Catal Lett (2007) 118:290–294
DOI 10.1007/s10562-007-9193-7

Modified Zinc Oxide for the Direct Synthesis of Propylene Carbonate from Propylene Glycol and Carbon dioxide

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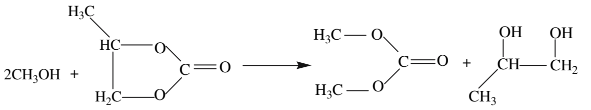
Received: 20 March 2007 / Accepted: 2 July 2007 / Published online: 28 July 2007

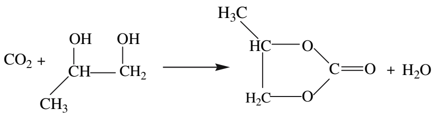
Abstract A series of modified zinc oxide catalysts were prepared and their catalytic activities were evaluated by the direct synthesis of propylene carbonate from propylene glycol and carbon dioxide in the presence of acetonitrile, which acted as not only the solvent but also the dehydrating reagent in the reaction. The reusability test indicated that the modified catalysts had the high stability. Ammonium carbonate was added into the reaction to significantly elevate the selectivity of propylene carbonate.

Keywords Propylene carbonate · Modified zinc oxide · Propylene glycol · Carbon dioxide

1 Introduction

Recently, the development of an environmentally friendly industrial process utilizing carbon dioxide has drawn much interest, and it has been well recognized that the utilization of carbon dioxide as a carbon resource is important [1, 2]. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates from carbon dioxide and cyclic oxide [3–6], which are commercially important compounds and are used as electrolytes in lithium batteries, as aprotic polar solvents, and as intermediates for producing polycarbonate and fine chemicals [7–9]. Moreover, a possible utilization of cyclic carbonates, such as propylene carbonate (PC) and ethylene carbonate (EC), is the transesterification with methanol to form dimethyl carbonate (DMC) and the corresponding glycol. It is well known that the transesterification of PC with methanol to form DMC is widely used in industrial synthetic process [10–14]. However, propylene glycol (PG) as by-product is always inevitable to be produced in the transesterification process (See Eq. (1)). The alcoholysis of urea with PG to synthesize PC is an available approach for making use of PG [15, 16]. However, it is a more perfect route to directly synthesize PC from CO_2 and PG (See Eq. (2)). In this way, not only can be PG recycled but also CO_2 can be utilized effectively. As a result, DMC is synthesized from methanol and CO_2 by using PC as a recyclable intermediate according to Eqs. (1) and (2).


(1)


(2)

Recently, CeO_2–ZrO_2, Bu_2SnO and $Bu_2Sn(OMe)_2$ have been developed to synthesize PC from PG and CO_2 [17–19] . However, PC yield was very low, which was only about 2%. This was attributed to the thermodynamic

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limitation and hence the removal of H_2O from the reaction system will help to enhance PC yield [19].

In the present work, PC synthesis from PG and CO_2 over modified ZnO was investigated in the presence of CH_3CN. CH_3CN in the reaction acted as not only the solvent but also the dehydrating reagent to remove the water produced in the reaction. So, the thermodynamic limitation was shifted and PC yield was improved obviously. In order to enhance the selectivity of PC, ammonium carbonate as the coupling reagent was added into the reaction system.

2 Experimental

2.1 Chemical Reagents

K_2CO_3, KOH, KI, KBr, KCl, KF, Na_2CO_3, NaOH and NaCl were produced by Beijing Chemical Reagent Factory. ZnO, $Zn(OH)_2$, $ZnCO_3$, $ZnCl_2$, propylene glycol and acetonitrile were supplied by Shanghai Chemical Reagent Factory. All the chemicals were of analytical grade and were used without further purification. CO_2 (>99.95%) was purchased from Beijing Analytical Instrument Factory.

2.2 Preparation of Modified ZnO Catalysts

Modified ZnO catalysts were prepared by impregnating ZnO with an aqueous solution containing certain amounts of alkali carbonate and alkali halide. Then, the slurry was placed at room temperature for 12 h and was dried at 120 °C for 10 h. The calcination of the catalysts was performed at 500 °C for 4 h.

2.3 X-ray Diffraction

XRD of the catalysts were measured in Rigaku D/max-A using Cu target with Ni filter and were operated at 50 kV and 30 mA, using a scan speed rate 0.2°/min (2θ).

2.4 BET Measurement

BET surface areas of the samples were performed with the BET method using a Micromeritics ASAP-2000 apparatus.

