared using co-precipitation methods. Take the Ca-Zn-Al oxide with  $n(\text{Ca}^{2+}):n(\text{Zn}^{2+}):n(\text{Al}^{3+}) = 1.6:3:1$  as an example: A mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (12.59 g),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29.75 g) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (12.50 g) was dissolved in 133 mL of distilled water to attain an aqueous solution designated as A. An aqueous solution of NaOH and  $\text{Na}_2\text{CO}_3$  with a molar ratio of 4 was prepared and designated as B. A and B were dropwise added into a beaker with 50 mL of distilled water under vigorously stirring, and the rate of solution A was maintained at 2 mL/min. The pH value of the mixed solution in the beaker was adjusted to about 9.5 by controlling the dropping rate of solution B. After aged at 40 °C for 24 h, the mixture was filtrated and the cake was washed several times with distilled water until the filtrate was neutral. Then the cake was dried at 110 °C for 12 h and calcined at 900 °C for 4 h to form Ca-Zn-Al oxide catalyst.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/max-2550 diffractometer (Rigaku International Corp., Japan) using  $\text{Cu K}\alpha$  radiation. The scan range covered from 5° to 90° at a rate of 8°/min.

The specific surface areas of the catalyst were obtained from  $\text{N}_2$  adsorption-desorption isotherm at 77 K with a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics Instrument Corp., USA), after degassing at 200 °C and 10  $\mu\text{m Hg}$  for 4 h. Multipoint BET analysis method was used to calculate the specific surface area.

The basicities of the Ca-Zn-Al oxide samples were measured by temperature-programmed desorption using  $\text{CO}_2$  as the probe molecule

( $\text{CO}_2$ -TPD). The measurements were performed on a Micromeritics AutoChem II 2920 Chemisorption Analyzer (Micromeritics Instrument Corp., USA). Prior to the test, 0.2 g of the sample was placed in a quartz sample tube and then heated to a temperature not higher than the calcination temperature of the sample and maintained for 1 h in an atmosphere of helium. When the temperature was decreased to 110 °C,  $\text{CO}_2$  was introduced to attain adsorption saturation. Then, the sample was purged by helium for 1 h to remove the physically absorbed  $\text{CO}_2$ . Finally, the TPD experiment started with a heating rate of 10 °C/min, and the  $\text{CO}_2$  desorption signal was detected by a thermal conductivity detector (TCD).

The elemental composition of the Ca-Zn-Al oxide samples was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) on an Optima 7300 V spectrometer (PerkinElmer, USA).

The morphological structure and element distribution of Ca-Zn-Al oxides were characterized with a Quanta 450 FEG Scanning Electron Microscope (SEM, FEI, USA) equipped with an Octane Plus Energy Dispersive Spectrometer (EDS, AMETEK Inc., USA).

### 2.4. One-pot synthesis of DMC

One-pot synthesis of DMC was conducted in two sequential reactions including the reaction of urea with PG to PC and the transesterification of PC with methanol to DMC. Urea, PG, and Ca-Zn-Al oxide catalyst were first added to a four-necked flask and then heated to the reaction temperature under stirring. During this period of reaction, a flow of pure  $\text{N}_2$  was introduced into the flask to remove the byproduct of ammonia from the reaction system quickly. After the completion of the first-step reaction, a Vigreux column was fixed to the four-necked flask to drive off the products of the upcoming transesterification reaction. During the period of transesterification reaction, a flow of methanol was continuously pumped into the four-necked flask by a metering pump to keep the volume of the reaction liquid steady in the flask. After the completion of reaction, the reaction system was cooled to room temperature. Finally, the distillate obtained from the Vigreux column and the residue left in the flask were collected separately for quantitative analysis.

### 2.5. Product analysis

The reaction products were quantitatively analyzed on a SP3420A gas chromatograph (Beijing Beifen Ruili Analytical Instrument Co. Ltd, China) with a PEG-20 M capillary column. Nitrogen was used as carrier gas at a flow rate of 30 mL/min. For the analysis of the distillate, the temperature of both injection port and FID was controlled at 180 °C. The column temperature was controlled according to the following program: an initial temperature of 50 °C and held for 3 min and then increased with a rate of 15 °C/min to 200 °C. An internal standard method was employed using *n*-propyl alcohol as the internal standard. For the analysis of the residue, the temperature of both injection port and FID was controlled at 220 °C. The column temperature was kept at 100 °C for 2 min, raised to 220 °C at a rate of 10 °C/min, and then held for 10 min. *n*-Butanol was used as the internal standard.

## 3. Results and discussion

### 3.1. Effect of preparation conditions on the catalytic performance of Ca-Zn-Al oxide

Ca-Zn-Al oxide catalysts were prepared using co-precipitation methods with calcium nitrate, zinc nitrate and aluminium nitrate as the precursors, and with NaOH and  $\text{Na}_2\text{CO}_3$  aqueous as the precipitant. The effect of pH value, Zn/Al molar ratio, Ca/Al molar ratio, NaOH/ $\text{Na}_2\text{CO}_3$  molar ratio, calcination temperature, and calcination time on the catalytic performance was investigated. The suitable reaction conditions obtained in our previous work were determined for the activity

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