



Catalysis, Kinetics and Reaction Engineering

Zn–Ca–Al mixed oxide as efficient catalyst for synthesis of propylene carbonate from urea and 1,2-propylene glycol☆

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ABSTRACT

A series of Zn–Ca–Al oxides with different CaO and ZnO contents have been prepared and evaluated in the synthesis of propylene carbonate (PC) from 1,2-propylene glycol (PG) and urea in a batch reactor. The effect of catalyst composition, basicity and reaction process parameters such as temperature, catalyst dose, molar ratio of PG to urea, purge gas flow and reaction time has been studied to find suitable reaction conditions for the PC synthesis. The PC selectivity and yield under the desired conditions could reach 98.4% and 90.8%, respectively. The best performing catalyst also exhibited a good reusability without appreciable loss in the PC selectivity and yield after five consecutive reaction runs. In addition, a stepwise reaction pathway involving a 2-hydroxypropyl carbamate intermediate was proposed for the urea alcoholysis to PC in the presence of Zn–Ca–Al catalysts, according to the time dependences of reaction intermediates and products.

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1. Introduction

Propylene carbonate (PC), as an excellent solvent with high boiling point, low toxicity and good biodegradability, finds many applications in organic synthesis, paint, battery electrolytes, etc. [1–3]. It is also a versatile reaction intermediate used for the production of poly(propylene carbonate) and dimethyl carbonate via transesterification with methanol [4–6]. PC is now industrially produced by the cycloaddition of CO₂ with propylene oxide derived from fossil resource at the elevated reaction temperature and pressure [7]. As the concern on sustainability from both public opinion and government increases, producing PC with renewable raw material in an environmentally friendly process is in great demand. Alcoholysis of urea with 1,2-propylene glycol (PG) to PC offers a practical route to fulfill the requirement of the desired sustainable chemical process, with PG derived from the biobased glycerol via hydrogenolysis [8] and urea reproduced from the released ammonia by reacting with greenhouse gas CO₂. In addition to the renewable or recyclable feedstock, urea alcoholysis has many advantages in synthetic process, such as mild reaction condition, safe operation and environmental benefit [1].

Many catalysts including (mixed) metal oxides [9–19], metal chlorides [20–22] and acetates [23,24] have been evaluated in the urea alcoholysis to PC, and Zn-containing catalysts, among these

candidates, have proven to be the most efficient because of their high activity towards the urea decomposition to form isocyanate species as reaction intermediates converted subsequently into PC. High PC yields of 94% and 92.4% [23] have been reported respectively on Zn acetate and ZnCl₂ catalysts, regardless of the difficult separation of catalysts from reaction mixture. Compared with the soluble Zn salts, ZnO exhibits better activity and durability for the PC synthesis, and the PC yield can reach as high as 98.9% under the reduced reaction pressure [1]. The recorded high PC yield was ascribed to the appropriate acidity and basicity of amphoteric ZnO, and the authors concluded also that strong alkaline catalysts, such as CaO, would increase the by-product yield due to the accelerated intramolecular dehydration of reaction intermediates in the presence of strong base [1,25].

To improve the utilization efficiency of the active Zn-contained compounds, supported catalysts have been widely used in the synthesis of PC from PG and urea. However, the overall catalytic performances of supported catalysts are greatly affected by the carrier properties. For example, zinc acetate immobilized on activated carbon led to a much lower PC yield of 78% than soluble zinc acetate (94%) under the identical reaction conditions [23]; while Zn–Mg mixed oxide [11] and Zn–Al hydrotalcite-like compounds [26] exhibited higher activity and selectivity than pure ZnO. In a similar work focused on the urea alcoholysis with ethylene glycol to produce ethylene carbonate on mixed metal oxides [27], the roles of catalyst acidity and basicity were related to the elimination of NH₃ and H₂O/CO₂, respectively. Urea alcoholysis with diols to synthesize cyclic carbonates seems to require a proper balance between active ZnO and acid–base property of support for the employed catalyst.

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γ - Al_2O_3 is an excellent catalyst carrier widely used in commercial catalysts due to its appropriate mechanical strength, high surface area and porosity, and γ - Al_2O_3 -supported catalysts are easily formulated to pelletized or extrudate particles for further use in chemical industries. So the design of alumina-based catalysts for the PC production is of great interest. However, the intrinsic acidity of γ - Al_2O_3 reduces its application as catalyst supports in many reactions sensitive to its surface Brönsted acid sites. Modifying γ - Al_2O_3 by alkaline or alkaline earth metal oxides makes it possible to act as a carrier for many catalysts. For example, Ca–Zn–Al mixed oxides could efficiently catalyze the urea alcoholysis by methanol to produce dimethyl carbonate (DMC), and the highest DMC yield of 82.9% was achieved on the catalyst with a Ca/Zn/Al molar ratio of 0.2/3/1 [6]. This indicates that an optimal combination of amphoteric ZnO, acidic Al_2O_3 and basic CaO with distinct acid–base properties was critical to the desired DMC yield. Nevertheless, little attention has been paid to exploring the catalytic performance of ZnO dispersed on the CaO-modified γ - Al_2O_3 in the PC synthesis from PG and urea, which may offer a potential route for the production of PC at an industrial scale.

In the present study, Zn–Ca–Al catalysts with various ZnO and CaO contents have been prepared and tested in the urea alcoholysis by PG to produce PC. Catalytic performance of Zn–Ca–Al mixed oxides has been analyzed in terms of catalyst composition, structure and basicity to select the optimal catalyst. Effect of reaction parameters such as temperature, molar ratio of PG/urea, catalyst dose, reaction time and the purge gas flow on the PC yield has been investigated to explore the suitable reaction conditions. Reusability of the best preferred Zn–Ca–Al catalyst has also been evaluated under the desired conditions. Moreover, the reaction pathway has been briefly discussed based on the variation of product distribution with reaction time stream.

