# Preparation of Zn–Al oxide catalyst and its catalytic performance in propylene carbonate synthesis from urea and propylene glycol on a fixed-bed reactor

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## ABSTRACT

The synthesis of propylene carbonate (PC) from urea and propylene glycol (PG) catalyzed by Zn–Al oxide catalyst was successfully performed on a fixed-bed reactor. The appropriate conditions for the preparation of Zn–Al oxide were obtained as follows: $Zn(NO_3)_2$ and $Al(NO_3)_3$ as the precursors of Zn–Al oxide, NaOH and $Na_2CO_3$ aqueous solution as the precipitant, using parallel-flow precipitation method, pH = 9.5, aging at 40 °C for 24 h, and calcination at 500 °C for 4 h. The structures, compositions, and acidities of the Zn–Al oxide catalysts were characterized by means of XRD, $N_2$ adsorption–desorption, ICP-AES and $NH_3$-TPD. Characterization and activity evaluation results indicate that Zn–Al oxide has an excellent catalytic performance for PC synthesis and specific surface area is the main factor influencing the catalytic performance of Zn–Al oxide. Under the suitable reaction conditions of $n$(PG):$n$(urea) = 6:1, Zn–Al oxide volume of 3 mL, reaction temperature of 140 °C and LHSV = 0.8 h$^{-1}$, the yield and selectivity of PC could reach 87.4% and 96.8%, respectively. Furthermore, the yield of PC was no less than 85% during the 60 h stability test, demonstrating that Zn–Al oxide catalyst exhibits a pretty stable activity. Additionally, React-IR was employed to investigate the reaction pathway for PC synthesis from urea and PG. The results show that the reaction of PC synthesis proceeds in two steps: 2-hydroxypropyl carbamate (HPC) is formed from urea and PG first and then PC is produced by elimination of an ammonia from HPC molecule.

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## 1. Introduction

Propylene carbonate (PC) is not only a solvent with high boiling point and high polarity but also an important organic chemical which has been used widely in the fields of organic synthesis, gas separation, electrochemistry, etc. [1,2]. Industrialization of dimethyl carbonate (DMC) synthesis from PC and methanol by transesterification has provided a new application for PC, increasing the demand of PC [3–7]. Now PC is mainly produced industrially by cycloaddition of propylene oxide with $CO_2$, which has many significant merits such as high atom economy and high product yield. However, there exist potential safety problems because this process must be conducted under high pressure and propylene oxide is a dangerous chemical substance [5,8,9]. Compared with the cycloaddition route, the route starting from urea and propylene glycol (PG) shows many advantages: cheap and easily available raw materials, mild reaction conditions, safe operations, environmentally friendly,

etc. [5–10]. The most important significance is that PG, as a by-product in the transesterification process for DMC synthesis, can be converted to the reactant PC and the released ammonia can be recycled to produce urea by reacting with $CO_2$ [7–10]. This would increase the utilization of raw materials for DMC synthesis by the transesterification.

Su et al. [11] described reactions of alkylene glycols with urea to synthesize alkylene carbonates using dibutyltin dilaurate catalyst and the selectivity of products was 84–99%. However, organotin catalyst suffered from some problems such as high toxicity, difficulty in separation and recycle use. Gao et al. [3] reported that $MgCl_2$ and $ZnCl_2$ showed excellent catalytic activity toward PC synthesis and the yields of PC reached 96.5% and 92.4%, respectively. However, these catalysts also suffered from the drawback of difficult separation. Masaharu et al. [12] synthesized alkylene carbonates using a catalyst containing zinc, magnesium, lead, calcium or its compounds under reduced pressure and found that zinc oxide showed a better catalytic performance; the highest yield of PC was 97.5%. Li et al. [5] also found that zinc oxide had a good catalytic activity for PC synthesis, and yield of PC could reach 98.9%. However, the operation under reduced pressure led to not only

an extra consumption of energy but also the loss of raw materials. Du et al. [13] studied the catalytic activity of metal-modified hydroxyapatite (M/HAP) catalysts and found that La/HAP exhibited the highest activity with a 91.5% yield of PC. Recently they [6] reported that the synergy between MgO and MgTiO$_3$ resulted in a high catalytic activity of MgTiO$_3$ and the highest PC yield reached 93.5%. However, with increasing the number of recycle, the catalytic activity of MgTiO$_3$ reduced because of the loss of MgO from the surface of MgTiO$_3$. Zhang et al. [10] reported that Zn–Mg mixed oxide exhibited high catalytic activity and stability: the PC yield was up to 94.8% and the catalyst can be reused for up to 5 times with less changed PC yield. We used Zn–Fe oxides [4], zinc acetate [8] and Pb/Fe$_3$O$_4$/SiO$_2$ [14] to catalyze the reaction of PC synthesis and the PC yield was 78.4%, 93.7% and 87.7%, respectively. All of the reports above for PC synthesis were performed in a batch reactor, in which some problems inevitably existed such as low productivity, difficulty in catalyst separation and reuse, and so on. Yu et al. [9] studied the reaction of PC synthesis from urea and PG on a fixed-bed reactor over ZnO/NaY catalyst and the PC yield reached a maximum of 82.3%. Furthermore, the PC yield was no less than 80% during the 35 h stability test. However, the operation at a reduced pressure consumed an extra energy.