2.5 Reaction Apparatus and Operations

The reaction was carried out in a 50 mL stainless-steel autoclave reactor equipped with a magnetic stirrer, in which the catalysts (0.5 g) were added to a solution of PG (7.6 g, 100 mmol) and CH_3CN (10 mL) as a typical process. And then CO_2 was introduced into the autoclave to displace the air three times with the pressure of 1.5 MPa. After that, the autoclave was pressurized with CO_2 and then was heated and constantly stirred during the reaction. After the reaction, the autoclave was rapidly cooled to ambient temperature in an ice-water bath and the excess of CO_2 was vented slowly. Products in liquid phase were quantitatively analyzed by a gas chromatograph (GC-920) equipped with a thermal conductivity detector and a packed column (GDX-203) using 2-propanol as an internal standard. And the qualitative analysis was further performed by GC–MS (HP G1800A) with a capillary column (HP-5MS).

3 Results and Discussion

3.1 PC Synthesis from PG and CO_2 over Different Catalysts

Table 1 illustrated the results of PC synthesis from CO_2 and PG over different catalysts in presence of CH_3CN. It could be seen that the reaction did not take place without catalysts (Entry 1). ZnO, $Zn(OH)_2$ and $ZnCl_2$ possessed quite high catalytic activity with PC yield of 18.5, 13.7 and 12.6%, respectively (Entries 2, 4 and 6). However, $ZnCl_2$ showed poor selectivity towards PC. The catalytic activity

Table 1 PC synthesis from PG and CO_2 over modified zinc oxide[a]

Entry	Catalyst	PG Conversion[c] (%)	Yield[c] (%)		
			PC	PG-2-acetate	DPGs
1	None	0	0	0	0
2	ZnO[d]	29.8	18.6	10.9	0.3
3	ZnO[d,f]	0	0	0	0
4	$Zn(OH)_2$	22.5	13.7	8.4	0.4
5	$ZnCO_3$	6.2	4.2	2.0	0
6	$ZnCl_2$	33.5	12.6	18.5	2.4
7	K_2CO_3/ZnO[b,d]	37.5	22.4	14.4	0.7
8	KOH/ZnO[b,d]	35.6	21.2	13.9	0.5
9	KI/ZnO[b,d]	42.6	26.0	15.8	0.8
10	KI/ZnO[b,e]	36.5	22.1	13.8	0.6
11	KBr/ZnO[b,d]	38.9	22.8	15.5	0.6
12	KCl/ZnO[b,d]	34.9	20.4	14.1	0.4
13	KF/ZnO[b,d]	13.8	8.5	5.3	0
14	Na_2CO_3/ZnO[b,d]	32.5	20.2	12.0	0.3
15	NaOH/ZnO[b,d]	31.8	19.2	12.1	0.5
16	NaCl/ZnO[b,d]	32.0	19.8	11.6	0.6

[a] Reaction conditions: PG (100 mmol), CH_3CN (10 mL), catalyst (0.5 g), CO_2 pressure (10 MPa), 160 °C, 15 h

[b] The content of alkali carbonate and alkali halide, 4 mmol/g

[c] Determined by GC using an 2-propanol as an internal standard

[d] Calcination at 500 °C for 4 h

[e] Without calcination

[f] Without CH_3CN

Table 2 BET surface areas of different samples

Samples	ZnO	K_2CO_3/ZnO	KI/ZnO	KBr/ZnO	KCl/ZnO	KF/ZnO	Na_2CO_3/ZnO
S_{BET}, m^2/g	4.86	4.32	4.43	4.55	4.72	4.61	4.44

of $ZnCO_3$ was quite low, where PC yield was only 4.2% (Entry 5). Obviously, ZnO was superior to other catalysts and PC yield over ZnO was much higher than that reported by others [17–19]. This was considered to be related to acidic and basic properties of ZnO, as revealed in the research of Bhanage et al. [20].

It was surprising that ZnO modified with potassium salt, such as K_2CO_3/ZnO, KOH/ZnO, KI/ZnO, KBr/ZnO and KCl/ZnO (Entries 7–12), possessed quite higher catalytic activity than ZnO for PC synthesis. Among them, the activity of KI/ZnO was the highest, over which PG conversion was 42.6% and PC yield was 26.0% (Entry 9). However, the activity of KF/ZnO decreased seriously, where PC yield was only 8.5% (Entry 13). The activity improvement of ZnO modified with sodium salts was not great in contrast to that of ZnO (Entries 14–16). Table 2 illustrated BET surface areas of different samples. From Table 2, it could be seen that ZnO possessed quite small surface area, which was only 4.86 m^2/g. When ZnO was modified with alkali salts, the surface areas of samples decreased in some sort and the surface area differences of all samples were not very obvious. So, the surface areas of different modified ZnO were not an important factor for the reaction.