2. Experimental

2.1. Catalyst preparation

CaO, γ - Al_2O_3 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Sinopharm Chemical Reagent Co., Ltd. were of analytical grade (AR) and used directly to prepare Zn–Ca–Al mixed oxides. A CaO– Al_2O_3 paste was prepared by mixing CaO and γ - Al_2O_3 powders enough in a 10 wt% HNO_3 aqueous solution, followed by extrusion, drying at 60 °C overnight and the subsequent calcination at 540 °C for 4 h. The obtained cylindrical Ca–Al mixed oxide was cut into pieces of 3–5 mm in length and 2 mm in diameter before impregnation in an ethanol solution of zinc nitrite. After separation and drying at 80 °C, the obtained solid was calcined again at 540 °C for 4 h to produce a ternary Zn–Ca–Al oxide. The final catalyst was designated as $\text{Zn}_x\text{Ca}_y\text{Al}$, in which y and x represented the theoretical mass percent of CaO to γ - Al_2O_3 and that of ZnO to Ca–Al binary oxide, respectively.

2.2. Characterization

Nitrogen adsorption isotherms were measured at –196 °C using an Autosorb-iQ analyzer (Quantachrome), and the specific surface area was estimated from nitrogen adsorption data in the relative pressure range from 0.05 to 0.30 using the Brunauer–Emmett–Teller (BET) method. Compositions of Zn–Ca–Al oxides were determined by an X-ray fluorescence spectrometer (S4 Explorer, Bruker). Powder X-ray diffraction (XRD) patterns of Zn–Ca–Al catalysts before and after reaction were recorded on a Shimadzu XRD-7000 X-ray diffractometer ($\text{CuK}\alpha$, $\lambda = 0.15418$ nm, 40 kV, 40 mA) at a scan rate of $2^\circ \cdot \text{min}^{-1}$. Morphology of catalysts was examined using a scanning electron microscopy (SEM, Shimadzu SSX-550) at an accelerating voltage of 20 kV. Amounts of the organic deposits on the used catalysts were quantified by thermogravimetric analysis (TGA) on a HCT-3 instrument (Beijing Henven) from room temperature to 800 °C in a dry air flow ($30 \text{ ml} \cdot \text{min}^{-1}$).

Temperature-programmed desorption of CO_2 (CO_2 -TPD) was taken on a Huasi DAS-7000 adsorption instrument. Typically, Zn–Ca–Al oxide (300 mg) was first treated at 500 °C for 1 h in a He flow ($30 \text{ ml} \cdot \text{min}^{-1}$) to remove the water and other molecules adsorbed on catalyst surface, then cooled to 50 °C in the He flow before exposure to a CO_2 flow ($30 \text{ ml} \cdot \text{min}^{-1}$) for 30 min at the same temperature. The CO_2 -saturated sample was purged again by the He flow at 50 °C until a constant baseline was recorded by the thermal conductivity detector (TCD) connected to the reactor, then heated to 1000 °C at a rate of $10^\circ \text{C} \cdot \text{min}^{-1}$, with the desorbed CO_2 continuously monitored by the TCD.

2.3. Catalytic test

Conversion of PG and urea to PC over Zn–Ca–Al catalysts was carried out in a three-necked flask equipped with a magnetic stirrer, thermometer, cycle reflux condenser and nitrogen inlet. In a typical run, PG (94.2 g, 1.24 mol), urea (25 g, 0.42 mol) and a specific amount of catalysts were added into the flask successively under nitrogen atmosphere ($250 \text{ ml} \cdot \text{min}^{-1}$), and the mixture was heated to 184 °C in an oil bath within about 20 min and kept at this temperature for 2 h. Afterward, the reaction mixture was cooled down to room temperature before filtration. The filtrate was analyzed by a gas chromatography (GC, Agilent 7890A) equipped with a flame ionization detector (FID) and a capillary column (Supelco-Wax, $30 \text{ m} \times 0.53 \text{ mm} \times 1 \mu\text{m}$) to separate PG, PC, 2-hydroxypropyl carbamate (HPC), 4-methyle-2-oxazolidone (MOD) and dipropylene glycol (DPG).

In the current paper, PC yield ($Y(\text{PC})$), selectivities to PC ($S(\text{PC})$) and other products are calculated as follows:

$$Y(\text{PC}) = \frac{n(\text{PC})}{n_0(\text{urea})} \times 100\%$$

$$S(\text{PC}) = \frac{n(\text{PC})}{n(\text{PC}) + n(\text{HPC}) + n(\text{MOD}) + 2n(\text{DPG})} \times 100\%$$

$$S(\text{HPC}) = \frac{n(\text{HPC})}{n(\text{PC}) + n(\text{HPC}) + n(\text{MOD}) + 2n(\text{DPG})} \times 100\%$$

$$S(\text{MOD}) = \frac{n(\text{MOD})}{n(\text{PC}) + n(\text{HPC}) + n(\text{MOD}) + 2n(\text{DPG})} \times 100\%$$

$$S(\text{DPG}) = \frac{2n(\text{DPG})}{n(\text{PC}) + n(\text{HPC}) + n(\text{MOD}) + 2n(\text{DPG})} \times 100\%$$

where $n_0(\text{urea})$ is the mole of fed urea, $n(\text{PC})$, $n(\text{HPC})$, $n(\text{MOD})$ and $n(\text{DPG})$ are the moles of PC, HPC, MOD and DPG, respectively, in the reaction mixture.

3. Results and Discussion

3.1. Catalyst composition

Zn–Ca–Al catalysts with different ZnO and CaO contents were examined in the urea alcoholysis to PC. The effect of CaO contents on both the structure and catalytic performance of Zn–Ca–Al composites was investigated when the theoretical ZnO loading was fixed at 10%, while the effect of ZnO contents was studied at a fixed CaO loading of 30%.