In recent years, the mixed oxides derived from hydrotalcite-like compounds were received much attention in view of their good activity owing to their large surface areas, suitable acid-base properties and high thermal stability [15–18]. Wu et al. [18] prepared Zn–Al oxide by thermal decomposition of hydrotalcite-like compounds and used it to catalyze the reaction of urea and methanol to DMC. The weak acidic and basic sites on the Zn–Al oxide catalyst were responsible for the high catalytic activity. Shu et al. [19] investigated the influence of divalent and trivalent cations in the hydrotalcite-like compounds on the catalytic performance of ZnO-Al$_2$O$_3$ and the influence of the reaction conditions on PC synthesis from PG and urea. But they did not study the effects of preparation conditions of the hydrotalcite-like compounds on its structural parameter and catalytic performance. In the present work, we prepared a Zn–Al oxide catalyst by co-precipitation method and used it to catalyze the reaction of PG and urea to PC under atmospheric pressure on a fixed-bed reactor. The catalyst preparation conditions and reaction conditions were optimized to improve PC yield and Zn–Al oxide stability. In addition, the reaction pathway for the reaction of PC synthesis from PG and urea was investigated by means of GC–MS and React-IR.

## 2. Experimental

### 2.1. Materials and reagents

Urea (AR, Tianjin Chemical Reagent Factory, China), Propylene glycol (AR, Tianjin Chemical Reagent Co. Ltd., China), Propylene carbonate (AR, Tianjin Chemical Reagent Research Institute, China), Zn(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, NaCO$_3$ and NaOH (AR, Tianjin Fengchuan Chemical Reagent Technology Co. Ltd., China).

### 2.2. Catalyst preparation

Zn–Al oxide catalysts were prepared using co-precipitation methods including normal precipitation method (aqueous solution of NaOH and Na$_2$CO$_3$ was dropped into aqueous solution of Al(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O), reverse precipitation method (aqueous solution of Al(NO$_3$)$_3$·9H$_2$O and Zn(NO$_3$)$_2$·6H$_2$O was dropped into aqueous solution of NaOH and Na$_2$CO$_3$) and parallel-flow precipitation method. Take the Zn–Al oxide prepared by parallel-flow precipitation method as an example: A mixture of Al(NO$_3$)$_3$·9H$_2$O (23.446 g) and Zn(NO$_3$)$_2$·6H$_2$O (55.780 g) was

dissolved in 200 mL of distilled water to attain an aqueous solution designated as A. An aqueous solution of NaOH and Na$_2$CO$_3$ with a molar ratio of 16 was designated as B. A and B were dropwise added into a beaker with 50 mL of distilled water in a parallel-flow manner under vigorously stirring, and the rate of solution A was maintained at 2 mL/min, and the pH value was adjusted to about 9.5 by controlling the dropping rate of solution B. After aged at 60 °C for 24 h, the mixture was filtrated and the cake was washed to neutral with distilled water. Then the cake was dried at 100 °C for 16 h to form Zn–Al hydrotalcite-like compounds (HTlcs). Zn–Al oxide catalyst was obtained finally by calcining HTlcs at 500 °C for 4 h.

### 2.3. Catalyst characterization

X-ray diffraction patterns (XRD) were recorded with a Rigaku D/max-2550 diffractometer (Rigaku International Corp., Japan) using Cu Kα radiation. The scan range covered from 5° to 80° at a rate of 8°/min.

The textural parameters of the catalyst were obtained from 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 μm Hg for 4 h. Multipoint BET analysis method was used to calculate the specific surface area. The pore volume and pore size were determined by the BJH method.

The elemental composition of the Zn–Al oxides was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on an Optima 7300 V spectrometer (PerkinElmer, USA).

The acidities of the Zn–Al oxides were measured by temperature-programmed desorption using NH$_3$ as the probe molecule (NH$_3$-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, NH$_3$ was introduced to attain adsorption saturation. Then, the sample was purged by helium for 1 h to remove the physically absorbed NH$_3$. Finally, the TPD experiment started with a heating rate of 10 °C min$^{-1}$, and the NH$_3$ desorption signal was detected by a thermal conductivity detector (TCD).

### 2.4. Catalytic test and reaction mechanism analysis

The reaction for synthesizing PC from urea and PG was carried out on a vertical fixed-bed reactor (i.d. 8 mm, length 600 mm) made of a stainless steel tube, and the ammonia formed in the reaction process was taken away by N$_2$. A typical operation process was as follows: a 3.0 mL of Zn–Al oxide catalyst was packed in the thermostatic zone of the reactor, and N$_2$ was introduced as a carrier gas. Then the mixed feed of urea and PG was pumped into the reactor after the catalyst bed was heated to the reaction temperature. During the reaction process, a regular sampling was withdrawn for quantitative analysis. The yield of PC was calculated based on urea while the selectivity of PC was calculated based on PG.

The reaction products were quantitatively analyzed on a SP3420A gas chromatograph (Beijing Beifen Ruili Analytical Instrument co. Ltd, China) with a PEG-20M capillary column. The analysis conditions were as follows: N$_2$ as carrier, FID temperature of 220 °C, injection port temperature of 220 °C and the program-controlled column temperature: initial oven temperature was kept at 80 °C for 3 min and then increased with a rate of 10 °C min$^{-1}$ to 220 °C and held for 10 min. An internal standard method using *n*-butyl alcohol