The activity of non-calcined KI/ZnO samples was a little lower than that of calcined ones (Entry 10). This could be due that calcination could improve the activity of catalysts. Generally, good dispersion of active component on the surface of the support would increase the number of active sites and the activity [21]. XRD patterns of samples showed that the characteristic peaks of KI declined after calcinations of KI/ZnO catalyst, as illustrated in Fig. 1. One possible reason was that KI was dispersed better on ZnO after calcinations or formed a new amorphous phase.

In order to further study the catalytic activity of KI/ZnO, the samples with different KI content were prepared and had been tested under the same reaction conditions. As listed in Fig. 2, the catalytic activity of KI/ZnO was improved with the increase of KI content within1–4 mmol/g. However, when KI content surpassed 4 mmol/g, the catalytic activity began to drop. This was due to that overmuch KI could make uneven dispersion of KI on the surface of ZnO, which resulted in the low catalytic activity for PC synthesis.

The presence of CH_3CN was very important and PC could not be detected in absence of CH_3CN (Entry 3). The water produced in the reaction could be consumed via the hydrolysis of CH_3CN. Then the thermodynamic equilibrium was shifted and improve PC yield. So, here CH_3CN acted as not only the solvent but also the dehydrating reagent in the course of the reaction. The main byproduct was propylene glycol-2-acetate (PG-2-acetate), which was attributed to the hydrolysis of CH_3CN. The hydrolysis of CH_3CN could generate acetamide, which could go on reacting with water to form acetic acid and ammonia (See

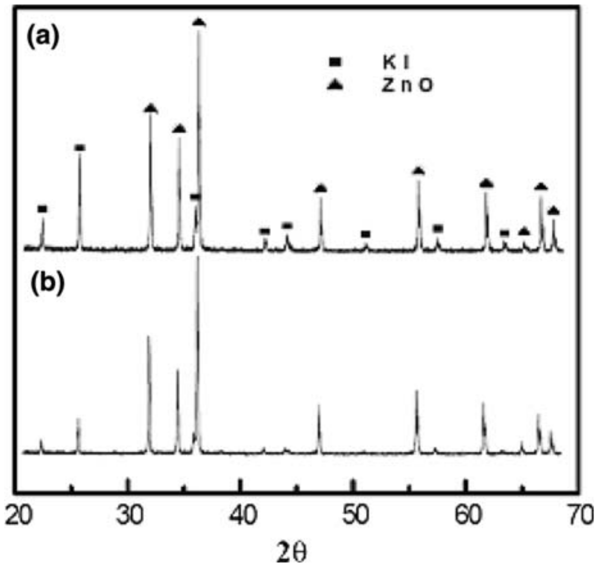


Fig. 1 XRD patterns of KI/ZnO catalyst. (**a**) without calcination; (**b**) with calcination

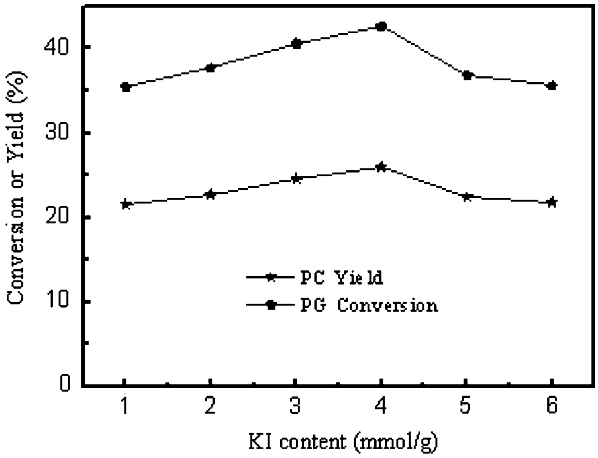
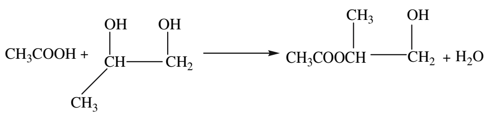


Fig. 2 Effect of KI content on PC synthesis. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), KI/ZnO (0.5 g), CO_2 pressure (10 MPa), 160 °C, 15 h

Eq. (3)). So-produced acetic acid could react with PG to produce PG-2-acetate (See Eq. (4)).

$$CH_3CN \xrightarrow{+H_2O} CH_3CONH_2 \xrightarrow{+H_2O} CH_3COOH + NH_3 \qquad (3)$$



$$CH_3COOH + \underset{CH_3}{\overset{OH}{CH}}\!-\!\overset{OH}{CH_2} \longrightarrow CH_3COO\overset{CH_3}{CH}\!-\!\overset{OH}{CH_2} + H_2O \qquad (4)$$

In addition, Dipropyleneglycols (DPGs) as expectable by-products in the reaction could be detected in a small amount by GC analysis, which were produced by the dehydration of PG [17, 18].