3.1.1. Effect of CaO contents

At a fixed ZnO content of 10%, an increase in the theoretical CaO contents from 20% to 90% results in the continuous decline in specific surface area of Zn–Ca–Al from 95.9 to $7.6 \text{ m}^2 \cdot \text{g}^{-1}$ (see Table S1 in supporting information), which is probably caused by the blockage of large pores in alumina and agrees well with the changes in catalyst surface morphology shown in Fig. 1. The relatively smooth surface of Zn–Ca–Al catalyst with low CaO contents turns to be much rough as the CaO contents increased; irregular decorations (Fig. 1(c)), and even

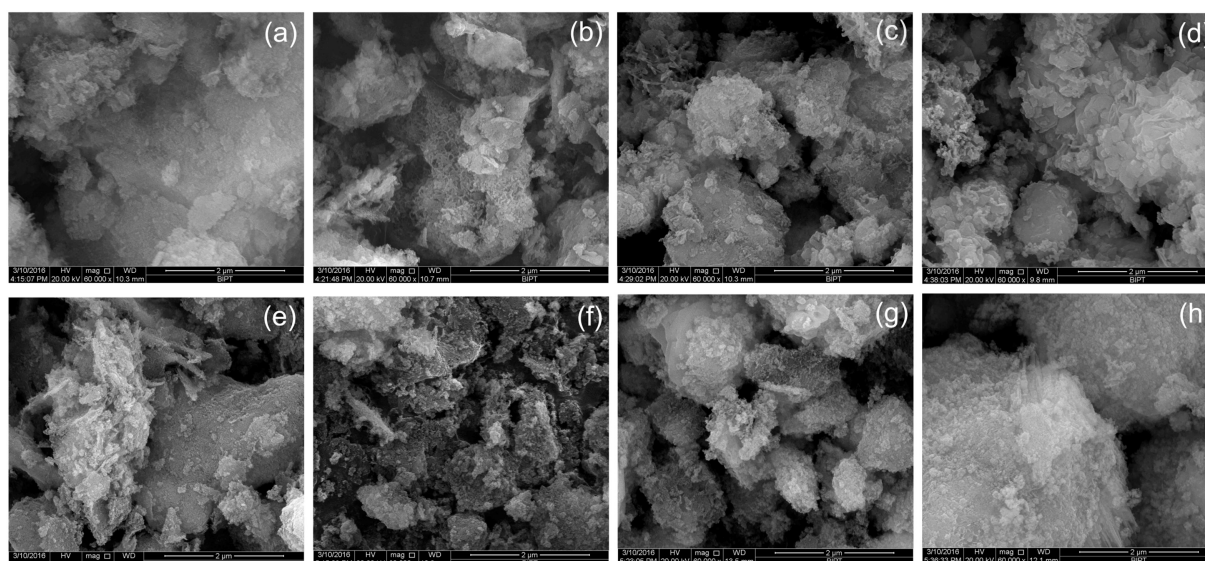


Fig. 1. SEM images of (a) Zn10Ca20Al, (b) Zn10Ca30Al, (c) Zn10Ca50Al, (d) Zn10Ca70Al, (e) Zn5Ca30Al, (f) Zn15Ca30Al, (g) Zn20Ca30Al, and (h) Zn25Ca30Al.

crystals in the shape of micron-scale flakes (Fig. 1(d)), are clearly seen on the SEM images of Zn–Ca–Al with higher CaO contents.

XRD results presented in Fig. 2(a) further reveal the structural evolution of Zn–Ca–Al oxides as CaO contents increase. The mixed oxides with CaO contents no higher than 30% show the identical spectra to that of γ - Al_2O_3 (not shown here), suggesting the highly dispersed Ca species on the catalyst surface. Previous studies [28,29] have confirmed that CaO starts to react with Al_2O_3 to form calcium aluminates above 700 °C. Undoubtedly, CaO should be the dominant species on the surface of Zn–Ca–Al with CaO contents lower than 30% since the employed calcination temperature was 540 °C. When the CaO content was increased to 50%, diffraction peaks at 2θ of 35.9°, 39.4°, 43.2°, 47.5° and 48.5° were observed and attributed to the crystalline calcite (JCPDS 47-1743). Further increasing the CaO content to 70% and even higher led to the simultaneous existence of CaO (JCPDS 48-1467, $2\theta = 32.2^\circ, 37.4^\circ, 53.9^\circ, 64.2^\circ$ and 67.4°), $\text{Ca}(\text{OH})_2$ (JCPDS 84-1264, $2\theta = 34.2^\circ, 47.2^\circ$ and 50.9°) and a little calcite on the catalyst surface. The flake particles seen in Fig. 1(d) are probably $\text{Ca}(\text{OH})_2$ crystals formed by the reaction of CaO-rich surface of Zn10Ca70Al with moisture during storage in air.

Accumulation of CaO and $\text{Ca}(\text{OH})_2$ on Zn–Ca–Al oxides at higher CaO contents caused not only the rapid decrease in catalyst surface areas, but also a sharp increase in the catalyst basicity. CO_2 -TPD spectra (Fig. S1(a)) and the related quantitative analysis (Table S1) show that the desorbed CO_2 corresponding to the strong basic sites increased from 0.17 to $2.77 \text{ mmol} \cdot \text{g}^{-1}$ as the CaO contents changed from 20% to 90%. However, catalytic performance of Zn–Ca–Al catalyst didn't change proportionally with its basicity. PC selectivity varied little, remaining around 97.5%, as

the CaO content increased from 20% to 50%; further increasing the CaO content to 90% caused the drastic decline in PC selectivity to 49.5%, with the DPG selectivity increased from 1.2% to 48.5% at the same time, as shown in Fig. 3. Formation of DPG has been considered as a result of the dimerization of PG in the presence of strong base, such as CaO and $\text{Ca}(\text{OH})_2$, which is capable of abstracting a proton for the adsorbed 1,2-propylene glycol, leaving a nucleophilic species actively involved in the sequential condensation with another PG molecule to produce a DPG [30]. As a consequence, PC yield exhibits a similar trend to that of PC selectivity, with a maximum of 85.5% recorded on Zn10Ca30Al catalyst. Thus, a medium CaO content of 30% is suitable for the desired PC selectivity and yield, avoiding overproduction of DPG and other by-products.

3.1.2. Effect of ZnO contents

At a given CaO content of 30%, an increase in the theoretical loading of ZnO from 5% to 30% have little influence on the textural properties of Zn–Ca–Al oxides, inducing a slight decrease in surface areas from 92.6 to $79.3 \text{ m}^2 \cdot \text{g}^{-1}$ (Table S2). This agrees with the morphological change of Zn–Ca–Al oxides: irregularly shaped catalysts with a low ZnO content tend to assemble into large spherical particles decorated with small crystals on surface as the ZnO content increases (Fig. 1). Further characterization by XRD (Fig. 2(b)) shows the typical ZnO diffraction peaks at 2θ of 31.8°, 34.5°, 36.3°, 47.6°, 56.7° and 63.0° when ZnO content was 15% or higher, confirming the presence of ZnO crystalline phase.

Effect of ZnO loadings on the PC selectivity and yield at the fixed CaO content of 30% in Zn–Ca–Al catalysts is plotted in Fig. 4. The PC selectivities for Zn–Ca–Al catalysts with different ZnO contents are about 98%, independent of ZnO loadings; while the PC yield increases initially

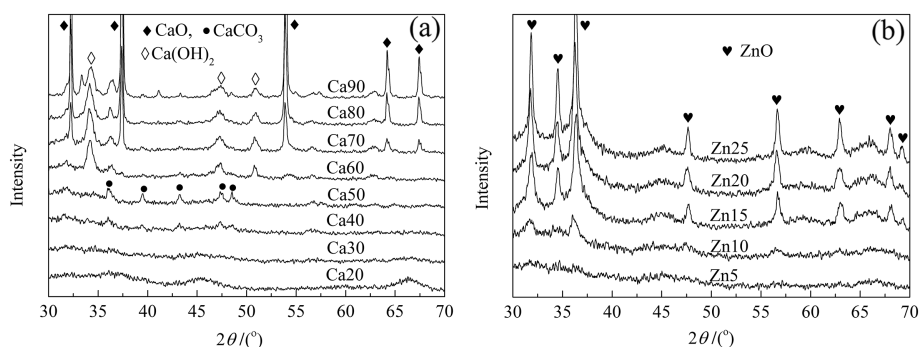


Fig. 2. XRD patterns of (a) Zn10CayAl and (b) ZnxCa30Al with different theoretical CaO and ZnO contents, respectively.

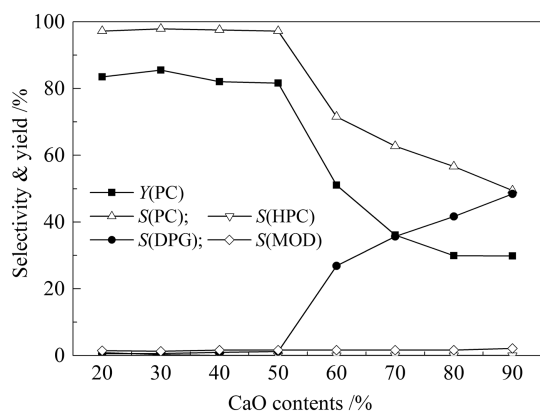


Fig. 3. Effect of CaO contents in Zn10Ca9Al on the reaction selectivities and PC yields. Conditions: 1 wt% catalysts, 184 °C, PG/urea = 3/1, 250 ml·min⁻¹ N₂, and data were collected after reaction for 3 h.

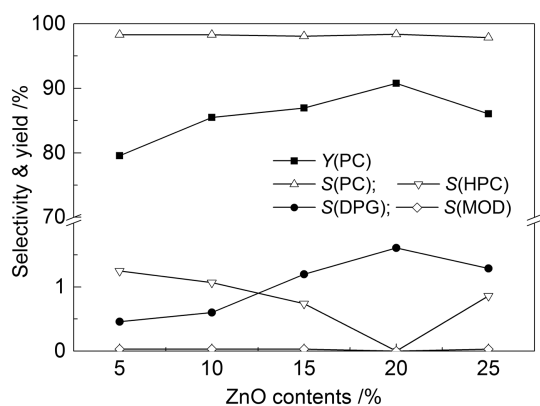


Fig. 4. Effect of ZnO contents in ZnxCa30Al on the reaction selectivities and PC yields. Conditions: 1 wt% catalysts, 184 °C, PG/urea = 3/1, 250 ml·min⁻¹ N₂, and data were collected after reaction for 3 h.

with ZnO contents, gets a maximum of 90.8% at 20% ZnO, and thereafter starts to decline. The decreased PC yield for Zn25Ca30Al has been probably caused by the undesired decomposition of urea to NH₃ and CO₂ in the presence of excess ZnO due to its high activity towards urea decomposition. By-products, such as HPC and DPG, change little with the increase in ZnO contents. Thus, the ZnO content of 20% is taken as optimum.

3.2. Reaction parameters

As discussed above, Zn–Ca–Al catalyst with CaO and ZnO contents of 30% and 20% respectively exhibited the best performance in the catalytic conversion of PG to PC. It was, therefore, used to evaluate the effect of process parameters such as reaction temperature, molar ratio of PG/urea, catalyst dose with respect to PG and the flow rate of N₂ purge gas on the selectivity and yield of PC. A single-factor-at-a-time method was employed in the following experiments.