3.2 Effect of the Reaction Conditions

KI/ZnO (KI content, 4 mmol/g) was chosen as a typical catalyst to optimize the reaction conditions and the results were listed below.

The effect of CH_3CN amount on PC synthesis was investigated. As shown in Fig. 3, PG conversion and PC yield increased remarkably with the rise of CH_3CN amount from 2 to 10 mL, and decreased by further increase in CH_3CN amount. This could be ascribed to that CO_2 was easily dissolved in CH_3CN and CO_2 concentration in the liquid increased with CH_3CN amount and led to high PC yield. However, more CH_3CN reduced PG concentration and then PC yield.

The effect of reaction temperature on PC synthesis was listed in Fig. 4. PG conversion and PC yield increased with reaction temperature in the range of 80–160 °C. Although further increase of the temperature led to the rise of PG conversion, there was a sharp decrease in PC yield, possibly due to the formation of side-products, such as DPGs [17, 18].

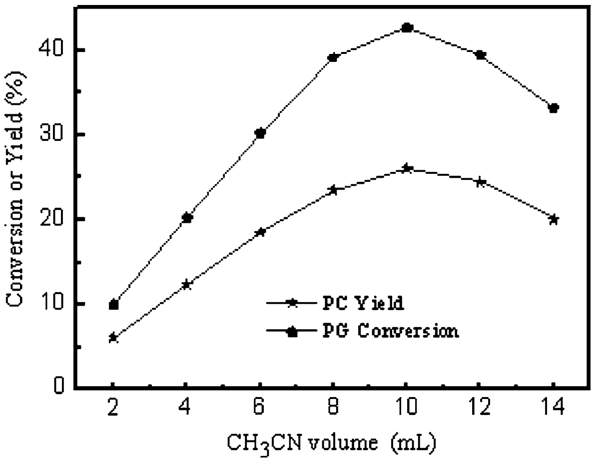


Fig. 3 Effect of the amount of CH_3CN on PC synthesis. Reaction conditions: PG (100 mmol), KI/ZnO (0.5 g), CO_2 pressure (10 MPa), 160 °C, 15 h

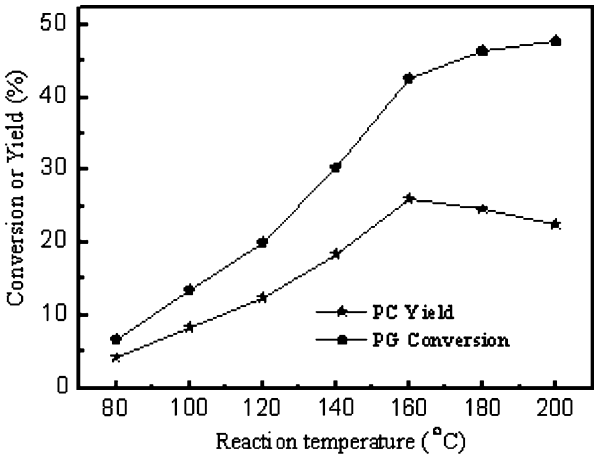


Fig. 4 Effect of reaction temperature on PC synthesis. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), KI/ZnO (0.5 g), CO_2 pressure (10 MPa), 15 h

Figure 5 showed the effect of CO_2 pressure on PC synthesis. It could be seen that PC yield was nearly proportional to CO_2 pressure in the range of 2–10 MPa. High CO_2 pressure was favorable for achieving high PC yield, which could be attributable to that CO_2 solubility in CH_3CN increased with CO_2 pressure and high CO_2 concentration in the liquid could promote PG conversion. However, when CO_2 pressure surpassed 10 MPa, the changes of PG conversion and PC yield were not significant.

3.3 Stability of KI/ZnO Catalyst

To investigate the reusability of KI/ZnO (KI content, 4 mmol/g), the recycling experiments were performed.