To determine the optimal PC yield, reaction temperature for the alcoholysis of urea to PC was varied from 160 °C to 190 °C, whereas the molar ratio of PG/urea was 3/1, catalyst dose was 1 wt% of PG, and the flow rate of N₂ purge gas was 250 ml·min⁻¹. The obtained results are shown in Fig. 5(a). The PC yield increase continuously with the rising reaction temperature, gets a maximum of 90.8% at 184 °C, and steps down at a higher temperature of 190 °C. Thermodynamic analysis indicates that the overall alcoholysis of urea to produce PC is endothermic with a reaction enthalpy change of 51.60 kJ·mol⁻¹ [24], an elevation of temperature will shift reaction equilibrium towards products and

promote the PC yield. However, the boiling point of PG is about 188 °C, an elevated temperature above it will cause fast evaporation of PG, especially in the case of a purge gas of 250 ml·min⁻¹, thereby resulting in the significant loss of urea and the consequent lower PC yield. Different from the PC conversions, the PC selectivities above 180 °C are around 98.5%, almost independent of temperature, suggesting side reactions such as the dimerization of PG to DPG and dehydration of HPC to MOD have little influence on the PC yields. The loss of PG reactant at 190 °C due to its fast evaporation, therefore, should be mainly responsible for the observed decline in PC yields at high temperature, and the suitable reaction temperature is proven to be 184 °C.

The influence of molar ratio of PG to urea on the PC yield under the conditions of 1 wt% catalyst, 184 °C and 250 ml·min⁻¹ N₂ purge flow is illustrated in Fig. 5(b). The PC yield rises with an increase in the molar ratio of PG/urea, reaches a maximum of 90.8% at the PG/urea ratio of 3/1, and then decreases when the ratio is beyond 3/1. Decomposition of urea into the undesired products is a competitive reaction accompanying the formation of PC, which is very sensitive to the concentration of urea and readily accelerated in the presence of active Zn–Ca–Al catalysts. As a result, increasing the molar ratio of PG/urea leads to a lower urea concentration and then a higher utilization efficiency of urea. However, a too large PG/urea ratio means a much lower concentration of urea, which causes a slow reaction rate and thus a low PC yield at a fixed reaction time of 3 h. The suitable molar ratio of PG/urea is therefore 3/1 for the PC synthetic process.

Fig. 5(c) shows the influence of catalyst dose on the PC yield and selectivity with other reaction conditions being: temperature = 184 °C; PG/urea molar ratio = 3/1; and N₂ purge flow = 250 ml·min⁻¹. An increase in catalyst dose from 0.5 wt% to 1.0 wt% with respect to PG improves obviously the PC yield from 83.3% to 90.8%. Further increasing catalyst dose up to 4 wt% has negative effect on the PC yield, reducing its value to 76.7% due to the accelerated decomposition of urea to NH₃ in the presence of excessive Zn–Ca–Al catalysts. On the other hand, the PC selectivity increases slightly from 97.8% to 98.8% as the catalyst dose varies from 0.5 wt% to 2.0 wt%, and thereafter reaches a platform whereas the selectivity to MOD decreases monotonically with increasing catalyst dose. This means that Zn–Ca–Al catalyst in excess is beneficial for the dominant PC product in reaction solution. However, higher catalyst doses above 1.0 wt% favor relatively the undesired decomposition of urea, thereby decreasing the overall PC yield.

Alcoholysis of a urea to produce a PC molecule releases two ammonia molecules, so removing ammonia from reaction system by purge gases or the reduced pressure is essential to shift the reaction equilibrium towards PC formation. Effect of the flow rates of N₂ purge gas on the PC selectivity and yield is presented in Fig. 5(d), with reaction temperature, molar ratio of PG/urea and catalyst dose fixed at 184 °C, 3/1 and 1 wt%, respectively. The PC yield increases as the N₂ flow rate increases from 50 to 250 ml·min⁻¹, gets a maximum of 90.8% at the N₂ flow of 250 ml·min⁻¹, then declines with further increasing the purge flow to 300 ml·min⁻¹. Nevertheless, the selectivities for both PC and by-products such as MOD and DPG change little as the purge gas increase from 50 to 300 ml·min⁻¹. These data suggest that a suitable purge flow of 250 ml·min⁻¹ facilitates the immediate removing of the released ammonia in the PC synthesis and promotes consequently the PC yield. Too large purge flow, however, causes the considerable loss of PG and a low PC yield, as well as a bad mass balance, due to the forced evaporation of PG by the strong purge at a temperature near to its boiling point.

According to the previously discussed influences of various experimental parameters on the yield of PC, the suitable reaction conditions for urea alcoholysis to PC, determined by using a single-factor-at-a-time method, contains the reaction temperature at 184 °C, the molar ratio of PG/urea at 3/1, the catalyst dose at 1 wt% of PG, and the N₂ purge gas at 250 ml·min⁻¹. Under such conditions, the PC yield is as high as 90.8%, but still a little lower than reported results in

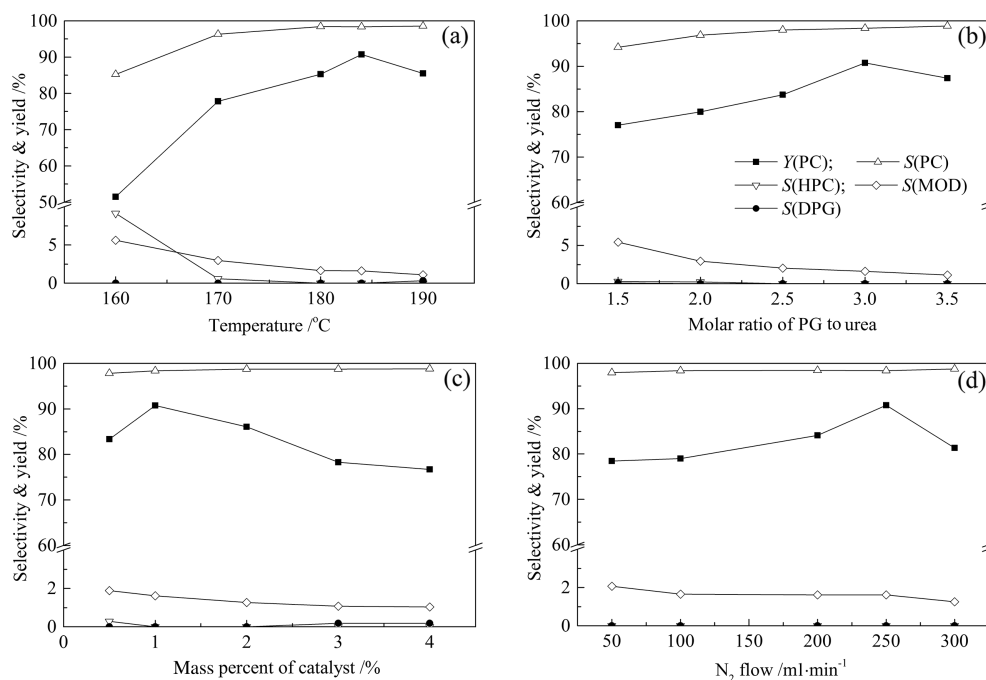


Fig. 5. Effects of (a) temperature, (b) molar ratio of PG/urea, (c) catalyst dose, and (d) purge flow rate of N_2 on the reaction selectivities and PC yields recorded after reaction for 3 h. Conditions: (a) 1 wt% catalysts, PG/urea molar ratio = 3/1, $250 \text{ ml} \cdot \text{min}^{-1} N_2$; (b) 1 wt% catalysts, 184°C , $250 \text{ ml} \cdot \text{min}^{-1} N_2$; (c) 184°C , PG/urea molar ratio = 3/1, $250 \text{ ml} \cdot \text{min}^{-1} N_2$; and (d) 1 wt% catalysts, 184°C , PG/urea molar ratio = 3/1.

literature (listed in Table 1). The relatively low PC yield recorded on Zn–Ca–Al catalysts was probably caused by the presence of CaO and/or $\text{Ca}(\text{OH})_2$, because such strong bases have been considered to promote the dehydration of HPC to form MOD and the decomposition of PC [1]. Anyway, the pretty high PC yield of 90.8% was obtained on Zn20Ca30Al catalysts under the suitable conditions, suggesting that active ZnO dispersed on the CaO-modified $\gamma\text{-Al}_2\text{O}_3$ may act as an industrial catalyst for the production of PC from PG and urea.

3.3. Reaction pathway

The Zn20Ca30Al catalyst was chosen as a candidate to catalyze the alcoholysis of urea to PC under the suitable reaction conditions determined above, and reaction components including PG, PC, HPC, DPG and MOD were continuously monitored and quantified by GC analysis.

Variation of product distribution and the PC yield along with the reaction time is shown in Fig. 6. The PC selectivity rises rapidly up to 93.2% in the first hour, increases gradually to 98.2% in the next hour and thereafter keeps almost constant; whereas the HPC selectivity exhibits the reversed trend, declining from 49.8% to zero within the same time range. Similar trend to PC is also seen for MOD, with its selectivity increasing to 1.8% in the first hour and fluctuating around it with prolonging reaction time. Moreover, the declining HPC selectivity is always accompanied by the rising total selectivity for PC and MOD, and the both values change synchronously in opposite directions. Such correlation suggests strongly HPC, derived from the reaction of PG with the primary decomposition product of urea, as a reaction intermediate for the synthesis of PC. The HPC intermediate can transform into a PC or MOD molecule via the intramolecular elimination of an ammonia or water molecule, respectively. The formation of MOD, however, seems much slower than that for PC, because MOD is not detected by GC

Table 1
Performance of representative catalysts in the urea alcoholysis to produce PC in a batch reactor

Catalysts	$n(\text{PG})/n(\text{urea})$	Temperature/ $^\circ\text{C}$	Reaction time/h	Catalyst dose/%	NH_3 removing	Yield/%	Refs.
MgCl_2	4	150	3	1.5	Vacuum	96.5	[20]
ZnCl_2	4	150	3	1.5	Vacuum	92.4	[20]
LaCl_3	2	160	3	2.3	5 kPa	94.3	[21]
PbCO_3	3	160	6	1.75	N_2 purge	98.2	[31]
MgO	2	160	4	3.2	N_2 purge	87	[10]
ZnO	1.5	170	3	0.79	37.3 kPa	98.9	[1]
Zn–Fe–O	4	170	2	1.4	N_2 purge	78.4	[18]
MgTiO_3	4	170	2	0.08	N_2 purge	93.5	[14]
Mg–Zn–O	2.5	170	0.5	1.05	40 kPa	94.8	[11]
NiFe_2O_4	4	170	5	0.8	Vacuum	93.4	[15]
Zn–Al hydrotalcite	4	170	5	0.25	N_2 purge	98.7	[26]
La/hydroxyapatites	4	170	2	0.64	N_2 purge	91.5	[13]
$\text{Zn}(\text{CH}_3\text{COO})_2$	4	170	3	1.63	N_2 purge	94	[23]
$\text{Na/MnO}_2/\gamma\text{-Al}_2\text{O}_3$	4	170	2	0.64	N_2 purge	91.6	[16]
Zn–Cr–O	1.5	180	6	1.67	N_2 purge	97.8	[2]
Pb–Zn carbonate	1.5	180	5	1.8	N_2 purge	96.3	[32]