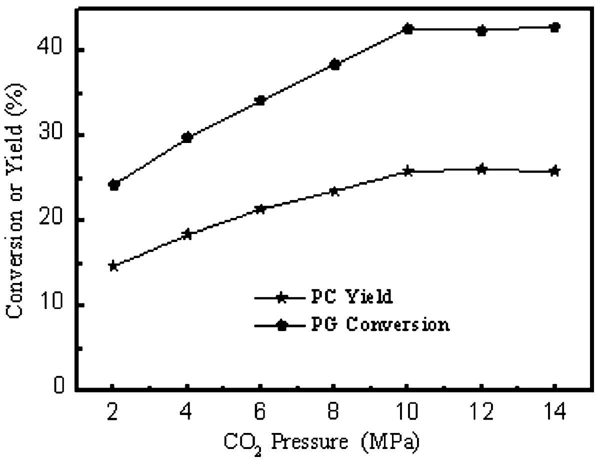


Fig. 5 Effect of CO_2 pressure on PC synthesis. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), KI/ZnO (0.5 g), 160 °C, 15 h

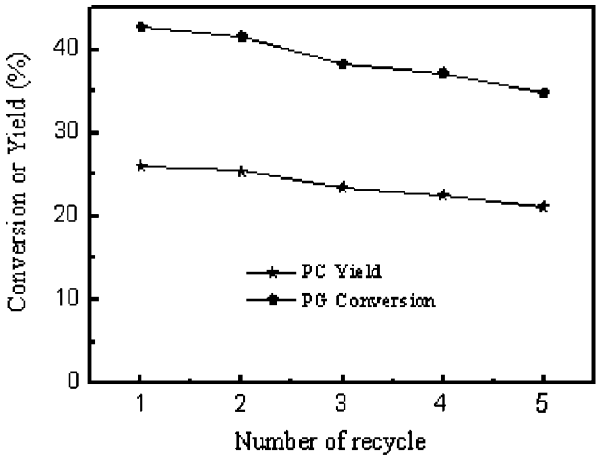


Fig. 6 Stability of KI/ZnO catalyst. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), KI/ZnO (0.5 g), CO_2 pressure (10 MPa), 160 °C, 15 h

After each reaction, KI/ZnO was separated by filtration and washed with 20 mL of CH_3CN three times, and then used for the next run. As shown in Fig. 6, KI/ZnO could be used several times with light decrease of the catalytic activity, which could be due to some loss of KI in the course of reaction. This result indicated that KI/ZnO had the high stability in the reaction.

3.4 Improvement for PC Selectivity

In order to enhance PC selectivity, ammonium carbonate as the coupling reagent was added into the reaction system. It was well known that ammonium carbonate was very easy to be decomposed to produce NH_3, H_2O and CO_2 (See Eq. (5)).

$$(NH_4)_2CO_3 \xrightarrow{\Delta} CO_2 + 2NH_3 + H_2O \qquad (5)$$

As a result, so-produced NH_3 could inhibit acetamide from further hydrolyzing to produce acetic acid and then improved PC selectivity. As shown in Fig. 7, when ammonium carbonate was added into the reaction system, PC selectivity was greatly improved. With the increase of the amount of ammonium carbonate, PC selectivity could reach 100%, although PC yield was found to decline to a certain extent. More ammonium carbonate was disadvantageous for the reaction, which resulted in an obvious drop of PC yield.

4 Conclusions

PC was effectively synthesized via the reaction of PG with CO_2 catalyzed by modified ZnO in the presence of acetonitrile. Among the catalysts, KI/ZnO showed the highest catalytic activity for PC synthesis. In the reaction, CH_3CN acted as not only the solvent but also the dehydrating reagent to eliminate water produced in the reaction, thus improving PC yield. The effect of the reaction conditions on PC synthesis was studied in detail and the highest PC yield could reach 26.0% under the optimal reaction conditions. Furthermore, the reusability test showed that KI/ZnO had the high catalytic stability. Interestingly, upon ammonium carbonate being introduced into the reaction system, PC selectivity was significantly enhanced.

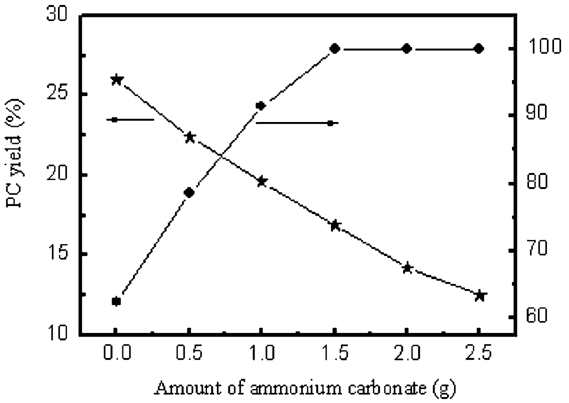


Fig. 7 Effect of the amount of ammonium carbonate on PC synthesis. Reaction conditions: PG (100 mmol), CH_3CN (10 mL), KI/ZnO (0.5 g), CO_2 pressure (10 MPa), 160 °C, 15 h

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