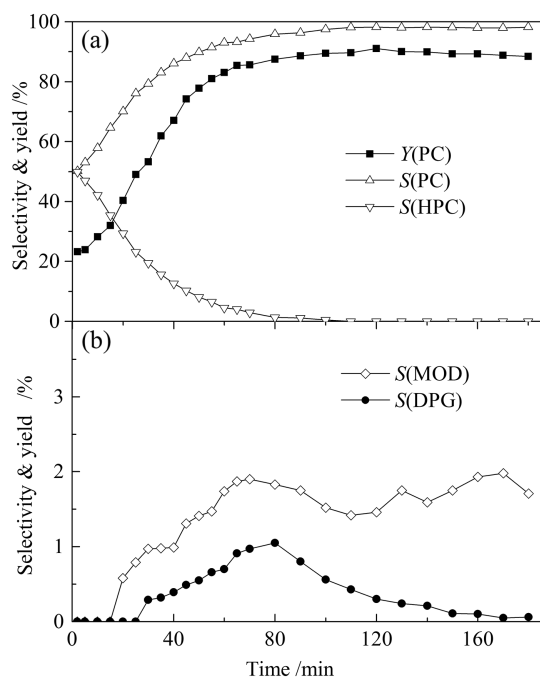


Fig. 6. Variation of reaction selectivities and PC yields with time stream in the conversion of PG to PC over Zn20Ca30Al catalysts. Conditions: 1 wt% catalysts, 184 °C, PG/urea molar ratio = 3/1, 250 ml·min⁻¹ N₂.

during the first 15 min. Differently from MOD, the selectivity to DPG exhibits a typical volcano curve with a maximum of 1.05% at 80 min. Dimerization of PG to DPG can be considered as a reversible reaction, and the reaction equilibrium is greatly affected by the concentrations of both reactant and product. So the observed DPG selectivity increases moderately during the initial reaction stage, and then gets a turning point at 80 min due to the shifted reaction equilibrium towards PG induced by the continuous depletion of reactant.

Based on the above discussion, a brief reaction pathway for the synthesis of PC from PG and urea is outlined as follows: isocyanic acids derived from the urea decomposition, which is not identified in the present work but has been confirmed by Li [1] and Bernhard [33] in previous studies, react with PG to form HPC, and the latter transforms into a PC via elimination of an ammonia. The whole process is, meanwhile, coexisted with several side-reactions, such as the undesired decomposition of urea to CO₂ and ammonia, the dimerization of PG to DPG, and the release of NH₃ from HPC to produce MOD, as shown in Fig. 7. Similar reaction pathways have also been described in the PC synthesis over ZnO [1], zinc acetate [22], and Zn–Al oxide catalysts [12], in good agreement with our observations.

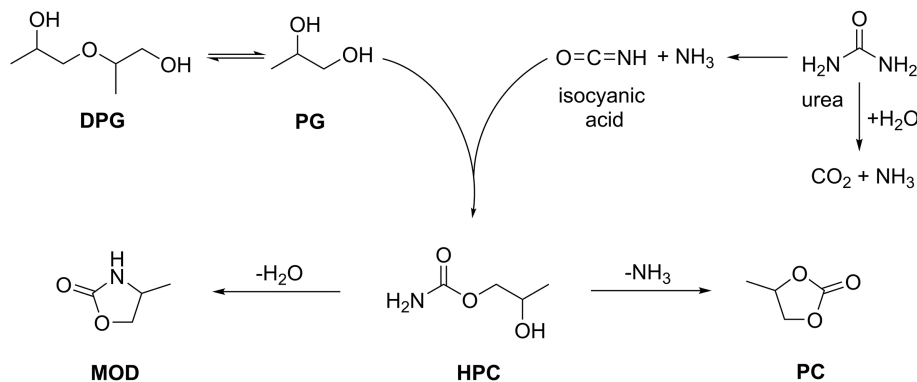


Fig. 7. Reaction pathway for the conversion of PG to PC over Zn–Ca–Al catalyst.

3.4. Catalyst durability

To examine the durability of Zn20Ca30Al catalysts, five consecutive batch reactions were conducted under the conditions of 184 °C, PG/urea molar ratio = 3/1, catalyst dose = 1 wt% of PG, and N₂ purge = 250 ml·min⁻¹. The catalyst after reaction for 3 h was recovered simply by filtration before reuse in the subsequent reaction cycle under the identical conditions. The obtained PC selectivity and yield against the run number are shown in Fig. 8. A slight decline in both PC selectivity and yield is seen as the run number increases up to five, changing from 98.4% to 95.3% and 90.8% to 86.9%, respectively.

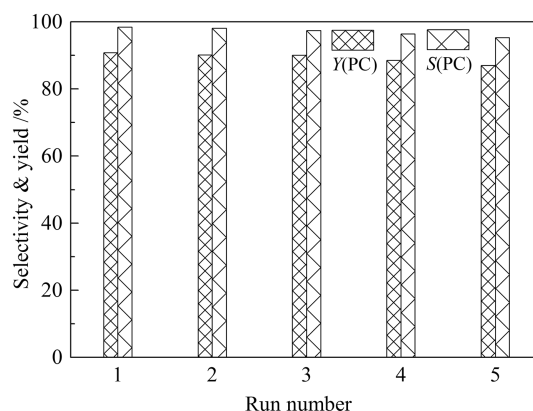


Fig. 8. Reusability of Zn20Ca30Al catalyst. Conditions: 1 wt% catalysts, 184 °C, PG/urea molar ratio = 3/1, 250 ml·min⁻¹ N₂, and reaction time = 3 h.

To interpret the declining catalytic performance, composition, morphology and structure of the employed Zn–Ca–Al catalyst before and after the consecutive reactions were studied carefully. Elemental analysis by XRF shows that the mass content of ZnO decreases from 20.2% for the fresh catalyst to 12.6% for the used one after five reaction cycles (see Table 2), in accordance with the measured Zn²⁺ concentration of 0.045 g·L⁻¹ in the reaction liquid after catalytic conversion of PC, urea and methanol to propylene carbonate over a Ca–Zn–Al catalyst [6], indicating the severe leaching of ZnO in the reaction. Morphology examination by SEM shows also clearly the cracked particles with much smaller size and rougher surface for the used catalyst (Fig. S2(b,c)), compared with the fresh Zn–Ca–Al oxide (Fig. S2(a)). The surface area of catalyst, as a consequence, increases from 78.9 to 154.8 ml·min⁻¹. The rising surface area might be attributed to the enhanced accessibility of pores of γ -Al₂O₃ as well as the relatively high content of γ -Al₂O₃ in the used catalyst, due to the partly loss of ZnO crystal phase covered previously on the catalyst surface.

Table 2
Physical properties of the fresh and used Zn₂₀Ca₃₀Al catalysts

Catalysts	Surface area /m ² ·g ⁻¹	Components/%		
		Al ₂ O ₃	CaO	ZnO
Fresh	78.9	60.9	18.9	20.2
1st run	137.9	60.6	21.1	18.3
5th run	154.8	67.9	19.5	12.6

Further XRD characterization of the used catalysts, shown in Fig. 9, exhibits a few peaks assigned to calcite instead of ZnO crystals, confirming the disappearance of ZnO crystals and the presence of calcite on the used catalysts. However, the disappearance of ZnO crystal phase couldn't be simply attributed to the leaching of Zn species, transformation of ZnO crystals into amorphous ZnO phase, which is probably induced by the involvement of ZnO in the activation of urea and the following intramolecular condensation of HPC intermediate to produce PC, should also be taken into account. This is supported by the invisible diffraction peaks of ZnO for the catalyst after the first reaction run when the leaching of ZnO content is only about 10%. On the other hand, calcite observed on the used catalyst has been probably caused by the reaction of CaO with water and CO₂ derived from the accompanying side-reactions in the PC synthesis. As reported previously by Zhang and co-workers [6], CaO in the catalyst reacted with water released in either the dimerization of PG to DPG or the intramolecular condensation of HPC to MOD to produce Ca(OH)₂, which would further react with CO₂ generated from the undesired decomposition of urea to form CaCO₃.

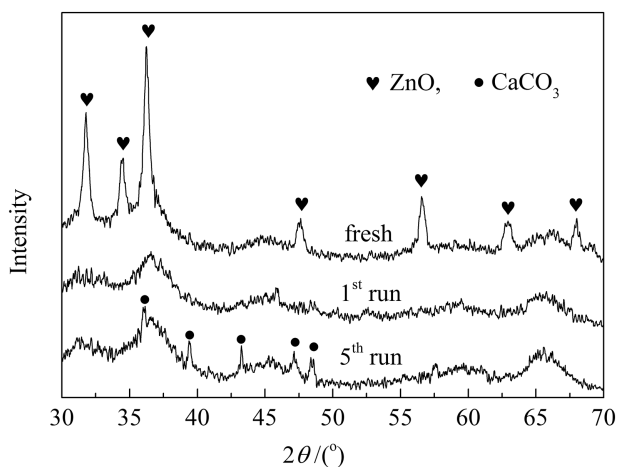


Fig. 9. XRD patterns of the used Zn₂₀Ca₃₀Al catalyst after consecutive reactions. Conditions: 1 wt% catalysts, 184 °C, PG/urea molar ratio = 3/1, 250 ml·min⁻¹ N₂, and reaction time = 3 h.

Apart from the structural evolution, coverage of catalyst surface by the deposited species is another factor to consider in determining the catalyst durability. TG-DTA analysis (Fig. S3) shows the amount of the deposited organic species on the used curves after the first and the fifth run was 11.2 wt% and 14.9 wt%, respectively. The slow deposition rate of organic species after the first reaction cycle suggests the accumulation of organic species should not be the main reason for the observed continuous decline in the PC yield against reaction run numbers. Considering other factors discussed above, the slight deactivation of Zn–Ca–Al catalyst in the PC synthesis is a result of comprehensive effect of the leaching of ZnO, partial transformation of CaO to calcite and the accumulation of organic deposits. A high PC yield of 86.9% has been, anyway, achieved after the five consecutive batch reactions over the optimized Zn–Ca–Al catalyst, without appreciable decrease in the PC yield compared to the fresh catalyst.

4. Conclusions

The catalytic process for the production of PC from PG and urea in a batch reactor has been investigated in terms of the composition of Zn–Ca–Al catalysts and reaction conditions such as temperature, molar ratio of PG/urea, catalyst dose, reaction time and the purge gas flow. The PC selectivity and yield could reach 98.4% and 90.8%, respectively, under the suitable conditions of temperature = 184 °C, molar ratio of PG/urea molar ratio = 3/1, catalyst dose = 1 wt% of PG, flow rate of N₂ purge = 250 ml·min⁻¹, and reaction time = 2 h. Moreover, Zn–Ca–Al catalysts exhibited the satisfactory reusability in the five consecutive batch reactions, with the PC yield decreasing slightly from 90.8% to 86.9% due to the leaching of ZnO content, partial transformation of CaO to calcite and gradual accumulation of organic deposits on the catalyst surface. An investigation of reaction pathway by means of monitoring the product distribution with time stream suggested that the alcoholysis of urea by PG to produce PC proceeds in two steps: HPC as reaction intermediate is formed from urea and PG, and then transforms into the desired PC by elimination of ammonia.

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Supplementary Material

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.cjche.2016.11.003>.

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